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INFRARED SPECTROSCOPY AND RADIATIVE LIFETIMES
OF MOLECULAR IONS

M. Okumura
(Ph.D. Thesis)

November 1986

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**Infrared Spectroscopy and Radiative Lifetimes
of Molecular Ions**

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Ph.D. Thesis**

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November 1986

Infrared Spectroscopy and Radiative Lifetimes of Molecular Ions

Mitchio Okumura

ABSTRACT

This thesis describes new experiments on the radiative lifetimes of small molecular anions and on the vibrational spectroscopy of weakly bound cluster cations, using an ion trapping photodissociation/photodetachment apparatus.

In Chapters 2 and 3, the radiative lifetimes of long-lived excited states of the CH_2^- and CH^- anions are reported. The ions are trapped in a high vacuum radio frequency octopole ion trap, where they can be confined without collisions for times as long as seconds. The radiative lifetimes of excited bending vibrations of CH_2^- are reported in Chapter 2 and compared to high level *ab initio* calculations by Lee, Handy, and Schaefer. The theory is somewhat successful, but cannot completely reproduce the experimental results. Chapter 3 describes experiments measuring the decay of excited CH^- . Two states have been observed: $v=1$ of the ground electronic state, with a short lifetime in excellent agreement with recent *ab initio* calculations,

and a very long-lived state, the $a^1\Delta$ state, which decays by a spin-forbidden process. These results also clear up a discrepancy in the literature over the electron affinity of the CH radical.

Vibrational predissociation spectroscopy of weakly bound ionic clusters is the subject of the last chapters. Chapter 4 presents infrared spectra of the hydrogen cluster ions $H_3^+ \cdot (H_2)_n$. The clusters dissociate after excitation of a single quantum in the ligand H_2 stretching vibrations; spectra are recorded by detecting the fragment ions as a function of photon energy. Despite extensive high resolution searches, no rotational structure has been resolved, implying some homogeneous broadening, or unusually congested spectra. Implications for the dissociation dynamics are discussed. Chapter 5 describes a new "messenger" technique used to obtain vibrational spectra of the hydronium ion hydrates $H_3O^+ \cdot (H_2O)_n$, $n=1,2,3$. Because a single quantum in an OH stretch cannot dissociate these clusters, the vibrational predissociation spectra of the messenger-bound clusters $H_3O^+ \cdot (H_2O)_n \cdot (H_2)$ are obtained, between 2300 cm^{-1} and 4200 cm^{-1} . The H_2 messenger forms a weak hydrogen bond with the cluster, and should ideally act as a mass label. With the exception of $H_3O^+ \cdot (H_2O)$, the H_2 is found to have a small but detectable effect on the infrared spectra of the hydrates. $H_3O^+ \cdot (H_2O)$ has a flat potential and is easily distorted, even by H_2 . Spectra of the clusters $H_3O^+ \cdot (H_2)_m$, $m=1,2,3$ provide additional information on the H_2 /ion interaction. The $H_3O^+ \cdot (H_2)$ spectrum presented in this chapter is the first example of a rotationally resolved spectrum of a weakly bound cluster ion.

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Chapter 1

The Experimental Apparatus

I. INTRODUCTION

In this chapter, we describe the ion trapping and photodissociation apparatus with which we have observed the radiative decay of long-lived excited states of ions and the vibrational predissociation spectra of molecular cluster ions. The machine was originally built by Bustamente, Carlson, Gerlich, and Lee, and is described in some detail elsewhere.¹ The apparatus, shown schematically in Fig. 1, is a tandem mass spectrometer with a radio frequency octopole ion guide between the two mass filters. The ion guide helps to confine very slow ions, with energies less than 1 eV, but can also be used as an ion trap, capable of storing ions for long times. The first mass spectrometer selects only the parent ions for injection into the octopole, where the ions are trapped and then photolyzed. The final mass spectrometer is used to mass-analyze the photodissociation products. The experiment is thus similar in concept to ion photodissociation experiments using ICR traps. With a time resolution of approximately 1 ms and trap region pressures of less than 10^{-9} torr, the apparatus is well suited for measuring vibrational and forbidden decays.

II. EXPERIMENTAL

A. The Radio Frequency Octopole Ion Trap

Ion traps have been used successfully to measure the lifetimes of a number of excited states of ions. For atomic ions, several forbidden transition lifetimes have been measured. The 58.6 ± 12.9 s lifetime of 2^3S_1 Li^+ , the 47 ± 16 s lifetime of $^5D_{5/2}$ Ba^+ , the 17.5 ± 4 s lifetime of $^5D_{3/2}$ Ba^+ , and the 0.090 ± 0.015 s lifetime of $^2D_{5/2}$ Hg^+ have been measured in ion traps by optical pumping schemes.² Knight has measured a 4.2 ± 0.6 ms lifetime for metastable $^5S_2$ N^+ by directly observing the decay of the spontaneous emission.³ Several workers have used rf quadrupole⁴ and ICR traps⁵ to determine allowed radiative lifetimes and collisional deactivation rates for molecular ions using laser induced fluorescence.

The confinement of ions in three dimensional radio frequency quadrupole (Paul) traps is well established. Because the equation of motion of ions can be solved analytically, the properties of quadrupole traps are well understood.^{6,7} Trapping properties are not however limited to quadrupole fields. In an oscillating, spatially inhomogeneous electric field the trajectory of a slowly moving ion can be separated into a fast, small amplitude oscillation (the micromotion) and a slower time-averaged motion,^{6,8} provided the frequency of oscillation is fast relative to the ion velocity. The micromotion creates an adiabatic effective potential for the time-averaged motion.

Teloy and Gerlich have pioneered the use of inhomogeneous rf fields for confining, guiding and trapping ions.^{9,10} For an ideal rf electric multipole field with $2n$ poles, the effective potential is given by

$$U_{\text{eff}}(r) = n^2 K \left(\frac{r}{r_0} \right)^{2n-2} \quad (1)$$

where

$$K = \frac{q^2 V_0^2}{4m\omega^2 r_0^2} \quad (2)$$

for a particle of charge q and mass m inside a multipole of radius r_0 . The voltage of the rf is V_0 , the frequency ω . For a dipole field, $n = 1$, for a quadrupole $n = 2$, and for an octopole field $n = 4$. These trapping potentials are valid within certain limits, which are discussed in detail by Teloy and Gerlich.

The rf octopole was primarily developed to guide low energy ions in experiments measuring integral cross sections of ion-molecule reactions.^{9,10,11} For a rf octopole field, the effective potential varies as $(r/r_0)^6$ while for a quadrupole field, it varies as $(r/r_0)^2$. Ions in the center of an octopole trap are thus less perturbed by the oscillating fields. Furthermore, the octopole trapping well is four times deeper than the quadrupole well at the same frequency, voltage, and mass. Thus, the octopole potential is flatter in the center and has steeper walls than the quadrupole effective potential. The depth of the trap also depends inversely on the mass; therefore, fragments created in the trap by photodissociation will experience a deeper potential well than their heavier parent ions. Further details can be found in discussions by Teloy and Gerlich^{9,10}, and by Ervin and Armentrout.¹¹

The octopole guide is made of eight parallel molybdenum rods, 50 cm long, 0.32 cm in diameter, equally spaced on a 1.25 cm diameter circle. Molybdenum is used to minimize surface charge, which would adversely affect low energy ions. Alternate rods of the octopole are at opposite phases. The leads are connected to a coil, and the octopole acts as the capacitor in the resulting resonant LC circuit. The circuit is driven inductively by a small rf power supply. The rf frequency is 14 MHz, with an amplitude of ~ 250 V. The rods are thicker than those used by Ervin and Armentrout.¹¹ As a result, the field probably deviates more from a pure hyperbolic octopole field, but the trapping volume is shielded more effectively from

potentials outside the trap.

The radio-frequency traps the ions radially, transverse to the axis of the ion octopole. The ions are confined inside the trap by raising the dc potential of the entrance and exit lens elements at either end of the rods. These lenses protrude into the trap, to minimize problems while trapping with rf fringe fields at the ends of the trap. The ions would thus bounce back and forth between these elements. To trap the ions, the potential of the lens was typically 10 V above the dc bias of the rods. When trapped, the average energy of the ions was about 0.65 eV.

For the quadrupole rf field, Dawson has shown that only certain initial ion trajectories found within an acceptance ellipse in phase space will be trapped.¹² Those with initial momenta or spatial position outside the acceptance ellipse are unstable and will be ejected. Similar conditions are imposed on the initial ion trajectories for the octopole trap. Approximately 50% of the parent ions are lost in the first 50 ms; however, the remaining ions are efficiently trapped. In an experiment with molecular oxygen ions, no additional loss of O_2^+ was observed for trapping times as long as 5 s.

B. Experimental Details

Fig. 1 is a schematic drawing of the machine. Ions were produced by a variety of sources, to be described later chapters. They included electron impact ionization, hot cathode discharge and high pressure corona discharge sources. In a typical experiment, the ions were extracted from the source, accelerated to about 350 eV, selected by a sector magnet mass filter, deflected 90°, and then pulsed into the ion trap. After a selected delay time, a pulsed laser was fired into the trap to dissociate the ions in the metastable state. The ions were released from the trap through the exit lens element. Products were selected by a final quadrupole mass filter,

and then counted by the ion detection system. The radio frequency applied to the trap was turned off for 5 ms to ensure that the ion trap was free of ions at the start of the next data cycle. The sequence was repeated—without the laser firing—to measure the background product ion counts. In the case of negative ions, the parent mas was detected, and subtraction of the background gave the laser-induced depletion. Spectra could be taken by scanning the wavelength of a tunable dye laser while keeping the trapping time fixed. Lifetimes were measured at fixed laser wavelengths by incrementing the trapping time.

The ions were focused, and then accelerated to 350 eV. The ions passed through a second differential chamber with ion optics, maintained at approximately 2×10^{-7} torr by a liquid-nitrogen trapped six inch diffusion pump. The ion beam was mass-selected by a 60° sector magnet mass analyzer with a 20 cm radius of curvature. To enhance the resolution and transmission, we used electrostatic quadrupole lens pairs¹³ to focus the beam when it entered into and exited from the magnetic field. The analyzer was scanned by tuning the magnetic field; the flight tube was at ground. Resolution was typically $M/\Delta M=150$ or better at an ion energy of 350 eV. Differential pumping kept the pressure in the mass analyzer region at approximately 2×10^{-8} torr.

After leaving the mass analyzer, the ions passed through a small tube which limited conductance between the sector magnet region and the ultrahigh vacuum chamber. The latter region was kept at pressures of approximately 8×10^{-10} torr by a 220 l/s ion pump. An electrostatic quadrupole field deflector, based on the design of Zeman,¹⁴ bent the ion beam by 90° into a path collinear with the laser. This deflector allowed the two beams to merge without introducing apertures which would perturb the field. The poles of the deflector were circular, approximating the hyperbolic equipotential surfaces of a quadrupole field. The fields of the poles

were terminated by grounded plates, but there were no shim electrodes to correct for aberrations. The ions were then slowed to about 5 eV by a constant gradient decelerator and focused into the trap, where their final energy was approximately 0.5 eV.

To trap the ions, the voltage of the input lens was kept low for 0.6 ms to focus the ions into the trap, then raised. The ions were kept in the trap for a delay time generated by the LSI-11 computer. The laser was then fired (on alternate cycles). The voltage of the exit lens element was lowered for 4.5 ms to release the ions.

After the ions left the trap, they were focused into a quadrupole mass spectrometer (Extranuclear Laboratories) and then detected using either a Ceratron (muRata Corp.) ceramic electron multiplier or a Daly detector.¹⁸ In this experiment, measurements were made by pulse counting, using the Daly detector only. Data acquisition was controlled by a Digital Equipment Corporation LSI-11 microcomputer interfaced with a Kinetic Systems CAMAC Crate.

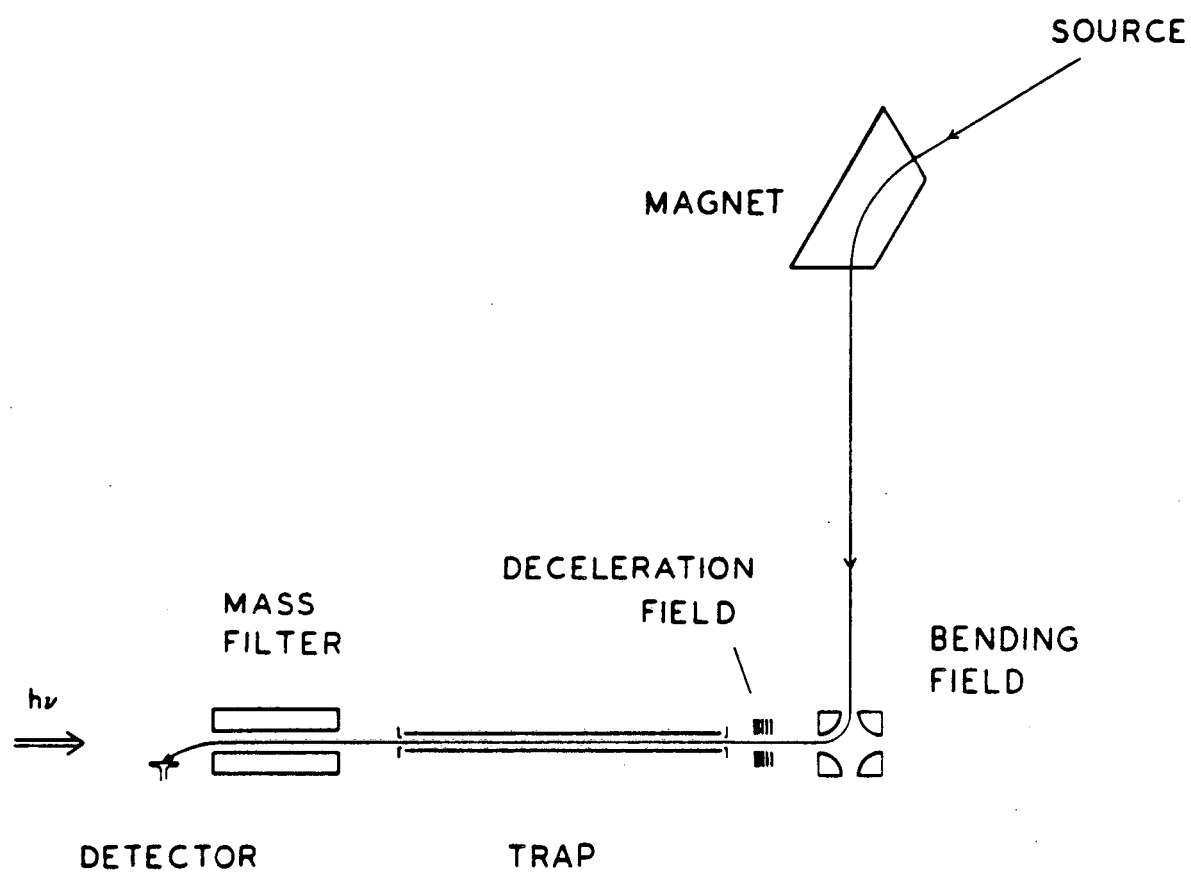
The spectrometer was built so that the laser beam could pass completely through the machine without striking any obstructions. The quadrupole mass filter, the octopole ion guide, and the ion optics were all collinear with the laser beam, while the detector components were off-axis. The laser beam entered the vacuum chamber through a sapphire window, down the axis of the ion optics, through the quadrupole deflection field, and out a second window. This design prevented spurious laser-correlated signal from photoelectrons or desorption caused by the laser pulse striking metal surfaces.

REFERENCES

1. S. W. Bustamente, Ph.D. thesis, University of California, Berkeley, 1983.
2. R. Schneider and G. Werth, *Z. Phys.* **A293**, 103 (1979).
3. R. D. Knight, *Phys. Rev. Lett.* **48**, 792 (1982).
4. C. C. Martner, J. Pfaff, N. H. Rosenbaum, A. O'Keefe, and R. J. Saykally, *J. Chem. Phys.* **78**, 7073 (1983) and references therein.
5. J. Danon, G. Mauclaire, T. R. Govers, and R. Marx, *J. Chem. Phys.* **76**, 1255 (1982).
6. H. G. Dehmelt, *Adv. At. Mol. Phys.* **3**, 53 (1967) ; *ibid.* **5**, 109 (1969).
7. D. J. Wineland, W. M. Itano, and R. S. van Dyck, *Adv. At. Mol. Phys.* **19**, 135 (1983).
8. L. D. Landau and E. Lifschitz, *Mechanics* (Pergamon Press, Oxford, 1960).
9. E. Teloy and D. Gerlich, *Chem. Phys.* **4**, 417 (1974).
10. D. Gerlich, in *Electronic and Atomic Collisions* (edited by D. C. Lorents, W. E. Meyerhof, and J. R. Peterson) (North-Holland, Amsterdam, 1985).
11. K. M. Ervin and P. B. Armentrout, *J. Chem. Phys.* **83**, 166 (1985).
12. P. H. Dawson and J. E. Fulford, *Int. J. Mass Spectrom. Ion Phys.* **42**, 195 (1982).
13. H. A. Enge, *Rev. Sci. Instrum.* **30**, 248 (1959).
14. H. D. Zeman, *Rev. Sci. Instrum.* **48**, 1079 (1977).
15. R. N. Daly, *Rev. Sci. Instrum.* **31**, 264 (1960).

FIGURE CAPTIONS

FIG. 1 Schematic of the ion photodissociation spectrometer. The ions are formed in a differentially pumped source region. The ions are then extracted, accelerated, mass selected by the sector magnet, decelerated, and trapped in the rf octopole ion trap. After photolysis of the trapped ions with a laser, the products are released from the trap and mass analyzed with a quadrupole mass spectrometer.



XBL 847-3011

FIG. 1

Chapter 2

Radiative Decay of Vibrationally Excited CH_2^-

I. INTRODUCTION

Hot bands are a potential problem in threshold measurements made by photoelectron and photodetachment spectroscopy of negative ions.^{1,2,3} The difficulty in creating a sufficient current of negative ions often forces experimentalists to use discharge, sputter and other high temperature ion sources. A large fraction of the ions produced in these sources may be in vibrationally excited states; and the task is to identify the signal arising from these states. Normally, the intensity of these hot bands can be altered by changes in sources, precursor gases, and extraction voltage, which affect the vibrational temperature. Frequency shifts from isotopic substitution can also help to assign hot bands. While these methods are usually sufficient, in the case of the photoelectron spectrum of methylene such an analysis failed to correctly establish the presence of hot bands.

The ground $\tilde{X}^2B_1$ state of the anion CH_2^- is similar in geometry to the $\tilde{a}^1A_1$ of the neutral, because the extra electron is in a non-bonding $1b_1$ orbital perpendicular to the plane of the molecule. As a result, detachment occurs primarily by bending transitions with $\Delta v_2 = 0$. This has been observed in the photoelectron spectrum^{4,5} as a single large peak, and in the photodetachment spectrum⁶ as a sharp threshold. In photodetachment to the ground $\tilde{X}^3B_1$ state of CH_2 , an electron in a slightly bonding $3a_1$ orbital is removed. There is a significant change in bond angle from

102.7° to 133.8°, and in the energy of the linear configuration, from 11500 cm⁻¹ to 1938 cm⁻¹. The poor Franck Condon factors for the $\Delta v_2 = 0$ bending transitions result in an extended vibrational progression above threshold, making it difficult to distinguish the true origin from the hot bands, which are weak steps below threshold.

Engelking *et al.*⁵ concluded that no hot bands were present in the photoelectron spectrum of CH₂⁻. They placed the threshold for detachment to the ground $\tilde{X}^3B_1$ state at the origin of the observed vibrational progression. The resulting electron affinity of 1630 cm⁻¹ for the ground state $\tilde{X}^3B_1$ (0.210 eV) led to a controversial value of $T_0 = 6820$ cm⁻¹ (0.84 eV or 19.5 kcal/mol) for the $\tilde{a}^1A_1$ state of CH₂⁻. The weight of experimental and theoretical work on methylene contradicted this result, and results from molecular beam photodissociation of ketene⁷ and high resolution LMR spectroscopy of methylene⁸ soon followed. The spectroscopic work gave a definitive value of 3165 ± 20 cm⁻¹ (0.392 eV ± 0.003 eV or 9.1 kcal/mol for the splitting between the singlet and triplet states.

Shavitt⁹ has given an excellent review of the controversy over the singlet-triplet gap. A correct simulation¹⁰ based on accurate spectroscopic constants fits the photoelectron spectrum of hot CH₂⁻ with an electron affinity of 5250 ± 160 cm⁻¹ (0.65 ± 0.02 eV) and a vibrational temperature of 2500K. The evidence now indicates that three (or possibly four) hot bands were present in the photoelectron spectrum, as was first suggested by Harding and Goddard¹¹ based on their ab initio GVB calculations. Recently, using an improved photoelectron spectrometer, Lineberger and co-workers^{12,13} were able to obtain well resolved spectrum of vibrationally cool CH₂⁻ formed in a flowing afterglow source. These new spectra confirm the expected value for the electron affinity and provide improved spectroscopic constants for the anion.¹⁴

In this chapter, we describe an experiment in which we measured the time dependence of photodetachment from CH_2^- at frequencies near threshold. By allowing the ions to cool radiatively in a trap for times up to 0.5 s before photodetachment, we have directly observed the existence of vibrationally excited states of CH_2^- formed in a hot cathode discharge. From the decay of the photodetachment signal at 4700 cm^{-1} , arising solely from hot band intensity, we have attempted to determine lifetimes for these states. Our work has stimulated Lee, Handy and Schaefer to perform very high level *ab initio* calculations of the radiative lifetimes of the ν_2 bending states.¹⁵ Because the CH_2^- bending vibration is a large amplitude motion, a large part of the potential and dipole surface are sampled. Such calculations are relatively difficult, and have not been systematically investigated. Furthermore, there are few calculations of vibrational intensities or lifetimes for polyatomic ions whose accuracy can be verified by experiment.

II. EXPERIMENTAL

Our approach is to store the CH_2^- in a high vacuum ion trap, and probe the radiative decay of vibrationally excited ions at various storage times by measuring the photodetachment signal, using photons of energy above and below the electron affinity. To obtain the decay rates, we increment the trap residence time and measure the photodetachment at each step. In our experiment, we observe the depletion of the parent anion population caused by photodetachment with infrared light. The signal is thus the sum over all energetically allowed transitions. At photon energies immediately above the electron affinity, all vibrational states can be photodetached, although the ground vibrational state can only detach by a $\Delta\nu_2 = 0$ transition. Due to the poor Franck-Condon factors, one expects a weak contribution from $\nu_2'' = 0$ despite its large population. Because the higher bending states have a larger cross

section, one expects a decay of the photodetachment signal to a constant level as the vibrationally excited CH_2^- relax. Below threshold, only the vibrationally excited states are photodetached. As we trap the ions for longer times, signal from the excited states will disappear, and the photodetachment should decrease to the ground state intensity for each frequency.

A 1-2 ms pulse of CH_2^- from a mass spectrometer is injected into a half meter long radio frequency (rf) ion trap. The ions are stored for some variable duration, after which a tunable infrared laser is fired into the trap. The ions are released, mass analyzed, and counted. The same cycle is repeated without the laser, to measure the background count rate. After summing over many cycles, the difference gives the average depletion caused by photodetachment. The experiment is performed by measuring the depletion while varying the trapping time at a fixed laser frequency. After normalizing to the background, the signal is independent of the time dependent trapping efficiency, low frequency plasma fluctuations, and other noise not correlated with the laser.

The CH_2^- are created by a hot cathode duoplasmatron, in a discharge of 60-300 millitorr of methane, with an emission current of about 1 milliamp. The ions are accelerated to 360 eV, and mass analyzed by a 60° sector magnet. The ion beam enters the ultra-high vacuum region where it is bent 90° by an electrostatic quadrupole deflection field into an axis collinear with the laser beam, and decelerated to 1 eV.

The ions are trapped inside a radio frequency octopole ion guide based on the design of Teloy and Gerlich.¹⁶ It consists of eight molybdenum rods, 50 cm long and 3 mm in diameter, positioned symmetrically on a 12.5 mm diameter circle. Approximately 150V of radio frequency are applied to the octopole rods, creating an effective potential that traps the ions transverse to the axis of the guide. By raising the potential of the lens elements at the entrance and exit of the ion guide,

these elements act as electrostatic mirrors, and the ions are confined within the trap. The ions are pulsed into the trap by lowering the voltage of the entrance lens element for 1-2 ms. After a computer-generated delay, the ions are released through the exit lens. The pressure in the trap region is typically below 5×10^{-9} torr. Collisions within the trap become important for times greater than one second.

The laser beam is collinear with the axis of the trap, and passes completely through the machine, entering and exiting through two sapphire windows. This arrangement minimizes light scattering and reduces problems due to desorption or photoionization as the light strikes surfaces in the machine. No depletion was observed using ions with higher thresholds; hence, no laser correlated noise was evident.

Tunable infrared radiation is generated by an optical parametric oscillator (OPO) similar to that developed by Byer.¹⁷ A LiNbO_3 crystal in a resonant cavity is pumped in the far field of a Quanta Ray Nd:YAG laser at 1.06μ . For frequencies from 5000 cm^{-1} to 7000 cm^{-1} it produces 10 ns pulses of 8-12 mJ at a 10 Hz repetition rate. There is no grating in the cavity, so the linewidths are typically $4\text{-}10 \text{ cm}^{-1}$, sufficient for the current experiment. The linewidth and divergence are anomalously large near 4700 cm^{-1} , where the two frequencies created by the OPO become degenerate. At degeneracy, the linewidth is about 200 cm^{-1} FWHM, the energy 13-16 mJ per pulse.

III. RESULTS

The time dependence of the photodetachment was taken at three frequencies: 4700 cm^{-1} , 5690 cm^{-1} and 6320 cm^{-1} . Photodetachment at 4700 cm^{-1} is below the expected threshold of 5250 cm^{-1} (0.65 eV). Three time ranges were scanned: 1 ms to 37 ms; 1 ms to 153 ms (at 4700 cm^{-1} only), and 1 ms to 501 ms.

The decay curves taken with photon energies above threshold are shown in Fig. 1. These curves are normalized to unity at $t=1$ ms. At both 5690 cm^{-1} and 6320 cm^{-1} , the signal decreases by about a factor of two within the first 200 ms, but then remains almost constant for times up to 500 ms. If we assume that the ions have almost cooled by 500 ms, then the photodetachment at that time will arise primarily from the ground vibrational state. The decay curve at 4700 cm^{-1} , shown in Fig. 2, is qualitatively different; the photodetachment signal has decreased by an order of magnitude at 500 ms. These observations clearly demonstrate the presence of excited states of the anion. The observed decay behavior suggest that the electron affinity of ground state CH_2 is bracketed by 4700 cm^{-1} and 5690 cm^{-1} , in agreement with the accepted results.

The decay of the photodetachment signal at 4700 cm^{-1} shown in Fig. 2 is clearly not a single exponential. In contrast, at a photon energy of 9398 cm^{-1} , approximately 67% of the ions are photodetached at all trapping times. The power dependence, shown in Fig. 3, reveals at least three different components, two of which are saturated. After 30 ms, the state with the largest cross-section has disappeared.

The photon energy of 4700 cm^{-1} is 500 cm^{-1} less than the electron binding energy. The multiple exponential decay arises because all states with more than 500 cm^{-1} of internal energy can in principle be photodetached. Assuming a temperature of 2500 K, derived from the photoelectron spectra by Sears and Bunker,¹⁰ the relative v_2 populations are 53%, 25%, 12%, 6%, and 3% for $v_2 = 0$ through 4. The contribution from each v_2 state depends upon the Franck-Condon factors as well as the number of final v_2 states accessible.

The problem of cascading decays of an N-level system is an elementary problem of formal kinetics, for which the set of first order differential equations can be solved analytically. The solution requires initial populations, all decay rates A_{ij} , and, for

our data, relative photodetachment cross-sections σ_i . A unique fit of our data with such a large number of parameters is impossible, but the solution can be reduced to a simple sum of exponentials

$$Y(t) = \sum_{i=1}^N Y_i e^{-t/\tau_i} \quad (1)$$

where τ_i is the radiative decay rate of the i th level, and the effective pre-exponential factor Y_i is a function of the initial populations, the A_i 's, and the cross-sections. The data were fit to Eq. 1 using the A_i 's and the Y_i 's as parameters.

The data were fit by a weighted nonlinear least squares to the sum of exponentials. Such a fit is notoriously difficult, especially if the decay rates are similar. We fit the data to a sum of three exponentials, and obtained lifetimes of 14^{+7}_{-7} ms, 70^{+50}_{-40} ms, and $524^{+\infty}_{-280}$ ms. In general, the most reliable fits require data over a time span covering at least two lifetimes. The large uncertainty in the longest lifetime stems from the lack of data beyond 500 ms. The relatively large uncertainties in the other lifetimes primarily reflect the extent to which these parameters are correlated with τ_1 .

A biexponential decay mechanism, yielding lifetimes of 20 ms and 296 ms, gave a significantly poorer fit. The signal-to-noise ratio was too poor to yield a unique fit to a four exponential model.

IV. DISCUSSION

Theoretical results obtained by Lee *et al.*¹⁵ are listed in Table I. These calculations used correlated functions with very diffuse basis sets, in order to accurately calculate properties of the anion. Both the bending potential and the dipole moment function were calculated over a wide range of bending angles ($\rho = -120^\circ$ to $+120^\circ$). Vibrational wavefunctions and rotationless transition moments were ob-

tained numerically using the semi-rigid bender Hamiltonian. The semi-rigid bender model should provide a far more accurate treatment of the large amplitude bending modes of CH_2^- than any harmonic approximation. Information on the CH stretching frequencies and transition moments were also calculated, but only within the double harmonic approximation (these results are discussed below).

We have initially assigned the three observed decays of 525, 70, and 14 ms to $v_2 = 1, 2$, and 3 respectively. The longest lifetime, 525 ms, agrees reasonably well with our theoretical $v_2 = 1$ lifetime of 431 ms. The latter is the most reliable of the theoretical lifetimes. The experimental values for the $v_2=2$ and $v_2=3$, 70 ms and 14 ms, however, are significantly smaller than the theoretical values of 207 ms and 108 ms. Thus, the lifetimes obtained from a fit with a three exponential model do not agree with theory.

The five- to seven-fold decrease in the experimental lifetimes with vibrational quantum number, however, seems anomalously large. The theoretical lifetimes decrease by only a factor of about two for each additional quantum in the bending mode. It is quite possible that an additional component with an intermediate lifetime is present but cannot be extracted from the data due to the signal-to-noise. Examination of the data reveals that there are not enough data points between 150 and 300 ms to preclude the existence of a such a component.

The discrepancy between the results of the fit and theory therefore indicate that four exponentials may be necessary. Although an unconstrained fit (eight parameters) of the data to a sum of four exponentials does not yield a unique result, we can fit the data if we reduce the number of variables. The trend in the theoretical results suggest that we can assume a geometric progression for the four lifetimes. We have thus performed several fits holding the ratio τ_i/τ_{i+1} constant. The range of lifetimes is large, and the lowest value of τ_i/τ_{i+1} that fits the data

is 3.0, with lifetimes of 15 ms, 45 ms, 135 ms, and 405 ms. The $v_2=1$ lifetime agrees with the computational value, and the $v_2=2$ lifetime is somewhat closer to the theoretical result, but the two smaller lifetimes are still significantly less than theory. Therefore, the lifetimes extracted from the data using a four component model with constant τ_i/τ_{i+1} still do not completely agree with the results of the *ab initio* calculation. Furthermore, the ratio $\tau_i/\tau_{i+1}=2.5$ gives a fit one standard error worse than the best fit, with lifetimes of 19 ms, 47 ms, 118 ms, and 296 ms. Thus, we cannot fit the data with the theoretical τ_i/τ_{i+1} of approximately two for a geometric progression of four lifetimes.

We have also tried to fit the experimentally observed curve in Fig. 1, setting all the A_i to the theoretical values, but have found that the data cannot be fit. The dashed curve in Fig. 2 is the result of such an attempt. Despite the ambiguities in fitting a multiple exponential decay, it is clear that the theoretical values for $v_2 = 1$ through 4 alone cannot reproduce the experimentally observed decay. The problem lies at the shortest times ($t < 30$ ms), where the experimental signal-to-noise is best, and the theory is the most uncertain.

The deviation of the dashed curve from the data suggest an alternative explanation for the disagreement. If the theoretical values for A_i for $i = 1, 2$, and 3 are used, along with a fourth decay that is allowed to vary, the data can be fit, with $\tau_4 = 15$ ms. This result implies that the theoretical results would be consistent with experiment if one postulates an alternative relaxation mechanism giving rise to a fast decay. We next consider possible sources for a fast decaying component.

One possibility is that the $v_2=5$ is populated, and contributes to the signal; however, Lee, Handy, and Schaefer have predicted that this state will have a lifetime of 40 ms, based on calculations with a TZ+diffuse+4P basis set. This lifetime is substantially longer than 14 ms. In addition, two objections might be raised. First,

even at a vibrational temperature of 2500 K, only 1.5% of the total population is expected to be in this level. Second, $\nu_2=5$ lies well above the threshold for electron detachment, and is therefore only metastable to electron loss.

The fast decay component could be the result of an experimental artifact; however, we have made a similar measurement of the excited state lifetimes of CH^- under almost identical experimental conditions, and observed lifetimes of 1.75 ms and 5.9 s,¹⁸ but no evidence for a decay of 14 ms. For that system, we also found that collision-induced decay rates were much less than 1 s^{-1} . At the pressure used in this experiment, it is unlikely that collisions would be responsible for a process with a lifetime as fast as 14 ms. Furthermore, contamination from other species is probably not a problem. The mass resolution of the sector magnet is high: $\Delta M/M \approx 150$. The only contaminants would be isotopes of CH^- , but the lifetimes we observed for CH^- would not account for a 14 ms decay. We therefore believe that the 14 ms lifetime arises from the decay of an excited state of CH_2^- .

We have thus far neglected contributions from the excited stretches $\nu_1=1$ and $\nu_3=1$. Based on isotope shifts and the Teller-Redlich rule, Leopold *et al.* estimate that the CH_2^- vibrational frequencies for ν_1 and ν_3 are 2580 cm^{-1} and 2635 cm^{-1} respectively.¹³ The theoretical harmonic values (2782 cm^{-1} and 2841 cm^{-1} respectively) are in reasonable agreement with these estimates, with both theoretical values being 7.8% higher. Bunker and Langhoff¹⁹ have calculated the stretching transition moments for the neutral $\tilde{a}^1A_1 \text{ CH}_2$, in the double harmonic approximation. These yield radiative lifetimes of approximately 15 and 28 ms for ν_1 and ν_3 respectively. These lifetimes match the fast component we observed. However, the analogous calculation for CH_2^- yields lifetimes of 1.6 ms and 2.7 ms respectively for the ν_1 and ν_3 modes. These excited states, however, are expected to have very small relative cross sections for photodetachment. The small change in the CH bond

length results in very poor Franck Condon factors for transitions of the stretches with $\Delta v \neq 0$. No such transitions were reported in any of the photoelectron spectra published to date. We observed, however, that the fast component possessed a large relative cross section; the transition appeared to be saturated at the intensities used in our experiment. Thus, it is difficult to reconcile the observed cross section with the expected poor Franck-Condon overlap, and the estimated lifetimes of the stretches are not entirely consistent either.

In their calculation, Lee *et al.* did not consider the possibility of a Fermi resonance. Because the stretching modes have relatively large transition moments, the strong coupling of a stretching mode with a bending level $v_2 = n$ could greatly reduce the lifetime of the latter. The $v_2 = 1$ frequency of 2580 cm^{-1} estimated by Leopold *et al.* is very close to the $v_2 = 2$ level at 2574 cm^{-1} obtained from our best potential, but the actual frequencies are not known well enough.

Another possibility is that we are observing vibrational autodetachment of highly excited rovibrational states with energies above the electron affinity. The $v_2=4$ state, for instance, lies very close to the electron continuum. In order for the electron of a vibrationally excited anion to detach, the mechanism must involve a breakdown of the Born-Oppenheimer approximation. Very little is known about vibrational autodetachment rates. Our fast component decays at a rate that is four to seven orders of magnitude slower than the NH^- rotational autodetachment rates observed by Neumark, Lykke, Andersen, and Lineberger,²⁰ and three orders of magnitude slower than the SF_6^- autodetachment rates.²¹ These experiments are sensitive to fast processes, and cannot measure slower rates, whereas the experiment reported here can only measure long decays. Thus, long-lived autodetaching states may have been present but unobserved in the earlier experiments. However, CH_2^- that are metastable to detachment are unlikely to be long-lived. There is a crossing of

the CH_2^- anion and neutral potential energy curves near $v_2 = 0$ of the neutral.^{11,14} The propensity rules of Simons indicate that such a crossing would result in rapid electron detachment from any anion states above the detachment threshold.²²

None of these possibilities is entirely satisfactory. Thus, the identity of a component with $\tau=14$ ms remains unclear, and the discrepancy between *ab initio* results and the experimental data is unresolved.

V. CONCLUSIONS

We have observed the presence of vibrationally excited CH_2^- created in a discharge, by measuring the photodetachment from CH_2^- as it radiatively relaxes in a high vacuum ion trap. We have used a tunable infrared laser to produce photons with energies above and below the expected threshold for removing an electron from the ground state. The time dependence of the photodetachment at three photon energies differ, and are consistent with the electron affinity of 5250 cm^{-1} (0.65 eV) obtained by previous workers for the ground $\tilde{X}^3B_1$ state of methylene.

The photodetachment signal at 4700 cm^{-1} thus arises solely from vibrationally excited CH_2^- . We have fit the observed decay to a three exponential model and determined lifetimes of $525_{-230}^{+\infty}$ ms, 70_{-40}^{+50} ms, and 14_{-7}^{+7} ms for $v_2 = 1, 2$, and 3. The best theoretical estimates of the radiative decay lifetimes of the bending mode of CH_2^- are 431 ms, 207 ms, 118 ms, and 68 ms for $v_2 = 1$ through 4. The last two experimental values are significantly smaller than the theoretical predictions. If the data are fit to a sum of four exponentials (assuming a geometric progression of lifetimes), we again find that the two shortest lifetimes are less than the theoretical values. We have considered several possibilities for the discrepancy, including alternative mechanisms resulting in a short lived state of CH_2^- , but have not resolved the disagreement.

REFERENCES

1. R. R. Corderman and W. C. Lineberger, *Annu. Rev. Phys. Chem.* **30**, 347 (1979).
2. B. K. Janousek and J. I. Brauman, in *Gas Phase Ion Chemistry* (edited by M. T. Bowers) (Academic Press, New York, 1979).
3. P. S. Drzaic, J. Marks, and J. I. Brauman, in *Gas Phase Ion Chemistry* (edited by M. T. Bowers) 167 (Academic Press, New York, 1984).
4. P. F. Zittel, G. B. Ellison, S. V. O'Neil, E. Herbst, W. C. Lineberger, and W. P. Reinhardt, *J. Am. Chem. Soc.* **98**, 3731 (1976).
5. P. C. Engelking, R. R. Corderman, J. J. Wendoloski, G. B. Ellison, S. V. O'Neil, and W. C. Lineberger, *J. Chem. Phys.* **74**, 5460 (1981).
6. D. Feldmann, R. Rackwitz, H. J. Kaiser, and E. Heinicke, *Z. Naturforsch.* **32A**, 600 (1977).
7. C. C. Hayden, D. N. Neumark, K. Shobatake, R. K. Sparks, and Y. T. Lee, *J. Chem. Phys.* **76**, 3607 (1982).
8. A. R. W. McKellar, P. R. Bunker, T. J. Sears, K. M. Evenson, R. J. Saykally, and S. R. Langhoff, *J. Chem. Phys.* **79**, 5251 (1983).
9. I. Shavitt, *Tetrahedron* **41**, 1531 (1985).
10. T. J. Sears and P. R. Bunker, *J. Chem. Phys.* **79**, 5265 (1983).
11. L. B. Harding and W. A. Goddard III, *Chem. Phys. Lett.* **55**, 217 (1978).
12. D. G. Leopold, K. K. Murray, and W. C. Lineberger, *J. Chem. Phys.* **81**, 1048 (1984).

13. D. G. Leopold, K. K. Murray, A. E. Stevens Miller, and W. C. Lineberger, J. Chem. Phys. **83**, 4849 (1985).
14. T. J. Sears and P. R. Bunker, J. Chem. Phys. **83**, 4856 (1985).
15. T. J. Lee, N. C. Handy, and H. F. Schaefer III private communication.
16. E. Teloy and D. Gerlich, Chem. Phys. **4**, 417 (1974).
17. S. J. Brosnan and R. L. Byer, IEEE J. Quant. Electr. **15**, 415 (1979).
18. See Chapter 3.
19. P. R. Bunker and S. R. Langhoff, J. Mol. Spectrosc. **102**, 204 (1983).
20. D. N. Neumark, K. R. Lykke, T. Andersen, and W. C. Lineberger, J. Chem. Phys. **83**, 4364 (1985).
21. J. E. Delmore and A. D. Appelhans, J. Chem. Phys. **84**, 6238 (1986).
22. J. P. Simons, J. Am. Chem. Soc. **103**, 3971 (1981).

TABLE I. Energy levels and radiative decay lifetimes of v_2 bending levels of $\tilde{X}^2B_1$ CH_2^- .

v_2	Energy, cm^{-1}		Lifetime, ms				
	<i>ab initio</i> ^a	Empirical ^b	<i>ab initio</i> ^a	Expt., 3 τ_i fit ^c		Expt., 4 τ_i fit ^d	
				Y_i	τ_i	Y_i	τ_i
1	1295	1230	431(574)	2.6%	525	3.1%	405
2	2572	2439	207(232)	3.2%	70	0.6%	135
3	3827	3622	118(114)	3.0%	14	2.3%	45
4	5051	4778	68(60)			2.8%	15
5			40				

^aSemi-rigid bender result using potential and dipole surface from CISD calculation with TZ+diffuse+4P basis set. Numbers in parentheses use TZ + diffuse + 3P basis set. From Lee *et al.*, Ref. 15.

^bFrom semi-rigid bender analysis of high resolution photoelectron spectroscopy of CH_2^- . See Ref. 13 through 15.

^cThis work.

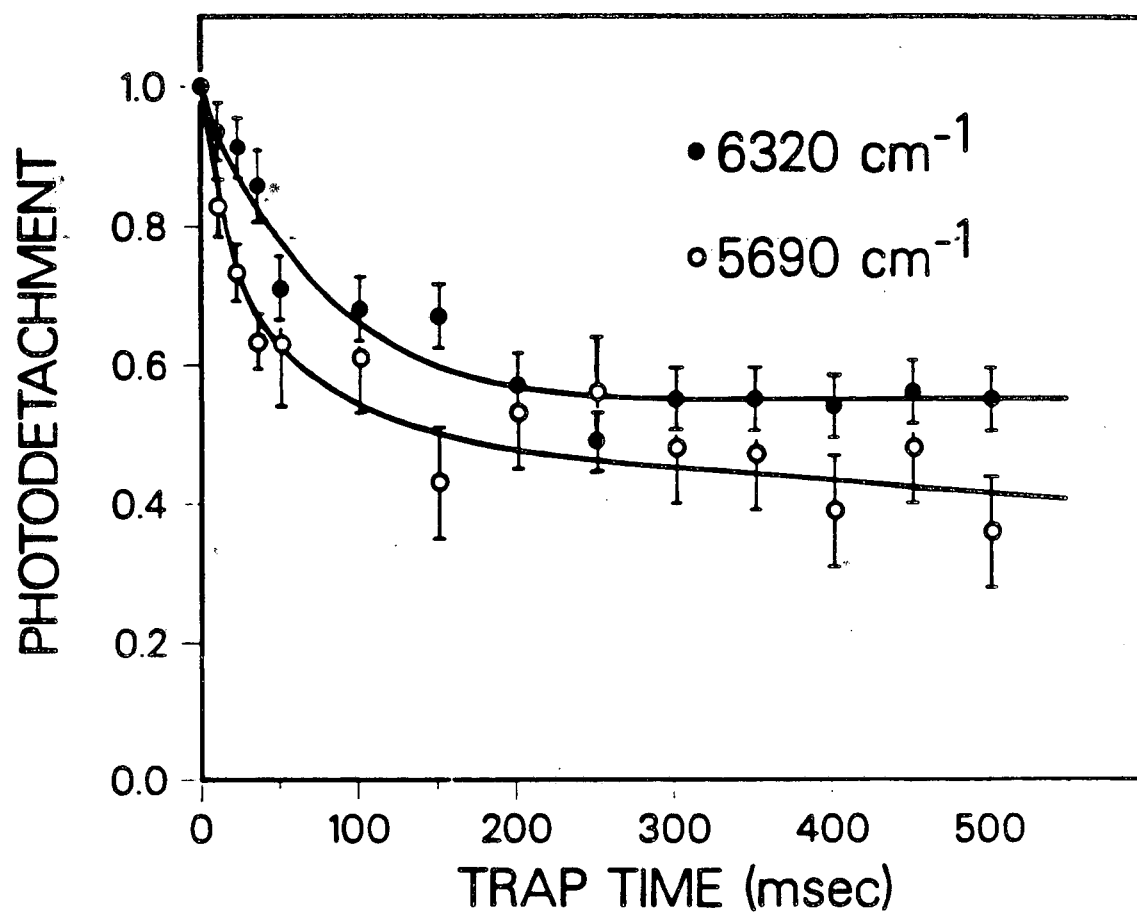
^dThis work. The four τ_i are constrained to a geometric progression with ratio $\tau_i/\tau_{i+1} = 3.0$.

FIGURE CAPTIONS

FIG. 1 Photodetachment signal from CH_2^- as a function of trapping time, normalized to unity at $t=1$ ms. Laser frequencies are above the detachment threshold at 6320 cm^{-1} and 5690 cm^{-1} .

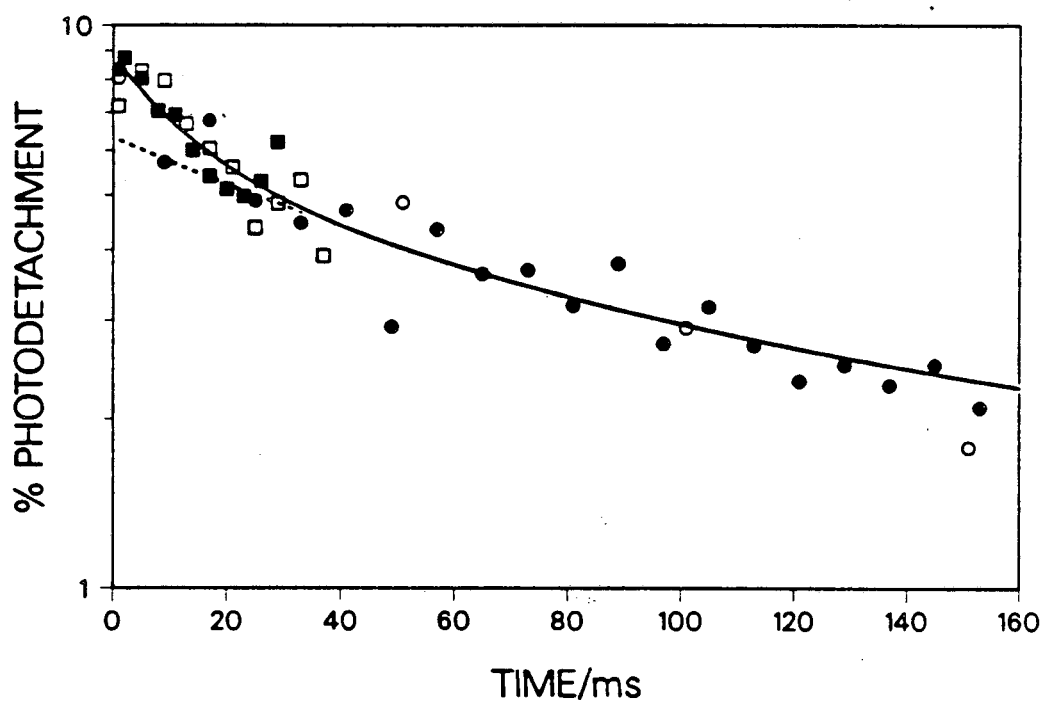
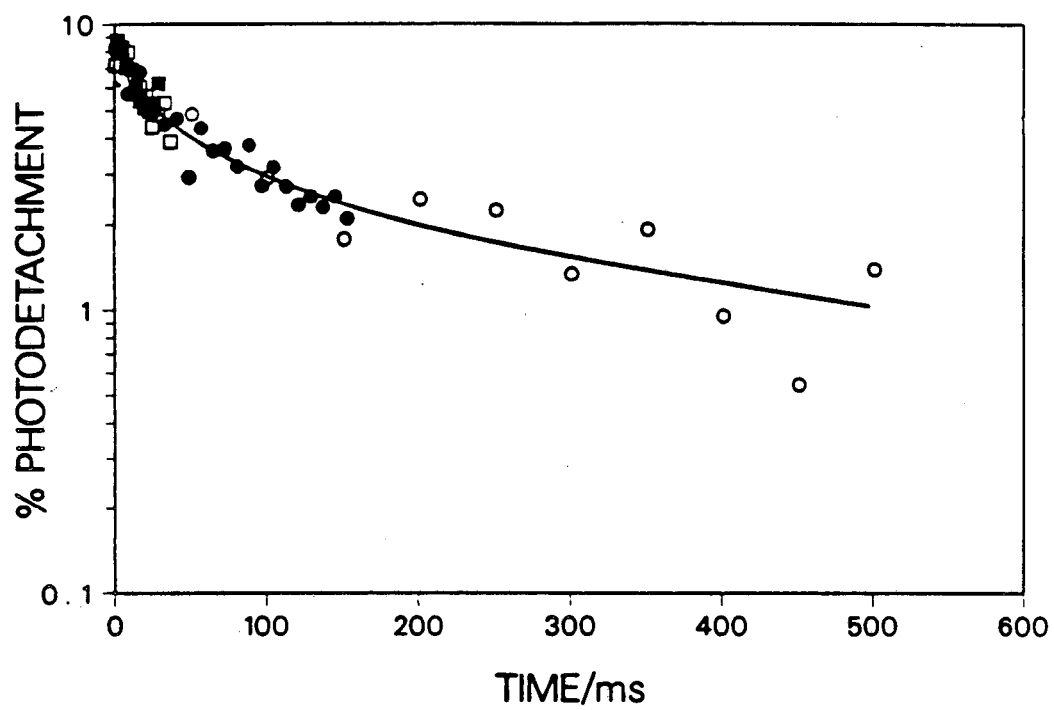
FIG. 2 Decay of the photodetachment signal at 4700 cm^{-1} . Curve is best fit of a triple exponential to the data, with lifetimes of 525 ms, 70 ms, and 14 ms. Lower plot shows detail of the first 160 ms of the upper plot. Dashed line is best fit to a sum of four exponentials, using the *ab initio* theoretical lifetimes for $v_2 = 1$ through 4 from Ref. 15.

FIG. 3 Power dependence of the photodetachment signal at 4700 cm^{-1} , taken at two trapping times. a) 1 ms and b) 30 ms. Intensity is in arbitrary units: abscissa full scale is approximately 5 MW cm^{-2} peak power over a 5 mm diameter spot for a 10 ns pulse.



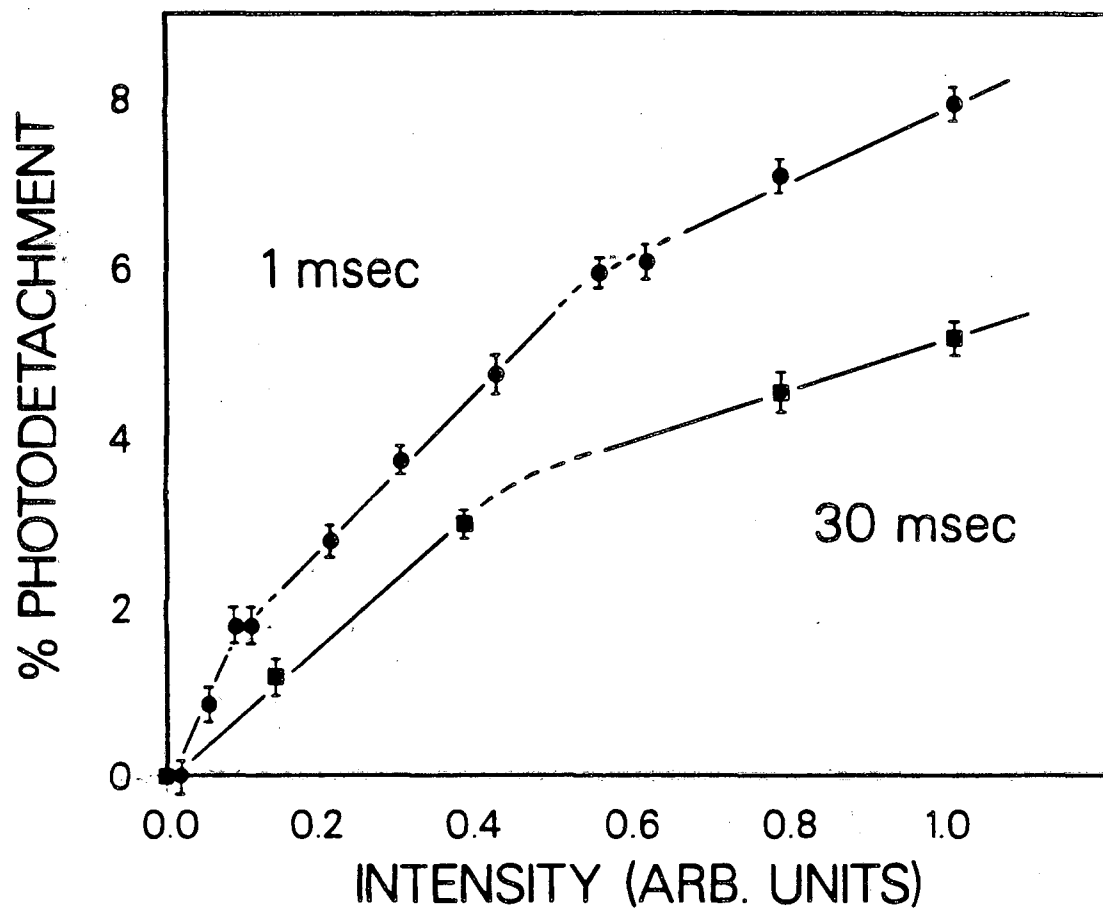
XBL 845-1706

FIG. 1



XBL 8610-3967

FIG. 2



XBL 845-1707

FIG. 3.

Chapter 3

The Lifetimes for Spontaneous Emission from the

$X^3\Sigma^-(v=1)$ and $a^1\Delta$ states of CH^-

I. INTRODUCTION

Although there has been considerable interest in the enhanced reactivity of metastable and vibrationally excited states of radicals and ions, the radiative lifetimes of such long lived states have rarely been measured. Several calculations of radiative transition probabilities for simple radicals and ions have appeared recently in the literature, with differing motivations: to aid spectroscopists in the search for infrared transitions of ions such as H_3O^+ ,¹ to help analyze chemiluminescence measurements of product densities of species like NO^+ ,^{2,3} and to better understand the effects of correlation in CI calculations of molecular properties.^{4,5,6} Theorists have also begun tackling the more difficult task of calculating quantitative rates of spin-forbidden processes.^{7,8} There is a paucity of experimental results on absolute intensities or lifetimes to compare to the theory, particularly for weak transitions. Common problems include collisions, space charge repulsion of ions, and difficulties in creating sufficient densities of transient species.

Ion traps provide a means of relaxing ions in a collisionless environment for long times. Some lifetime measurements have been made in three dimensional radio frequency, Kingdon, and Penning traps, including allowed electronic transitions of diatomic molecules⁹ such as HBr^+ , HCl^+ and the forbidden decays of metastable

atomic ions.^{10,11,12,13} We have recently measured the radiative lifetimes of metastable $a^4\Pi_u$, O_2^+ and vibrationally excited CH_2^- in a radio frequency (rf) octopole trap.^{14,15} The ions are created and mass selected before being injected into the trap, allowing the trap pressure to be kept below 5×10^{-9} torr. The ions could be trapped without collisions for times on the order of a second. The radiative decay is measured indirectly by probing the excited state population. In the case of negative ions, only ions in excited states are lost by photodetachment at photon energies below the ground state threshold. At a given trap time, we can determine the excited state population by measuring the depletion of trapped ions using sub-threshold photons.

In this chapter, we report an investigation of the radiative decay of excited CH^- . An energy level diagram of CH and CH^- is given in Fig. 1. Previous work has shown that there are two bound electronic states of CH^- : From the photoelectron spectrum of CH^- , Kasdan, Herbst and Lineberger¹⁶ have found the electron detachment threshold of the ground $X^3\Sigma^-$ state to be 1.238 ± 0.008 eV. They have also found a second state, bound by 0.393 ± 0.015 eV, which they have assigned as metastable $a^1\Delta$ CH^- . Several other peaks have been observed and assigned, including detachment from the ground state to the previously unseen $a^4\Sigma^-$ state of the neutral, placing that state 0.742 eV above the neutral $X^2\Pi$ state.

Theoretical calculations have supported their assignments.^{17,18} In the best CI calculation, Rosmus and Meyer¹⁹ predict an electron binding energy of 1.06 eV for the $X^3\Sigma^-$ state, slightly less than the experimental value. This result follows a trend in the first row diatomic hydride electron affinities, for which the theoretical values are somewhat lower than the experimental values. The identity of the metastable state is also confirmed by theory. Using quasidegenerate many-body perturbation theory, Sun and Freed²⁰ have calculated excited states and Feshbach resonances

of CH^- and found a bound $^1\Delta$ excited state of CH^- . In the best calculation to date, Manz *et al.*²¹ have recently performed a MCSCF-CI calculation and found that the CH^- $a^1\Delta$ state is bound, and lies 7057 cm^{-1} above the ground state. This calculation agrees to within 200 cm^{-1} of the value obtained from the photoelectron work.

The results of the photoelectron spectrum differ markedly from an earlier photodetachment experiment of Feldmann.²² He has observed two sharp thresholds at 0.74 eV and 1.95 eV, which he assigns as detachment from the $X^3\Sigma^-$ state of the anion to $\text{CH } X^2\Pi$ and $\text{CH } a^4\Sigma^-$ respectively. The higher threshold agrees well with Kasdan's analysis, but there is no clear explanation for the discrepancy between the measurements of the origin. Electron affinities of other systems reported by Feldmann in the same paper, including C_2 , SO , and SO_2 , are all shown to be in agreement with more recent photoelectron spectroscopy results. Thus, the marked difference between the threshold values of Kasdan *et al.* and Feldmann is puzzling.

In our experiment, we can distinguish between the two assignments by measuring the time dependence of the photodetachment signal from the trapped ions, using a photon energy of about 1 eV. This energy is below the ground state threshold of Kasdan *et al.*, but above Feldmann's threshold. If Kasdan *et al.* are correct, only excited state CH^- will be photodetached, and the signal will decrease to zero as the excited state radiatively decays. If Feldmann is correct, ground state CH^- will also be photodetached, and the signal will be nearly independent of time. This last result would be less conclusive. Since $^1\Delta$ states of diatomics are very long lived,⁷ the excited CH^- could live much longer than the collision free trapping time of the experiment. However, recent matrix isolation work on the isoelectronic species NH has yielded a value of 3.3 s for the radiative lifetime of the $a^1\Delta$ state.²³ With our apparatus, we would be able to detect a decay of this duration.

II. EXPERIMENTAL

The experiment is described briefly here, and is discussed in more detail in Chapter 1. The ions were created in a hot cathode discharge of methane, then extracted and accelerated to 360 eV. The ion beam was mass analyzed in a 60° sector magnet to select the CH^- , and deflected 90° by an electrostatic quadrupole field to be collinear with the laser beam. The CH^- ions were then decelerated and injected into a radio frequency octopole ion trap. The ions were stored for a variable time, ranging from 1.0 ms to 5 s. A pulsed infrared or visible laser was then fired into the trap. After laser irradiation, ions were released from the opposite end of the trap, mass selected in a quadrupole mass filter (Extranuclear Laboratories, Inc.), and detected with a Ceratron electron multiplier (muRata Co.). Pulse counting techniques were used.

In this experiment, we measured the fraction of CH^- depleted by the laser. To do this, the above sequence was repeated with the laser off to measure the total ion count at a given trap time. Pairs of cycles were repeated 10 to 100 times in a given run to signal average. The relative difference between the two cycles (laser on and laser off) gave the fractional loss of CH^- caused by photodetachment. Normalizing to the "laser off" ion count compensated for any losses that were not laser correlated, e.g. leakage from the trap. Lifetimes were measured by incrementing the trapping time under computer control.

The trap consisted of eight molybdenum rods, 50 cm in length and 0.25 cm in diameter, equally spaced on a 1.25 cm radius. Alternate rods were of opposite phase. The radio frequency voltage applied to the rods, typically 200 V and 7 MHz, created an effective potential well transverse to the axis of the trap, along its entire length. The ions were confined inside the octopole by raising the dc potentials of the lens elements at the ends of the octopole. The ions could be collected in the

trap by lowering the entrance lens voltage for 1.0 ms. The ions were released by lowering the exit lens voltage for several ms, beginning 1 ms after the laser had fired. In this arrangement, approximately half the ions escaped in the first 50 ms, but the remainder were trapped indefinitely. The laser beam was coaxial to the trap and passed completely through the machine, to prevent spurious effects caused by light striking metal surfaces.

The CH^- ions were created in a hot cathode duoplasmatron discharge of methane. The methane was ultra-high purity from Matheson, used without further trapping or purification. Experiments were run with and without a center electrode. This electrode, which helped in negative ion formation,²⁴ was a tungsten rod 0.3 cm in diameter which ran down the middle of the source to within 0.5 cm of the anode. It made the negative ion current more stable, enhanced the excited state population, and narrowed the energy spread of the ions. The last point was important, because only ions within a narrow energy range were efficiently trapped. The source pressure was 50 to 70 mTorr, the emission current 0.5 to 2 mA, and the discharge voltage 100 to 180 V.

The resolution of the magnetic mass spectrometer was approximately $m/\Delta m=150$ or higher. Thus, there was no contamination from other masses. One potential problem was signal from $^{13}\text{C}^-$; a metastable ^1D state of C^- could have yielded time dependent photodetachment signal at the photon energies used here. No time dependent photodetachment was observed during extensive experiments on $^{12}\text{C}^-$; therefore, we concluded that there was no contribution from $^{12}\text{C}^-$ to the CH^- decay.

The experiment was performed at two laser frequencies: the 9390 cm^{-1} (1.16 eV) fundamental of a YAG laser and the 14300 cm^{-1} (1.68 eV) output of a dye laser. The YAG laser was a Q-switched Quanta-Ray Nd:YAG laser, with a pulse width of approximately 10 ns. The laser beam, which had a donut shaped transverse mode

pattern, was propagated 20 m; diffraction resulted in a nominally Gaussian beam spot 0.7 cm in diameter. Typical power was 100 mJ per pulse, at a 10 Hz repetition rate. The dye laser was a Quanta-Ray PDL-1 laser with LDS 698 dye, pumped by the second harmonic of the YAG. The pulse energy was approximately 20 mJ per pulse at 10 Hz. The transverse mode pattern was irregular, resulting in poorer overlap with the trapped ions.

Precautions were necessary to eliminate systematic laser power variations with trapping time. For maximum thermal stability of the laser and nonlinear optics, we had to maintain the 10 Hz repetition rate, regardless of the trapping time. For long delays, we used two schemes for selecting the appropriate laser shot.

Dye laser pulses were selected using a shutter. Thus, in a 1 s delay, the laser fired ten times while the ions were trapped, but the shutter blocked all except the last shot. The YAG fundamental output was too intense to use the shutter. When we used the YAG laser alone, the flashlamps were fired at 10 Hz, but actual lasing was controlled by triggering the Q switch.

In both cases, the 10 Hz was synchronized with the data acquisition, so that the desired laser pulse occurred at the correct time in the data cycle, to within 50 μ s or better.

III. RESULTS

The photodetachment signal at the lower photon energy, 1.16 eV (0.08 eV below the threshold observed in the photoelectron spectrum), exhibited a biexponential decay with time, as shown in Fig. 2. There was a fast component, which decayed in the first several milliseconds, and a much slower component, which decayed in seconds.

To accurately measure the fast decay, we decreased the trap input time to 0.1 ms

from 1 ms and scanned the trapping time from 1.0 to 9.0 ms. The decay was effectively completed after approximately 5 ms. In Fig. 3, we fit the faster decay to a single exponential, after subtracting the long-lived component, and obtained a lifetime of 1.75 ± 0.15 ms. The uncertainties are reported as one standard error.

The spatial distribution of ions in the trap reached a steady state after 2 to 3 ms. To check for systematic errors arising from variable laser/ion overlap in this time regime, we repeated the experiment with CH_2^- , reducing the laser power with a filter to prevent saturation. Because the photon energy was above threshold for detachment to both the X^3B_1 and a^1A_1 states of the neutral,^{25,26} no time dependence was expected, and none was observed.

To measure the slower decay, we trapped the ions for as long as 5 s. We fit the decay to a single exponential. The long time decay, shown in curve b of Fig. 4, had the short time decay subtracted for clarity. A least squares fit to the data in Fig. 4 (curve b) yielded a lifetime of 5900^{+800}_{-600} ms. We again measured the photodetachment of CH_2^- over the same time range, and observed no time dependence, thus ruling out systematic errors such as drop in laser power with trapping time.

For such long times, collisional processes could become significant at pressures on the order of 10^{-9} torr. We therefore measured the photodetachment decay at three pressures: 3.0×10^{-9} , 4.6×10^{-9} , and 6.5×10^{-9} torr. The decay rates were equal within our uncertainty. The 5.9 s decay was not collision-induced.

In contrast, the absolute ion count (independent of the laser) did decay as a function of trapping time. We had found previously that, after the first 50 ms, strongly bound ions such as O_2^+ could be trapped for several minutes without loss.¹⁴ Any loss of weakly bound ions at longer times therefore arose from collision. The loss rate of CH^- was proportional to pressure, as shown in Fig. 5, indicating that collisional destruction of the CH^- was occurring. At 3.0×10^{-9} torr, the

collisional lifetime was 29 s, five times longer than the lifetime of the laser-induced signal. There was about a factor of two systematic uncertainty in the absolute pressure measurements, because the ion gauge (Varian nude ion gauge UHV-24) was calibrated for air. The background gas probably consisted of mainly H_2 and CO, the gases typically found in stainless-steel, ultra-high vacuum chambers.

Collisional losses could be neglected as long as the loss rate was much longer than the radiative decay. Furthermore, because the photodetachment signal was measured as the fraction depleted by the laser, trapping and collisional losses were exactly compensated if the excited and ground states had the same non-radiative loss rates. Only relative differences in the collision cross section would affect our radiative lifetime measurements. That the laser-induced signal was independent of pressure implies that the collisional decay rate of the long-lived excited state was slow compared to the radiative decay.

We measured the power dependence of the 1.16 eV photodetachment at trapping times of 1.0, 25, and 100 ms. The power dependence at 25 ms and 100 ms were identical, so only the 25 ms results are shown in Fig. 6. As seen in Fig. 6, the signal at 25 ms was completely saturated at full power (300 mJ per pulse). At 1 ms, the signal was less saturated; there was an additional absorption that was not fully saturated. The difference between the 1 ms and 25 ms curves, plotted as curve c in Fig. 6, is the power dependence of the 1.75 ms state. The fast component, which would only contribute to the 1 ms signal, thus appears to have a much weaker cross section for photodetachment than the slow component, by over an order of magnitude.

Curve a of Fig. 4 shows the CH^- photodetachment using the dye laser at 1.68 eV (700 nm). The signal was 40% photodetached, and did not change with trapping time up to 5 s. This high fraction of photodetachment was obtained with approxi-

mately 20 mJ per pulse, more than an order of magnitude less power than we used at 1.16 eV (1064 nm). The transition was partially saturated. In comparison, 70% of the CH_2^- ions were depleted by the 1.16 eV light (well above threshold) at saturation. The CH_2^- signal was presumably an upper limit on the fraction that could be detached, imposed by incomplete overlap of the laser beam and the trapped ions. Thus, despite incomplete saturation, we were able to detach over half the CH^- ions in the trap.

Because we were at or near saturation, we could estimate the populations for the two components. Extrapolating to zero trapping time yielded observed depletions of 8.5% and 7.8% for the slow and fast components respectively. Correcting for incomplete irradiation of the trap, which resulted in a maximum observable depletion of 70%, gave a population of 12% for the long-lived state.

For the fast component, there were two additional considerations. The transit time from the source was 0.05 ms. In addition, the trap entrance was "open" for 0.1 ms; therefore, the average additional time from source to zero trapping time was 0.1 ± 0.05 ms. Extrapolating to true zero time (at the source) yielded a value of 8.2% for the depletion, and $12 \pm 1\%$ for the true population. This estimate might be low, if the detachment signal was not fully saturated.

IV. DISCUSSION

A. Electron affinity of CH

The biexponential decay of the photodetachment signal at 1.16 eV clearly indicates the presence of at least two excited states of CH^- . Although we did not observe the signal decay to zero, we can rule out the possibility of a weak contribution from the ground state at this energy, because we expect a large photodetachment cross

section for the $X^3\Sigma^-$ state. A nonbonding p electron is detached to an outgoing s-wave, resulting in a sharp threshold. Furthermore, the Franck-Condon factors are favorable, because the ground states of the neutral and ion have similar bond lengths. The signal at this lower energy therefore arises from excited states alone. In contrast, at 1.68 eV, the signal is large and independent of time, indicating that ground state CH^- are being detached. Our results thus provide bounds for the CH electron affinity: $1.16 \text{ eV} < \text{E.A.} < 1.68 \text{ eV}$, and are consistent with the analysis of the photoelectron spectrum.¹⁶ Our results contradict Feldmann's photodetachment results, in which he observed the same photodetachment cross section at the two energies studied here. We can therefore rule out Feldmann's value for a threshold of 0.74 eV, although we do not have any explanation for his results.

Only two peaks in the photoelectron spectrum fall within these limits; the larger one was assigned as the origin. The Franck-Condon factors favor a diagonal transition, and one expects a strong peak. The only uncertainty is the possibility of C^- signal, caused by the poor mass resolution of the Wien filter. Kasdan *et al.* discount this problem, on the grounds that the C^- peak is 0.003 eV higher in energy.

B. The lifetime of vibrationally excited $X^3\Sigma^- \text{CH}^-$

The fast decay is almost certainly an excited vibrational state of $X^3\Sigma^- \text{CH}^-$. The weakness of the absorption is consistent with a $\Delta v \neq 0$ transition, for which the Franck-Condon factor is small. The photon energy of 1.16 eV is only 0.08 eV below the threshold, and well above the $v=1$ detachment threshold. The fast component has a smaller detachment cross section and therefore could not be decaying to the slow component; otherwise, the photodetachment signal would increase during the first 5 ms.

We are probably not seeing decay of $v=2$ or higher vibrational levels. In our

experiment, we can excite both $v=1$ and $v=2$ to the continuum (see Fig. 1). Both states will contribute signal; however, the second vibrational level, expected to be 5000 cm^{-1} above the ground state, probably has a small population at typical plasma temperatures (1000K to 2000K). Furthermore, the $v=2$ state should decay faster than the $v=1$ state, but we do not begin measurements for 1.1 ms after the ions have been extracted from the source. The fast decay appears to be a single exponential, with no observable curvature in the log plot over a range of more than two lifetimes. We therefore assign the 1.75 ms lifetime to the $v=1$ level of the $X^3\Sigma^-$ CH^- .

The observed lifetime of 1.75 ms is fast for a vibrational state, making CH^- a very strong IR emitter, but it is similar to the $v=1$ lifetimes of other diatomic hydrides. Compare this value to the following $0 \rightarrow 1$ lifetimes obtained from theory or experiment: NeH^+ 1.60 ms,²⁷ HF 5.29 ms,²⁸ HF^+ 1.62 ms,⁴ OH^- 7.30ms, OH 82.0 ms, OH^+ 3.80 ms,^{5,6} and BeH^+ 64.4 ms.²⁹

The 1.75 ms lifetime which we measured is in reasonable agreement with a recent MCSCF-CI calculation done by Manz, Zilch, Rosmus and Werner.²¹ They have obtained a value of 1.96 ms, which deviates from our result by slightly more than one standard error. The calculated $v=2$ lifetime is 1.09 ms. They have also calculated a value for the Franck-Condon factor for the $0 \rightarrow 1$ transition of 0.018, which is consistent with our observed power dependence. Properties of anions are known to be more difficult to calculate than those of the corresponding neutrals.³⁰ The good agreement here is encouraging, and suggests that the lifetimes of simple diatomic anions can be calculated accurately.

Based on the observed fast component population, we can estimate the $v=2$ population. We assume that there is a Boltzmann distribution of vibrational states, and that the observed fast component is saturated and includes both the $v = 1$

and $v = 2$ states (*v.s.*). Manz *et al.* have calculated the (v following vibrational constants for the $X^3\Sigma^-$ state: $\omega_e = 2577 \text{ cm}^{-1}$ and $\omega_e x_e = 80 \text{ cm}^{-1}$. We obtain a $v=2$ population of 1.5% of the total beam current. The populations relative to $v=0$ are 0.14 and 0.02 for $v=1$ and $v=2$ respectively, giving a vibrational temperature of 1700 K. This value is typical for a hot cathode discharge. Factors which play a role in determining the vibrational temperature include source design, discharge conditions, and collisional heating during extraction.

Using the estimated populations and a scaled value of the theoretical $v=2$ lifetime, we have modeled the vibrational decay. When a single exponential is fit to the data derived from the model, the resulting parameters deviate by less than one standard error from the true values. These results show that neglecting the $v=2$ decay in the fit does not significantly change our results.

This is the first reported observation of vibrationally excited CH^- . Neither Feldmann nor Kasdan *et al.* report a hot band in their spectra. It is quite possible that vibrationally excited CH^- was present in the photoelectron experiment. In that experiment, as in ours, the CH^- were created in a hot cathode discharge of methane. They used a Branscomb type source, while we used a duoplasmatron. Both sources had electrical and magnetic confinement of the discharge, and physically shielded the aperture in the anode. The $\Delta v = -1$ band is expected^{19,21} to be 0.3 eV to the red of the threshold. The broad feature at 1.5 eV electron energy in the photoelectron spectrum, which Kasdan attributed to CH_2^- , could be reassigned as a hot band; or as a combination of the two. In addition, because of the poor Franck-Condon factors, they may not have seen hot bands if their laser power was too low.

C. The lifetime of metastable $a^1\Delta$ CH^-

Both the photoelectron work¹⁶ and the *ab initio* calculations^{19,21} establish that the $a^1\Delta$ state is bound. This state would radiatively decay by a spin-forbidden transition to the $X^3\Sigma^-$ state. The long lifetime of the slow component is consistent with a spin-forbidden transition, so we have assigned the slow decay as the metastable $a^1\Delta$ state of CH^- . Furthermore, we expect detachment from this state to be a strong transition, for the same reasons cited for the ground state. The power dependence shows that the observed transition is indeed much stronger than the $v=1$ photodetachment hot band.

The radiative decay of the $a^1\Delta$ state to the ground state is forbidden by spin selection rules. The transition occurs because these two states are not pure spin states, but mix with other electronically excited states by spin-orbit coupling. All of these other states are Feshbach resonances, states imbedded in the ionization continuum. The nearest feasible state appears to be the $A^3\Pi$ state (see Fig. 1), calculated to be 2.6 eV ($21,000\text{ cm}^{-1}$) above the metastable state.²⁰ The Franck-Condon factors coupling these states appear to be unfavorable, leading one to expect a slow decay of the metastable state.

Spin forbidden transitions in diatomics often exhibit multiple exponential decays, with a strong J dependence.³¹ Considered in a Hund's case (a) basis, this J dependence results from different decay rates for states with different values of the spin projection quantum number Σ . The observation of a single exponential decay is consistent with the decay of a singlet state, for which there is no spin degeneracy.

Recent work on the isoelectronic species NH yield values for the radiative lifetime of the $a^1\Delta$ state that are quite similar to our results for CH^- . Esser *et al.* have recently measured the lifetime of $a^1\Delta$ NH in rare gas matrices.²³ They extrapolated their data and predicted a gas phase radiative lifetime of 3.3 s. Marian

and Klotz,⁸ however, point out that there is a great deal of uncertainty in such extrapolations. They have performed an *ab initio* MRD-CI calculation on NH, and obtained a radiative lifetime of 1.7 s for the $a^1\Delta$ lifetime. Both of these results are qualitatively similar to our own measurements for CH⁻. A calculation of the $a^1\Delta$ radiative lifetime of CH⁻ would be interesting but difficult, given the presence of the ionization continuum.

V. SUMMARY

There is a discrepancy in the literature concerning the experimental electron affinity of CH. By measuring the photodetachment from trapped CH⁻ ions as a function of trapping time, we have shown that at 1.16 eV, the photodetachment decays biexponentially with trapping time, and thus occurs only from excited states. At 1.68 eV, the photodetachment is independent of time, indicating that the photon energy is above the ground state threshold. Our results, which put bounds on the electron affinity ($1.16 \text{ eV} < \text{E.A.} < 1.68 \text{ eV}$), contradict Feldmann's photodetachment spectroscopy results ($\text{E.A.} = 0.74 \text{ eV}$), and support the photoelectron work of Kasdan, Herbst and Lineberger ($\text{E.A.} = 1.238 \text{ eV}$). We have found the radiative lifetime of the $X^3\Sigma^-$ ($v=1$) state to be $1.75 \pm 0.15 \text{ ms}$, and that of the metastable $a^1\Delta$ state to be $5.9^{+0.8}_{-0.6} \text{ s}$. Assuming a Boltzmann distribution, the estimated vibrational temperature is 1700 K.

REFERENCES

1. M. E. Colvin, G. P. Raine, and H. F. Schaefer III, J. Chem. Phys. **79**, 1551 (1983).
2. F. P. Billingsley II, Chem. Phys. Lett. **23**, 160 (1973).
3. H. J. Werner and P. Rosmus, J. Mol. Spectrosc. **96**, 362 (1982).
4. H. J. Werner, P. Rosmus, W. Schatzl, and W. Meyer, J. Chem. Phys. **80**, 831 (1984).
5. H. J. Werner, P. Rosmus, and E. A. Reinsch, J. Chem. Phys. **79**, 905 (1983).
6. H. J. Werner, J. Chem. Phys. **80**, 5080 (1984).
7. R. Klotz, C. M. Marian, S. D. Peyerimhoff, B. A. Hess, and R. J. Buenker, Chem. Phys. **89**, 223 (1984).
8. C. M. Marian and R. Klotz, Chem. Phys. **95**, 213 (1985).
9. C. C. Martner, J. Pfaff, N. H. Rosenbaum, A. O'Keefe, and R. J. Saykally, J. Chem. Phys. **78**, 7073 (1983) And references therein.
10. D. J. Wineland, W. M. Itano, and R. S. van Dyck, Adv. At. Mol. Phys. **19**, 135 (1983).
11. R. D. Knight and M. H. Prior, Phys. Rev. **A21**, 179 (1980).
12. R. Schneider and G. Werth, Z. Phys. **A293**, 103 (1979).
13. F. Plumelle, M. DeSaintfuschien, J. L. Duchene, and C. Audoin, Opt. Commun. **34**, 71 (1980).

14. S. W. Bustamente, PhD thesis, University of California, Berkeley, California, 1983.
15. See chapter 2.
16. A. Kasdan, E. Herbst, and W. C. Lineberger, *Chem. Phys. Lett.* **31**, 78 (1975).
17. P. E. Cade, *Proc. Phys. Soc.* **91**, 842 (1967).
18. P. F. Zittel, G. B. Ellison, S. V. O'Neil, E. Herbst, W. C. Lineberger, and W. P. Reinhardt, *J. Am. Chem. Soc.* **98**, 3731 (1976).
19. P. Rosmus and W. Meyer, *J. Chem. Phys.* **69**, 2745 (1978).
20. H. Sun and K. F. Freed, *J. Chem. Phys.* **76**, 5051 (1982).
21. U. Manz, A. Zilch, P. Rosmus, and H. J. Werner, *J. Chem. Phys.* **84**, 1683 (1986).
22. D. Feldmann, *Z. Naturforsch. A* **25**, 621 (1970).
23. H. Esser, J. Langen, and U. Schurath, *Ber. Bunsenges. Physik. Chem.* **87**, 636 (1983).
24. W. Aberth and J. R. Peterson, *Rev. Sci. Instrum.* **38**, 745 (1967); V. P. Golubev; G. A. Nalivaiko, and S. G. Tsepakin, in *Proceedings of the Proton Linear Accelerator Conference*, (Los Alamos National Laboratory Report LA-5115, 1972) p. 356; W. Aberth, R. Schnitzer, F. Eugener, and M. Anbar, in *Proceedings of the Second Symposium on Ion Sources and Ion Beam Formation* (Lawrence Berkeley Laboratory Report LBL-3399, 1974) p. I-7.
25. T. J. Sears and P. R. Bunker, *J. Chem. Phys.* **79**, 5265 (1983).

26. D. G. Leopold, K. K. Murray, and W. C. Lineberger, *J. Chem. Phys.* **81**, 1048 (1984).
27. R. N. Sileo and T. A. Cool, *J. Chem. Phys.* **65**, 117 (1976).
28. P. Rosmus and E. A. Reinsch, *Z. Naturforsch. A* **35**, 1066 (1980).
29. F. F. Ornellas, W. C. Stwally, and W. T. Zemke, *J. Chem. Phys.* **79**, 5311 (1983).
30. T. J. Lee and H. F. Schaefer III, *J. Chem. Phys.* **83**, 1784 (1985).
31. T. C. James, *J. Chem. Phys.* **55**, 4118 (1971).

FIGURE CAPTIONS

FIG. 1 Energy level diagram of the lowest lying states of CH^- and CH , based on the results of Kasdan, Herbst and Lineberger, Ref. 16. The vertical arrows are the transitions excited in this experiment. As indicated by the dashed arrow, a 9390 cm^{-1} photon cannot detach an electron from the ground state.

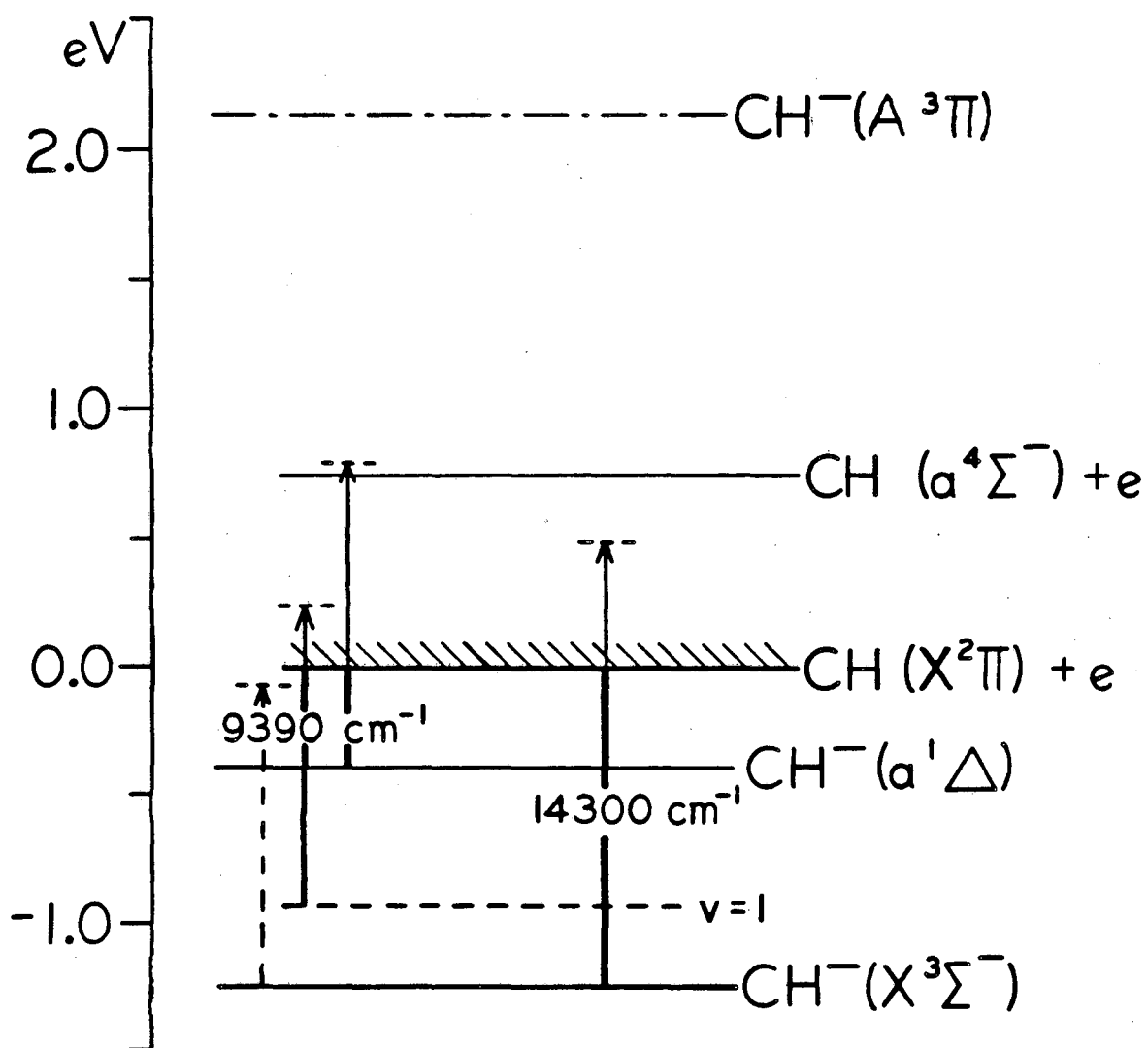
FIG. 2 The decay of the photodetachment signal from CH^- at short times. The photon energy is 9390 cm^{-1} (1.16 eV). The curve is obtained from the fits shown in Fig. 4 and 5.

FIG. 3 Log plot of the data at short times, with a long decay component subtracted. The photon energy is 9390 cm^{-1} (1.16 eV).

FIG. 4 The decay of the photodetachment signal from CH^- at long times. The photon energy in curve a) is 14300 cm^{-1} (1.68 eV). The photon energy in curve b) is 9390 cm^{-1} (1.16 eV). The short time decay has been subtracted from this curve, and would appear as a spike at $t=0 \text{ s}$ in this time scale.

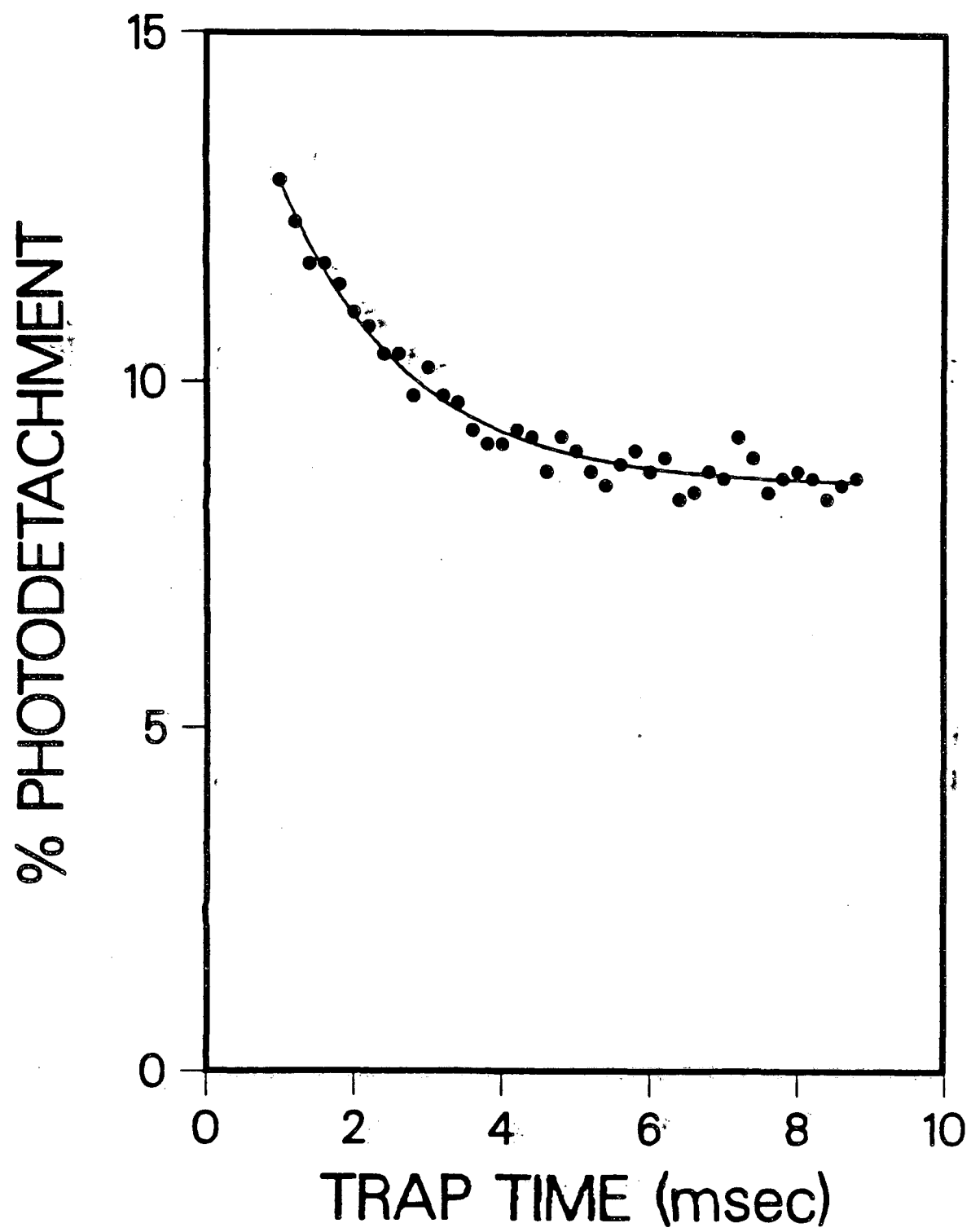
FIG. 5 Decay of the trapped ions caused by collisional loss, at four pressures of background gas.

FIG. 6 The power dependence of the photodetachment signal at 9390 cm^{-1} . Curve a) is measured at 1 ms trapping time. Curve b) is measured at 25 ms trapping time. Curve c) is the difference between curves a) and b). The curves are hand-drawn through the points.



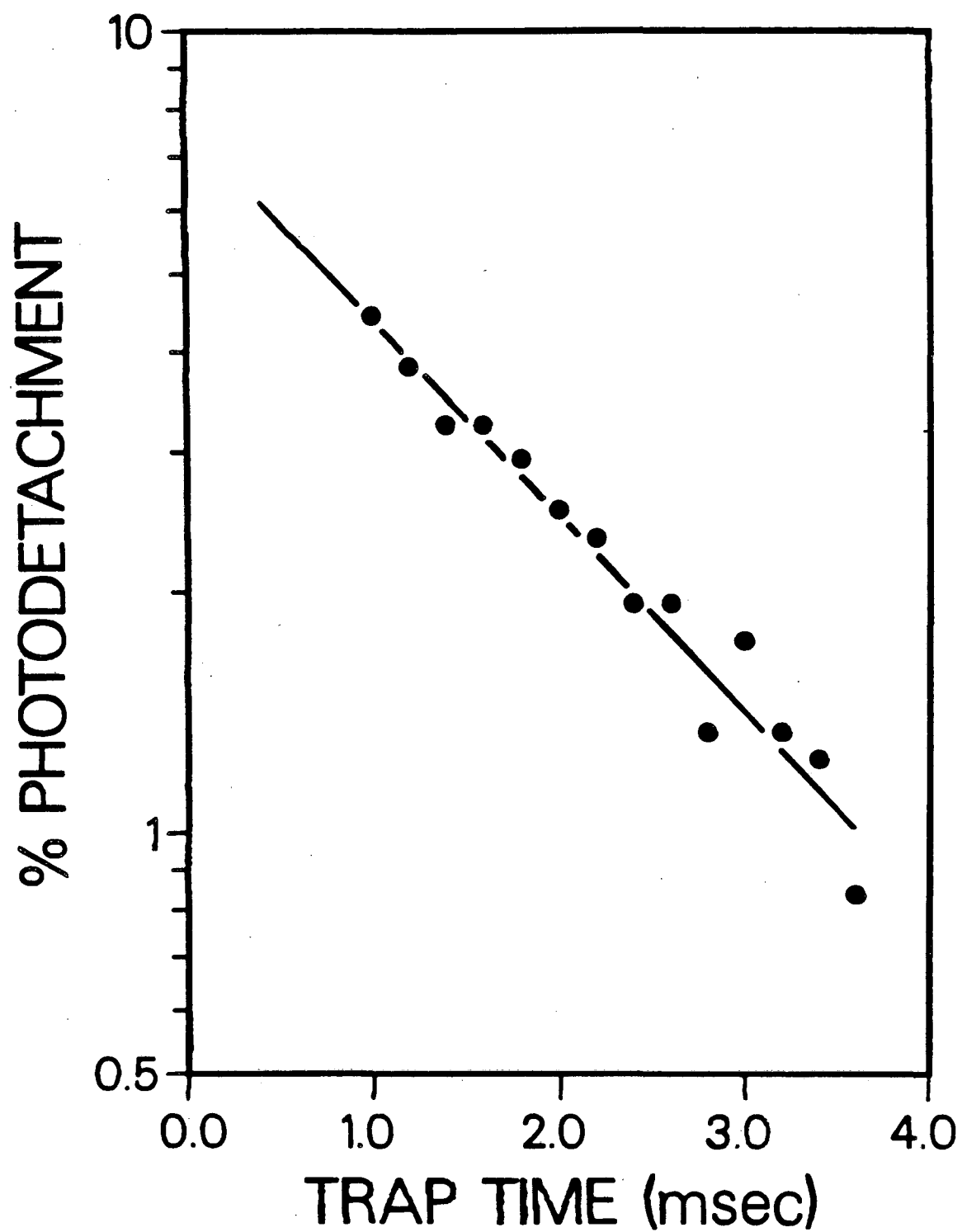
XBL 847-3076

FIG. 1



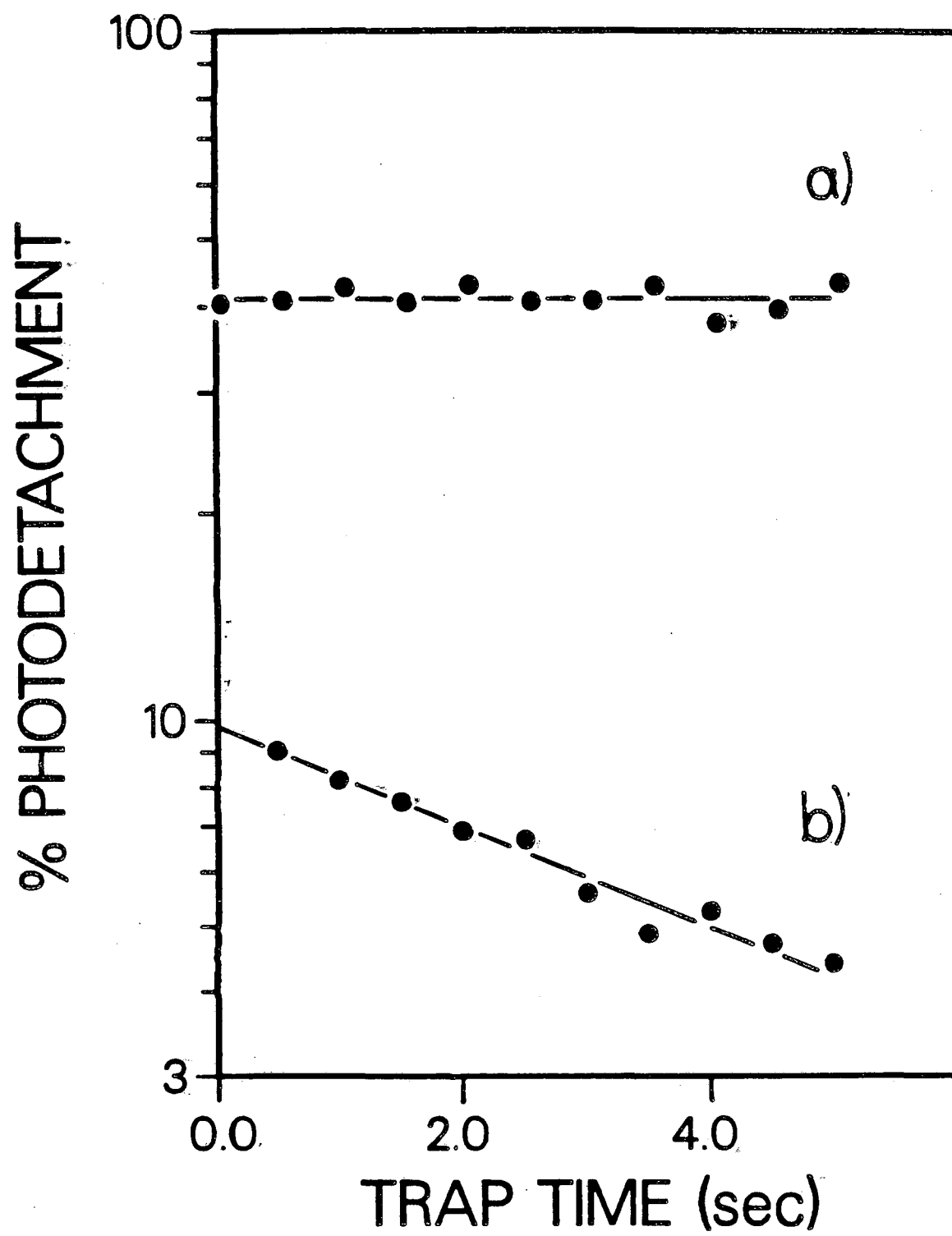
XBL 848-3514

FIG. 2



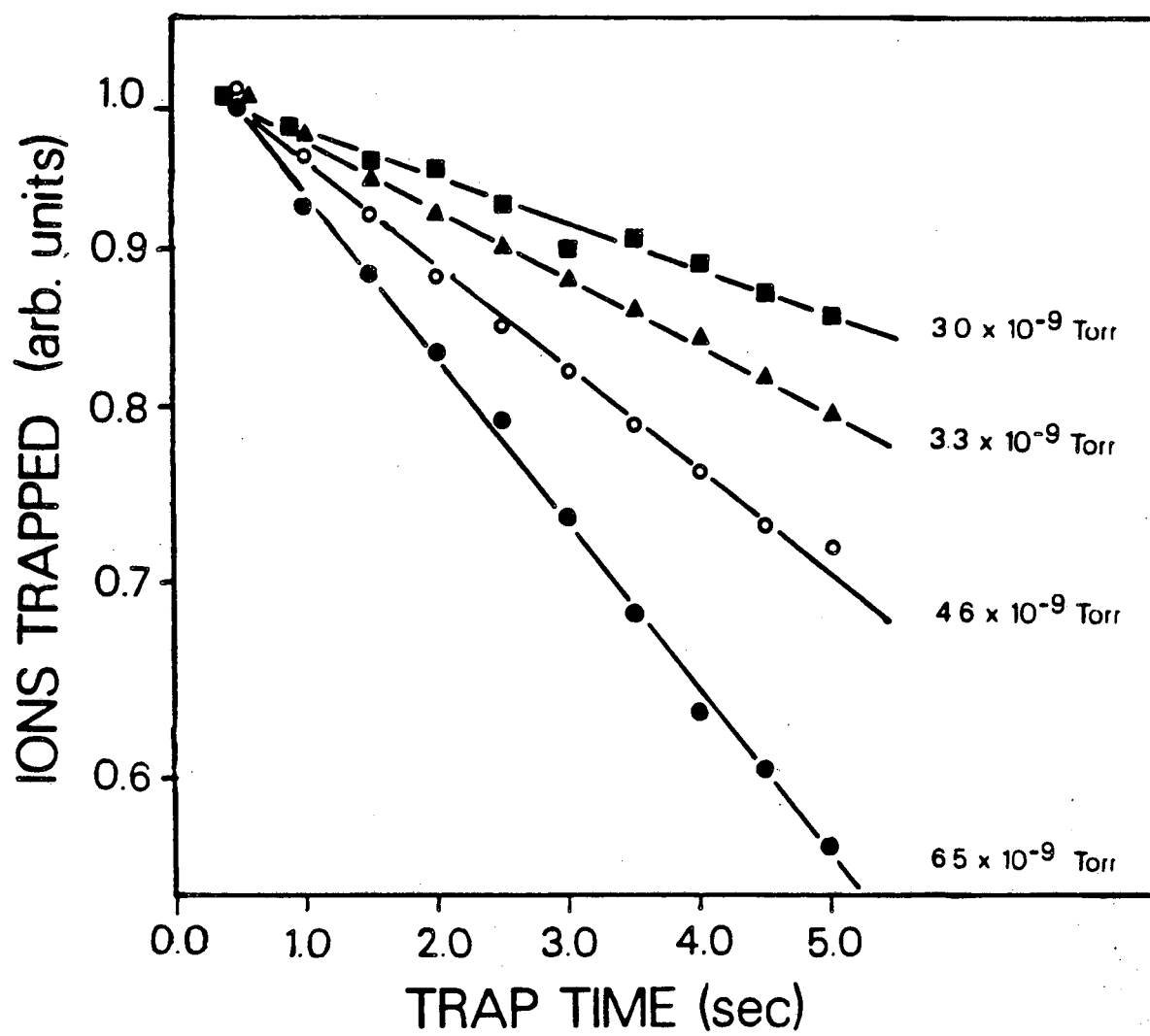
XBL 847-3261

FIG. 3



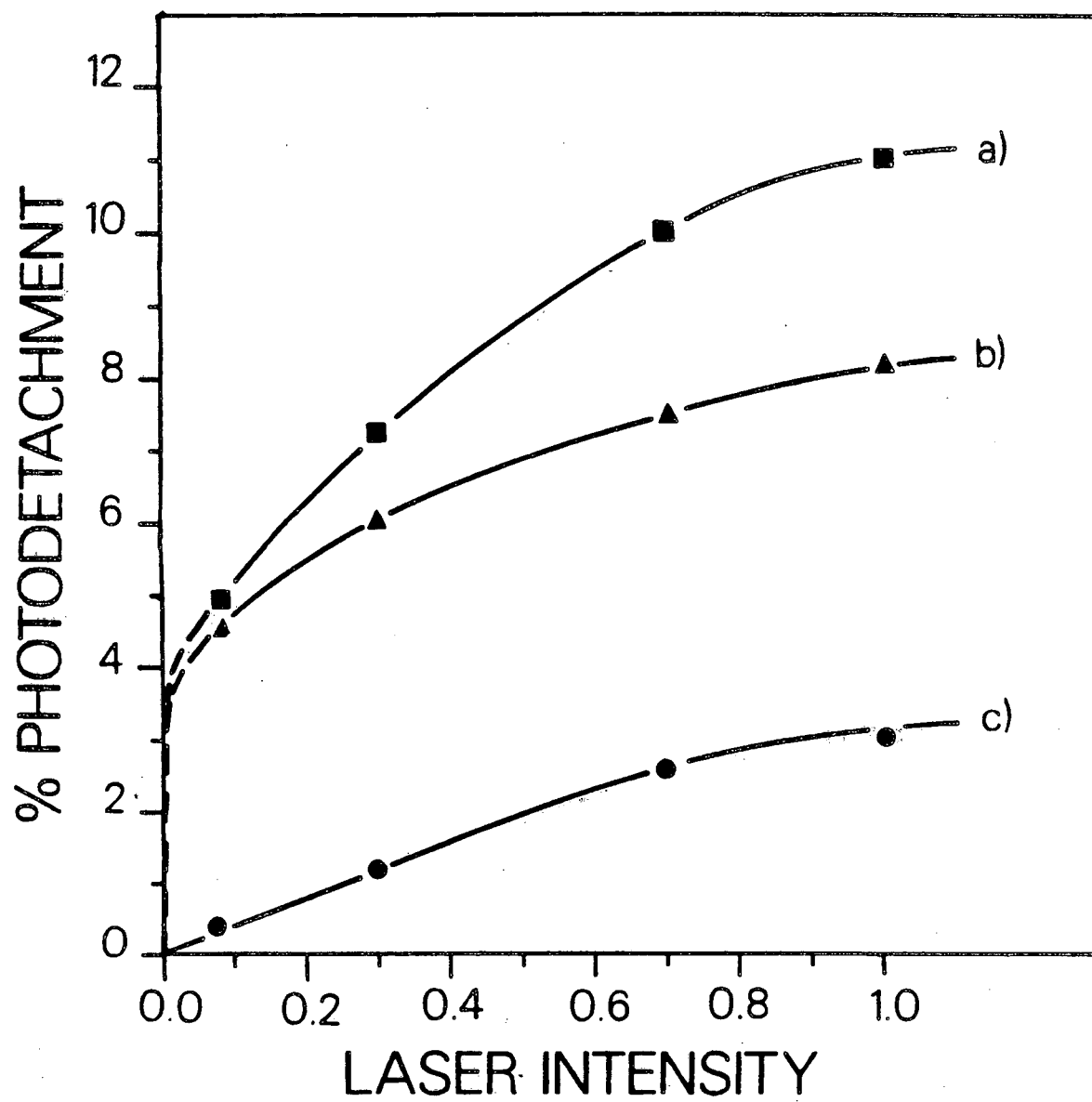
XBL 847-3262

FIG. 4



XBL 847-3259

FIG. 5



XBL 847-3260

FIG. 6

Chapter 4

Infrared Spectroscopy of Protonated Hydrogen Clusters

I. INTRODUCTION

Cluster ions have been investigated by a variety of experimental techniques.^{1,2} Many, including photodissociation and photoionization studies, have focused on determining cluster size distributions. Techniques such as high pressure mass spectrometry have yielded a large body of thermochemical data, including enthalpies and entropies of association.³ Such results have revealed trends in cluster stability as a function of solvent number. Studies of ion beam photodissociation have provided a wealth of information about the dynamics of dissociation. Still, questions about the structure and vibrational motions of these clusters remain largely unanswered. Only a handful of spectroscopic investigations have been done, but there have been several promising developments in the past year. Kennedy and Miller⁴ for example have recently reported vibronic spectra of the clusters $C_6F_6^+ \cdot He$, and from observation of transitions involving the intermolecular vibrations, have estimated the geometry and force field for this cluster. Smalley and co-workers⁵ have reported electronic spectra of Nb_2^+ and Ni_2^+ using a two photon dissociation scheme to probe the bound intermediate state. Photoelectron spectra of several anionic clusters have recently been observed by Bowen and co-workers.⁶ In this chapter we report a study of the infrared spectra of the hydrogen cluster ions.

In the past decade, the spectroscopy of molecular ions has developed rapidly. Much of the new information has come from the high resolution infrared spectra

of small, strongly bound ions such as H_3O^+ and HNN^+ , which are abundant in discharges.⁷ The spectra of these closed shell species often cannot be detected by more conventional visible or UV methods. Velocity- and discharge-modulation techniques have provided the sensitivity needed for the infrared absorption spectroscopy of these small ions in glow discharges.

The spectroscopy of cluster ions has proven to be very difficult using this direct absorption technique.⁸ Higher pressures and lower temperatures are required to prevent the fragile clusters from breaking up. Under these conditions, however, one is likely to produce a broad distribution of cluster sizes with a concomitant increase in spectral congestion. Furthermore, these clusters are expected to have many large amplitude vibrational degrees of freedom. Therefore, while the spectra of the smaller ions are relatively straightforward to analyze, a fully resolved room temperature spectrum of a cluster ion may be very complex.

To overcome these difficulties, we have pursued the infrared spectroscopy of cluster ions trapped in a radio-frequency(rf) ion trap. Our apparatus, possessing a tandem mass spectrometer, allows us to mass select the parent cluster ion extracted from one of a variety of sources, and trap them. Once we have collected ions in the trap, we can excite them with a tunable infrared laser. For weakly bound clusters, absorption of a single infrared photon by a high frequency stretching mode can lead to predissociation of the cluster. By detecting the fragment ions produced upon dissociation as a function of laser frequency, we can measure the absorption spectrum of the parent ion. Vibrational predissociation spectroscopy is a well known technique in the study of neutral van der Waals complexes,⁹ but has had limited success due to both the inability to mass select parent species and the uncertainties stemming from cracking of the products upon electron impact ionization during detection.

We have chosen to begin our studies on the simplest of the ionic molecular complexes, the hydrogen cluster ions. The H_5^+ ion was first positively identified by Dawson and Tickner in 1962.¹⁰ Larger odd mass clusters were subsequently observed by Buchheit and Henkes in mass spectra¹¹ and by Clampitt and Gowland using low energy electron bombardment of solid hydrogen.¹² Later workers have observed odd mass hydrogen clusters in size distributions from ionization and collisional fragmentation studies.^{13,14,15,16,17} The structure of these clusters has generally been described as H_2 molecules surrounding the H_3^+ ion, $H_3^+ \cdot (H_2)_n$. H_3^+ itself is a dominant ion in many hydrogen discharges¹⁸ and plasmas, such as the interstellar medium, where reactions of H_3^+ may be important in the isotopic fractionation of hydrogen. The proton affinity of H_2 is 101 kcal/mol,¹⁹ so the H_3^+ ion is strongly bound. Many thermochemical experiments have measured the enthalpy and entropy of association for the ionic hydrogen clusters,^{20,21,22,23,24,25,26} and found that they are bound by energies at least an order of magnitude smaller. The most recent measurements^{25,26} give $\Delta H_{300}^\circ = 5.8$ and 6.6 kcal/mol for $H_5^+ \rightleftharpoons H_3^+ + H_2$ and $\Delta H_{110}^\circ = 3.1$ kcal/mol for $H_7^+ \rightleftharpoons H_5^+ + H_2$.

There have been many *ab initio* results on these clusters.^{27,28,29,30,31,32,33,34,35,36,37,38} Their small size makes these clusters ideal for accurate computational study. Theorists have found that these clusters are very weakly bound, and require fairly large basis sets and correlation for converging results. Table I contains a compilation of the experimental results and a selection of *ab initio* calculations for the H_n^+ dissociation energies. The best calculation to date,³⁸ by Yamaguchi *et al.* on H_5^+ , is in good agreement with the most recent experimental values. There is general consensus that in these clusters, the first three H_2 molecules are bound to the three corners of the H_3^+ . Structures of H_n^+ , $n = 5, 7$, and 9, are shown in Fig. 1. The theory also confirm the finding of Hiraoka and Kebarle²³ that the binding energies of the

following H_2 molecules to H_3^+ are much smaller.

The *ab initio* theory has found that the potential energy surface for the H_3^+ ion is very shallow.^{28,36,38} The result has been that calculations for the dissociation energy and equilibrium geometries have not converged well. Yamaguchi, Gaw, Remington, and Schaefer have performed impressive full CI calculations³⁸ with large basis sets for ten stationary points below the dissociation energy. The equilibrium geometry, shown in Fig. 1, has C_{2v} symmetry, but there are three saddlepoints lying less than 0.6 kcal/mol above it. Perhaps the most important is the D_{2d} structure, with the central H atom symmetrically between the two H_2 . This barrier for the proton transfer $\text{H}_3^+ + \text{H}_2 \rightarrow \text{H}_2 + \text{H}_3^+$ has a mere 0.08 kcal/mol height. Three of the other saddlepoints lie only 4.8 kcal/mol above the equilibrium geometry. The H_3^+ ion is therefore predicted to be a very nonrigid molecule.

While most calculations have focused on the structure and energetics of these ions, Yamaguchi, Gaw, and Schaefer³⁶ have recently published calculations of the vibrational frequencies of H_6^+ , H_7^+ , and H_9^+ . Their calculations predict that the H_2 ligands in these clusters have allowed vibrational transitions at approximately 4000 cm^{-1} (11.4 kcal/mol), well above the cluster dissociation energies. Therefore, these clusters can be dissociated by exciting the solvent H_2 .

Encouraged (provoked?) by the theorists, we have searched for the H_2 stretching bands of H_n^+ , $n = 5, 7, 9, 11, 13$, and 15. We have initially created the ions using electron impact ionization of neutral $(\text{H}_2)_n$ complexes. In addition to low resolution observations of vibrational bands, we have sought rotationally resolved spectra using high resolution lasers. In this experiment, we have focused our high resolution efforts on the H_3^+ ion. The light H_3^+ molecule has a rotational spacing in the P and R branches of $2B \approx 6\text{ cm}^{-1}$; therefore, we expected to observe well-resolved rotational structure, even at laser linewidths of 0.5 cm^{-1} . Electron impact,

however, creates highly excited ions, which can lead to severe spectral congestion. We have therefore developed a high pressure discharge source as well. Here, the plasma created by a corona discharge is thermalized and then expanded into the vacuum. The resulting ions are internally cold, at room temperature or less, but the beam current is weaker.

Vibrational Frequencies

Yamaguchi, Gaw, and Schaefer³⁶ have reported harmonic vibrational frequencies for H_n^+ using both (DZ+P basis set) Hartree Fock SCF calculations for $n = 5, 7$, and 9 , and (DZ+P basis set) single and double configuration interaction calculations (CISD) for $n = 5$ and 7 . Since then, Yamaguchi, Gaw, Remington, and Schaefer³⁸ have performed higher level theory for H_5^+ , including (DZ+P) full CI as well as CI calculations with larger basis sets. Our experiments were guided by their theoretical predictions for the vibrational frequencies of the H_n^+ ($n = 5, 7$, and 9) ions.

As mentioned above, the calculated harmonic frequencies tend to systematically overestimate the true harmonic frequencies, as well as neglecting anharmonic effects. The theorists can crudely compensate for these errors by scaling the frequencies. In the case of H_5^+ , the highest frequency mode ν_1 is in large part an H_2 stretch. This mode is scaled by assuming that the error in the ν_1 frequency is proportional to the error in calculating the H_2 monomer frequency at the same level of theory:

$$\omega_0(H_5^+, \nu_1) = \omega_e^{calc}(H_5^+, \nu_1) \frac{\omega_0(H_2)}{\omega_e^{calc}(H_2)} \quad (1)$$

where ω_0 is the true vibrational frequency, and ω_e is the calculated harmonic frequency. This scaling is subject to size consistency errors; therefore, in CI calculations, one must be careful. For example, the H_5^+ CISD calculation must be compared to a CISD of H_2 and H_3^+ together, held asymptotically far apart.

In Table II, we have listed the highest frequency modes predicted by Yamaguchi *et al.* The highest frequency mode is close to the H_2 monomer stretch frequency³⁹ at 4161 cm^{-1} , and can be considered as the stretching of the solvent H_2 . This mode is actually red-shifted from the true H_2 frequency; the nearby charge decreases electron density and weakens the H_2 bond. These shifts are 100 to 250 cm^{-1} , far larger than those seen in neutral H_2 complexes. In $\text{Kr}\cdot\text{H}_2$, for example,⁴⁰ the shift is only 5 cm^{-1} . Even in solid H_2 ⁴¹ the para $Q_1(0)$ line ($v = 1, J = 0$) is shifted by only 11 cm^{-1} . Bernholdt *et al.*⁴² predict that H_2 hydrogen bonded to HF will have a vibrational red shift of 20 cm^{-1} . Furthermore, this normal mode of the ion now possesses a fairly large transition moment. In the H_2 molecule alone, this vibration is a dipole-forbidden transition. In H_5^+ , the oscillator strength is picked up by coupling of the H_2 stretch with motion of the central proton. As this proton moves, the center of charge moves with respect to the center of mass, creating a very large vibrational transition dipole. IR intensities are commonly enhanced in ions by this mechanism. Using Yamaguchi's notation,³⁶ we label this band ν_1 .

The next highest mode correlates with the $\text{H}_3^+ A_1$ symmetric stretch. Again, this mode is dipole-forbidden in H_3^+ alone, and in fact has only been observed in the partially deuterated species HD_2^+ and H_2D^+ . Only the antisymmetric E stretch at 2521 cm^{-1} , first observed by Oka^{43,18} has been studied. One theoretical estimate^{44,45} places the A_1 mode at 3178 cm^{-1} . The theory predicts that the unscaled harmonic frequency will be blue-shifted in the H_5^+ complex by 258 cm^{-1} (using a DZ+P full CI calculation). In H_5^+ , Yamaguchi *et al.* label this mode ν_2 . An increase in a vibrational frequency when a complex is formed is unusual. In H_5^+ , the H_3^+ ion is distorted. As the shared proton is pulled, the partial charge on the remaining two H atoms decreases, and this H_2 bond tightens up. The symmetric stretch takes on more of the character of an H_2 stretch. The absorption intensity is predicted to

be equal to that of the H_2 stretch in H_5^+ , but an order of magnitude weaker in the larger clusters.

Yamaguchi *et al.*, in their subsequent study³⁸ of H_5^+ , calculated not only the geometries but also the vibrational frequencies for a number of stationary points on the H_5^+ surface. The lowest lying saddlepoint is the D_{2d} geometry transition configuration for proton transfer. Despite a very small change in bond lengths, they have found that some of the vibrational frequencies change by 200 to 400 cm^{-1} , including both the ν_1 and ν_2 modes. The predicted frequencies for the D_{2d} geometry are also listed in Table II. Because the D_{2d} geometry appears to lie at almost the same energy as the C_{2v} minimum energy geometry, it is not clear that either will provide the correct vibrational frequencies.

Even the largest experimental value for the H_5^+ dissociation energy (the 9.6 kcal/mol value for ΔH_{300}° obtained by Hiraoka and Kebarle²³) is less than the energy having one vibrational quantum in either the ν_1 or ν_2 modes in H_5^+ . The larger clusters have even smaller dissociation energies. Based on the scaled frequencies, both of these modes are predicted to be above the dissociation limit, and are thus predissociating states. By exciting rovibrational transitions to these states, we can expect to dissociate the H_5^+ clusters, if the predissociation lifetimes are shorter than the radiative lifetimes or experimental trapping times (typically several milliseconds for both).

II. EXPERIMENTAL

The hydrogen cluster ions were produced either by electron impact ionization of neutral H_2 clusters, or within a high pressure (~ 200 torr) room temperature discharge. In the former, the ions were created with substantial amounts of excess internal energy; in the discharge, the ions were expected to be near room temper-

ature. The sources are described in more detail below. After extraction from the source, the beam of ions was mass-selected with a 20 cm radius sector magnet. The ion beam was decelerated to approximately 5 eV, then focused into a radio-frequency (rf) octopole ion guide. The pressure in this region was typically 1 to 3×10^{-9} torr. Collisions in the trap were found to be negligible on the timescale of the experiment. After 0.1 to 1.0 ms, the potential of the entrance lens was raised, and the ions trapped inside the octopole ion guide. After 1 ms to 2 ms, a laser was fired through the trap. In this experiment, we used one of three tunable infrared lasers; an optical parametric oscillator, a difference frequency laser, and a F center laser, discussed in detail in the following section.

After excitation with the laser, the ions were then released, mass analyzed with a quadrupole mass spectrometer, and detected with a Daly ion detector. Standard ion counting techniques were used. When measuring the parent ion signal, the ion count rate was often greater than 10^{+6} s^{-1} . In that case, the photomultiplier gain was reduced, and the (amplified) ion current measured.

The laser was fired or chopped in alternate data cycles; the signal was the difference between cycles with the laser on and cycles with the laser off. This eliminated background fragment counts resulting from decay of metastable ions, and collision-induced dissociation in the trap. The laser power was measured after passing through the trap, for normalization of the spectra.

The trap is 0.5 m long. Trapped ions bounce back and forth between two lens elements, on either side of the octopole, held at a d.c. potential about 20 V above the trap bias. The rf on the octopole creates an effective potential well perpendicular to the trap axis, confining the ions to the center of the octopole region. The Doppler width of the ions is broader than a room temperature width, because the laser beam is collinear to the trap. For H_5^+ at a mean energy of 0.5 eV, the expected Doppler

width is approximately 0.08 cm^{-1} .

A. Infrared Lasers

Three tunable infrared lasers were used in this experiment, covering the range from 2200 cm^{-1} to 6500 cm^{-1} , providing a choice of average power and frequency resolution.

The optical parametric oscillator (OPO)⁴⁶ was a LiNbO_3 crystal pumped by the far-field output (1 W) of a Quanta Ray DCR-1A Nd:YAG laser. No line narrowing elements were in the OPO cavity; thus, the linewidth was as broad as 20 cm^{-1} (at 4200 cm^{-1}), but was more typically $5\text{--}10 \text{ cm}^{-1}$ at the wavelengths used ($3500\text{--}4000 \text{ cm}^{-1}$). This laser gave the highest powers, and was used for preliminary searches. The wavelength was calibrated using an 0.3 m monochromator. The laser produced 8-10 mJ per pulse at 10 Hz.

A commercial difference frequency laser was used for some moderate resolution spectra. The Quanta Ray Infrared Wavelength Extender mixes the 1.06μ output of a Nd:YAG laser with the output of a near infrared dye laser. The laser linewidth was measured to be 1.2 cm^{-1} . The pulse energy was 0.8-1 mJ at 4000 cm^{-1} and 0.5 mJ at 3500 cm^{-1} . The laser was operated at 10 Hz.

Both of the above lasers utilize nonlinear mixing in LiNbO_3 crystals. This material has an unfortunate infrared absorption between 3460 and 3490 cm^{-1} caused by OH absorption. In the case of the difference frequency system, the output dropped over an order of magnitude, to 0.05 mJ per pulse or less in this range.

For high resolution experiments, spectra were taken with an F-center laser (Burleigh Instruments Inc.). Without an intra-cavity etalon, the laser produced 5 to 40 mW, cw, with a nominal linewidth of 0.5 cm^{-1} . With the etalon in place, the linewidth was specified as 1 MHz ($3 \times 10^{-5} \text{ cm}^{-1}$), far below the expected

Doppler limit for trapped ions of approximately 0.08 cm^{-1} . Because this laser was continuous, the experiment timing was modified. When the ions were trapped, the laser beam was flagged on with a shutter (A. W. Vincent Associates) for 20 ms. As before, the laser was flagged on during alternate cycles. The low duty cycle resulted in a significant decrease in average power and signal, relative to spectra taken with the pulsed lasers. The laser wavelength was calibrated using a Burleigh λ meter.

B. Sources

1. *Electron Impact Ionization of Neutral $(\text{H}_2)_n$ Clusters*

Most of the spectra reported here were of ions produced by electron impact of neutral hydrogen clusters $(\text{H}_2)_n$. The neutral clusters were formed by supersonic expansion of pure hydrogen (99.999% pure, from Matheson or Scientific Gas Products) through a 10μ nozzle. The stagnation conditions were 20–30 atm, at a temperature of 110 K. The expansion was skimmed with a Beam Dynamics electroform skimmer 7 mm from the nozzle. The first region was pumped with a liquid nitrogen trapped ten inch VHS diffusion pump backed by a 150 l/s roots pump. The chamber following the skimmer was pumped by a trapped, six inch diffusion pump, giving a background pressure of 0.5 to 1×10^{-5} torr. This region contained both the ionizer and electron optics. The molecular beam was ionized in a conventional Brink's ionizer. The electron energy was 80–100 eV, and the ionizer emission current was ≈ 4 mA. The upper panel of Fig. 2 shows the mass spectrum. H_2^+ and H_3^+ were the dominant ions; the H_5^+ current was approximately 100 pA. The beam intensity decreased monotonically with cluster size, but always showed a definite drop after H_9^+ .

Upon ionization of the $(\text{H}_2)_n$ clusters, the reaction



proceeds within the cluster. The excess energy in the reaction of 40 kcal/mol is deposited as internal energy in the cluster. Since, for larger clusters, the average binding energy of an H_2 is 3 kcal/mol or less,²³ the cluster probably fragments extensively. Several H_2 molecules evaporate from the cluster to carry off the excess energy.

The ionization and subsequent rearrangement leaves the cluster internally excited. We observed that approximately 0.1% of the ions fragment in the trap within the first 2 ms, predominantly by loss of a single H_2 . The fragmentation in the trap arises from metastable ions which have survived the 50 μs flight from source to trap. Any fragments from in-flight dissociation would not have enough energy to enter the trap. Previous experiments with weakly bound ions have shown that, under similar conditions, collisional processes have far smaller contributions for the trapping times used here. Furthermore, such fragmentation was not observed for ions created internally cold. Thus we have direct evidence for metastable cluster ions with predissociation lifetimes on the order of milliseconds.

The background counts arising from the metastable fragmentation were comparable to the laser induced signal. These daughter ions thus reduced the signal to noise for spectra recorded with the



channel. For H_5^+ , this was the only channel. The background counts were equal to the signal counts at the peak of the absorption bands, causing a significant decrease in the signal-to-noise. For the larger clusters, loss of one H_2 was a secondary dissociation channel; thus, the signal to noise was very poor, but better spectra could be recorded using the other dissociation channels.

2. Corona Discharge Source

To eliminate spectral congestion and to reduce the background of fragment ions, a source of internally cold ions was needed. Several such sources have been developed, all involving ionization at relatively high pressures ($p > 1$ torr). There must be enough collisions for the rotational and vibrational degrees of freedom to be at least partially equilibrated with the source temperature. These sources tend to create thermodynamically stable ions,^{3,47,48} often terminal ions "at the end of the food chain." Since the density of charged species is low, the presence of trace impurities can have a pronounced effect on the mass spectrum. For example, in a high pressure hydrogen discharge, the dominant ion may be not H_3^+ but H_3O^+ . The proton affinity of water is 165 kcal/mol,¹⁹ 64 kcal/mol higher than that of H_2 . As a result, unless the source and gas is thoroughly dried, all H_3^+ will react with trace water by very exothermic proton transfer.

Corona discharges have been used as sources of ionic clusters in a number of previous experiments.^{49,50} Searcy and Fenn^{51,52} developed a corona discharge source to study water cluster nucleation about an ion during a supersonic expansion, while Beuhler, Ehrenson and Friedman²⁵ used one for measurements of hydrogen cluster ion equilibria prior to expansion. In the apparatus of Searcy and Fenn, a discharge was struck from a tungsten needle to a tungsten grid; the volume between the grid and a nozzle was a field-free drift region, in which the ions could equilibrate. Beuhler *et al.* did not use such a drift region. Beuhler *et al.* reported ion currents of only 10^4 ions per second; however, they used very small apertures ($12\ \mu$) to minimize cooling effects after the nozzle.

The corona discharge source used in this experiment, shown in Fig. 3 was built by L. Yeh. The body of the source was copper and was in thermal contact with a reservoir. It was designed for cooling with liquid nitrogen, although Freon-12

and Freon-22 were the primary coolants in this experiment. The electrode was a nickel-plated steel sewing needle which could be translated to vary the distance from body to point. We expected that the discharge would be located in a conical-shaped region. This tapered down at 30° to a cylindrical volume 1.0 mm in diameter, 1.7 mm in length before the nozzle in which the ions would react and equilibrate. The drift time in this region was estimated to be approximately 0.5 ms. The nozzle was a $70\ \mu$ aperture in a platinum disk (Ted Pella, Inc.). The source was floated at +350V above ground.

The needle was fixed at a minimum distance of 3.3 mm from the tapered wall of the source, 5.7 mm from the beginning of the drift region. It was in series with a 1 M ballast resistor. Typical discharge conditions were 2.5 kV and $30\ \mu\text{A}$. Ultra-high purity hydrogen (99.999 % pure, as in the previous source) at 100 to 200 torr was used. The gas was always passed through a liquid nitrogen cooled trap containing Linde 13X molecular sieve. The inlet line and the source were baked out daily and pumped to a base pressure of 10^{-5} torr or less. Without these precautions, no hydrogen cluster ions appeared. Instead, for temperatures above approximately -10°C , protonated water clusters were the dominant species in a dirty source. If the source was cooled further, the water clusters were replaced by protonated nitrogen clusters. Hydrogen cluster ions could only be produced in useful currents by keeping the source and inlet system clean.

The skimmer aperture was 1.4 mm, and was approximately 7 mm from the nozzle. The skimmer was kept to within 1 V or less of the nozzle voltage, to prevent acceleration and subsequent collisional heating of the ions. A grid surrounding this region and held at the same potential as the source was necessary to prevent stray fields from penetrating into the nozzle-skimmer region. The skimmer was followed by a conical extractor, 2 cm behind, at a potential of 10 to 20 volts below the

skimmer. Variations of this voltage could alter the ion size distribution. This result was probably due to extraction and focusing effects, because there was never any indication of collisional heating. The ions were then accelerated and focused. During normal operation, the pressure of the source differential chamber was 1 to 2×10^{-4} torr, while the post-skimmer/ion optics region was 6×10^{-6} torr.

A mass spectrum using the sector magnet is shown in Fig. 2 at two source temperatures. The H_5^+ current through the machine was about 3×10^5 counts/s at a source temperature of 260 K. At lower temperatures (80 K), the ion current was dispersed over a large range of cluster sizes; the intensity of a given cluster was relatively low.

III. RESULTS

A. Clusters Formed by Electron Impact Ionization

Low resolution OPO spectra were recorded from 3800 cm^{-1} to 4200 cm^{-1} for the ions H_n^+ ($n = 5, 7, 9, 11, 13$, and 15) created by electron impact ionization. With the exception of H_5^+ , all ions had a single, slightly asymmetric peak in this region. For each parent ion, we searched for spectra with the OPO at all possible fragment masses; in general, only one or two channels were important. Fig. 4 shows the branching ratios of the different dissociation channels with the laser set at the peak of each absorption. In general, the major channel for each cluster was consistent with loss of the maximum number of solvent H_2 energetically allowed.

The spectrum of H_5^+ is shown in the upper panel of Fig. 5. This spectrum was taken with the OPO, detecting the H_3^+ fragment. The peak lies at 3910 cm^{-1} , red-shifted 250 cm^{-1} from the vibrational origin of unbound H_2 monomer at 4161 cm^{-1} . In addition to an asymmetric peak, there is a long shoulder going to higher frequen-

cies, extending over 300 cm^{-1} .

The OPO spectrum of H_7^+ is shown in the middle panel of Fig. 5. Two spectra are shown, one for dissociation to H_3^+ and one for dissociation to H_5^+ . The two spectra are similar, with absorption maxima at the same frequency. The peak is more symmetric than in H_6^+ , with a much smaller high frequency shoulder. The spectrum arising from dissociation to H_3^+ is slightly broader, and has a larger relative contribution from the high frequency shoulder. The peak lies at 3980 cm^{-1} , 70 cm^{-1} to the blue of the H_6^+ peak.

The peak of the H_9^+ absorption at 4020 cm^{-1} shown in Fig. 5, is at an even higher frequency than those of the smaller clusters. The shift is only 40 cm^{-1} from the H_7^+ maximum. Again, spectra recorded detecting different fragments are similar, with the H_3^+ channel yielding the broadest peak, and the H_7^+ channel the narrowest. The signal-to-noise in the H_7^+ channel is low, in part because the background is higher, and in part because it is a weak channel. The dominant products are H_5^+ and, to a lesser extent, H_3^+ , as seen in Fig. 4.

When detecting the H_7^+ fragment, an additional feature appears in the spectrum. There is a small depletion in the background H_7^+ counts, resulting in a negative signal on the low frequency side of the peak. This is caused by laser photodissociation of the background H_7^+ that were created from (laser independent) dissociation in the trap of metastable H_9^+ . The absolute number of ions is small, relative to the number of parent H_9^+ , and does not make a significant contribution to the signal at mass 5 or mass 3.

In the larger clusters H_{11}^+ , H_{13}^+ , and H_{15}^+ , the peak positions are close in frequency to that of the H_9^+ peak. Dissociation with loss of only one H_2 molecule is not observed. A clear depletion signal is observed at these frequencies when detecting the channel H_{n-2}^+ .

Spectra were recorded for all parent ions, at selected daughter ions, using the color center laser. The spectra shown in Fig. 6 were all taken at a resolution of 0.5 cm^{-1} , with the intracavity etalon removed. Additional scans were taken with the intracavity etalon in place, giving a laser line width of $\approx 3 \times 10^{-5} \text{ cm}^{-1}$ and Doppler limited resolution. We did not fully cover the peaks observed at low resolution, but did try to scan selected $5\text{--}10 \text{ cm}^{-1}$ wide segments. We searched the H_5^+ spectrum the most intensively. In no case was any additional spectral structure resolved with the higher resolution. The signal-to-noise was worst in the high resolution scans, usually no better than 10:1 after signal averaging. An individual scan with the intra-cavity etalon in place had a range of at most 1 cm^{-1} , and more typically 0.5 cm^{-1} .

Based on the calculations of Yamaguchi *et al.*^{36,38} we expected the mode in H_5^+ correlating to the H_3^+ symmetric stretch to occur near 3400 cm^{-1} . Fig. 7 shows the peak we observed using the color center laser with 0.5 cm^{-1} resolution. It had a maximum at 3532 cm^{-1} , with an intensity equal to that of the 3910 cm^{-1} peak. No rotational structure was observable at this resolution. The intensity of this band is, within 20%, identical to the 3910 cm^{-1} band, as predicted by Yamaguchi, Gaw and Schaefer at the DZ+P SCF level. We also scanned from 3000 cm^{-1} to 3600 cm^{-1} , searching for the corresponding band in H_7^+ and H_9^+ , but found no absorption. Any peak would therefore have to be at least an order of magnitude less intense to go unobserved.

B. Results with the Corona Discharge Source

As stated above, the hydrogen cluster beam intensity of the corona discharge source was two to three orders of magnitude less intense than that of the electron impact source, and was predominantly H_5^+ at these temperatures. Thus, it was

difficult to take spectra of the larger clusters. We therefore limited scans for the most part to the H_5^+ cluster.

The lower plot of Fig. 8b shows the H_5^+ spectrum taken with the OPO in the region of the ν_1 mode, compared to the spectrum of the ions formed by the electron impact source (Fig. 8a). There was a significant difference in the band contour, when compared to the spectrum of H_5^+ created by electron impact. The main peak at 3910 cm^{-1} did not shift, but became somewhat narrower. The high frequency shoulder decreased in intensity, except near 423 cm^{-1} . Thus, the spectrum of cold H_5^+ appears to have an additional weak band 340 cm^{-1} above the main band. The spectrum of H_5^+ formed by electron impact ionization could be reproduced if either the grid voltage was set to ground, or if there were a voltage drop of 10 to 30 V across the nozzle and skimmer. The difference between the two spectra is therefore caused by the different internal temperatures of the ions created in the two sources. Fig. 9 shows the H_5^+ ν_1 spectrum taken with the difference frequency laser at a resolution of 1.2 cm^{-1} . The band has a more sharply defined peak, with a relatively flat shoulder at lower frequencies, but otherwise contains no further structure. A similar band contour was seen in the spectrum of hot H_5^+ using the F center laser. The detail in the lower panel was taken with the WEX at 0.75 cm^{-1} , and reveals the lack of structure in the spectrum.

Again, we took extensive scans of the peak with the F-center laser, at both 0.5 cm^{-1} and $3 \times 10^{-5}\text{ cm}^{-1}$ resolution, but still found no evidence of resolvable structure within our signal-to-noise. Scans over sections of the H_7^+ and H_9^+ bands also revealed no resolvable rotational structure. We also scanned sections of the H_7^+ and H_9^+ spectra using both the F center laser and the difference frequency laser, but again saw no evidence of resolvable lines.

The observation of a weak band at 4230 cm^{-1} for H_5^+ prompted a search for other

weak combination bands or overtones at higher frequencies. We scanned 3900 cm^{-1} to 5300 cm^{-1} using the difference frequency laser (1.2 cm^{-1} resolution) in the H_5^+ spectrum, but found no new features, despite the higher laser power obtainable at these wavelengths from the difference frequency laser.

IV. DISCUSSION

A. Spectra

Table II lists the frequencies of the observed peak maxima for all H_n^+ with $n = 5, 7$, and 9 along with the frequencies predicted by various levels of *ab initio* theory. Full CI values are available only for H_5^+ ; frequencies at the CISD level have been computed for H_7^+ . Yamaguchi *et al.*³⁶ have calculated vibrational frequencies for clusters as large as H_9^+ .

One must use care in comparing the experimental and theoretical vibrational frequencies. The experimental frequencies are maxima of unresolved bands, not true vibrational band origins. Band heads and other pileups of lines could lead to band maxima displaced from the origin. This uncertainty is particularly important for H_5^+ , which has an asymmetric band shape.

One of the largest uncertainties in the theoretical values lies in the scaling of frequencies to estimate both the systematic error and the anharmonic correction. In most cases, *ab initio* calculations overestimate the harmonic vibrational frequencies. Furthermore, the normal mode analysis is inadequate for weakly bound complexes with large amplitude vibrations. Recent advances⁵³ in the computation of anharmonic constants using analytic second derivatives should improve the accuracy of the calculations, but in cases with large anharmonic coupling, as in floppy molecules, such an expansion may not be satisfactory.

The ν_2 mode of H_5^+ cannot be properly scaled, because the symmetric stretch of H_3^+ has not been experimentally observed. We can still estimate the scaling factor, if we use a theoretical prediction for the H_3^+ symmetric stretch. This calculation involved numerically solving the vibrational hamiltonian on a potential energy surface derived from *ab initio* points. The calculation has proved to be very accurate for the ν_1 mode of both HD_2^+ and H_2D^+ , which have been observed, as well as the ν_2 mode of H_3^+ . Agreement with observed band origins from high resolution spectra is a few wavenumbers or less. The predicted H_3^+ symmetric stretching frequency is 3178 cm^{-1} ,⁴⁴ resulting in a scaled value of 3407 cm^{-1} for the frequency of the ν_2 mode of H_5^+ at the C_{2v} geometry, compared to our observed band at 3532 cm^{-1} .

Despite the uncertainties, the theoretical and experimental values are in good agreement. The worst agreement is for the H_7^+ cluster. Even the full CI estimate is off by 41 cm^{-1} . The theoretical predictions for the frequencies at the saddle point geometry D_{2d} do not agree at all with the experimentally observed frequencies.

The observed peak frequencies of the H_2 stretch are plotted as a function of cluster size for all observed clusters in Fig. 10. As noted above, the peaks are red-shifted from the vibrational frequency of the H_2 monomer. As the cluster size increases, the frequency shift relative to the monomer frequency decreases; however, after H_9^+ , the frequency shift changes very little. This result can be understood if we consider the H_9^+ cluster to be a H_3^+ ion with a complete inner shell of solvating H_2 ligands, as depicted in Fig. 11. In the larger clusters, the H_9^+ forms a largely unperturbed inner core. The *ab initio* calculations^{28,30,36} indicate that H_2 molecules bind first to the three corners of the H_3^+ ion. After the first three H_2 bind, additional H_2 molecules are bound far more weakly. The reason for the lack of change in the spectrum is two-fold. First, the three H_2 molecules at the corners are strongly perturbed by the ion, and thus possess the most oscillator strength at $\approx 4000\text{ cm}^{-1}$.

The outer H_2 molecules (darkened in Fig. 11) are far less perturbed, and thus do not absorb. Second, these outer H_2 do not strongly perturb the H_9^+ core; thus, the H_2 at the corner absorb at a similar frequency, despite the added H_2 molecules.

As mentioned above, such a description of the larger clusters is supported by both the *ab initio* calculations and the trends observed in the ΔH° . However, the trend is not as convincing in the experimental data. The difference between the enthalpies²³ for H_9^+ and H_{11}^+ , 3.8 and 2.4 kcal/mol, is not so dramatic; furthermore, only Hiraoka and Kebarle have measured the enthalpies of clusters larger than H_7^+ , but their measurements for the smaller clusters disagree with the most recent experiments, implying possible systematic error.

We see only a small change in the spectrum at H_{16}^+ relative to the smaller clusters. H_{16}^+ may have some enhanced stability if it is the completion of a second solvation shell; this is not known. This is the cluster which Clampitt and Gowland observed to be especially abundant in their sputtering experiment.¹² They attributed this result to stability due to octahedral coordination of the H_2 ligands about the H_3^+ . Such a dramatic change in the structure is not evident from our spectra. The H_{16}^+ abundance they observed may in fact be kinetic; H_{16}^+ dominated their reported nascent distribution, but was only a minor peak in the supposed equilibrium distribution. No thermochemical experiments have measured the enthalpy or entropy of dissociation for this cluster. More recent cluster distributions obtained from electron impact ionization of neutral clusters reveal some extra stability of H_{15}^+ , and Reuss and others^{14,15,16,17} see evidence from collisional dissociation for some stability of H_{15}^+ . We did not obtain the H_{17}^+ spectrum, and the results we have cannot contribute to this question. If the stability of this ion is due to formation of a second solvation shell, then it is not certain whether such a weak effect would be evident from the IR spectrum, and would be relative to the H_{17}^+ spectrum in any case.

The weak band at 4230 cm^{-1} in H_3^+ could be either a combination band or an overtone. It lies 340 cm^{-1} above the ν_1 band at 3910 cm^{-1} . Two lower frequency modes are good candidates.^{36,38} Both ν_4 (H_3^+ asymmetric stretch) and ν_8 (intermolecular stretch) modes involve large motions of the central proton, and consequently large changes in the dipole moment. These two modes are in fact the strongest absorbers of the nine vibrational modes of H_3^+ , with predicted intensities in the double harmonic approximation over five and ten times larger (for ν_8 and ν_4 respectively) than the ν_1 and ν_2 modes.

The *ab initio* calculation³⁸ predicts that the low frequency stretch ν_8 of the complex bond has a harmonic frequency of 478 cm^{-1} . This mode is clearly anharmonic, and the frequency is undoubtedly much lower. Thus, the weak band could be the $\nu_1 + \nu_8$ combination band. If the 4230 cm^{-1} band is assigned as the combination band $\nu_1 + \nu_8$, then the ν_8 vibrational frequency is 340 cm^{-1} . This raises the question of where the $\nu_2 + \nu_8$ combination mode would lie. We predict that it would occur at 3870 cm^{-1} , only 40 cm^{-1} below the observed ν_1 band. This might give rise either to spectral congestion, or even the possibility of a Fermi resonance, since both modes will have a_1 symmetry.

The 4230 cm^{-1} band could also conceivably be an overtone. Yamaguchi, Gaw, Remington, and Schaefer predict a mode, the strong ν_4 mode, to have a harmonic frequency of 1746 cm^{-1} . Again, this number may seriously overestimate the true vibrational frequency. The scaled value for this mode is 1641 cm^{-1} , placing the second overtone at less than 4900 cm^{-1} .

The above discussion suggests an alternate assignment of the 3532 cm^{-1} band, as the first overtone of the 1746 cm^{-1} ν_4 mode. The intensity of the band is what one would expect, given that overtone intensities are approximately one order of magnitude weaker than the corresponding fundamentals. However, the position of

the band is somewhat high; twice the calculated harmonic frequency is 3492 cm^{-1} but this is an upper bound and should severely overestimate $2\omega_e - 6\omega_e x_e$. Twice the scaled frequency is 3282 cm^{-1} , well below the observed band. Therefore, this is an unlikely candidate for the assignment of the 3532 cm^{-1} band.

B. Linewidths

Despite using high resolution lasers, we were unable to resolve rotational structure in any of the vibrational bands. These clusters are relatively light, and from the predicted rotational constants, the rovibrational spectrum should be resolved for $n = 5, 7$, and 9 . There are several possible explanations for the absence of rotational structure. The asymmetry of the peaks, particularly those of H_5^+ , and the observed narrowing of the spectrum with temperature indicate that at least part of the linewidth is inhomogeneous. We can rule out some instrumental artifacts, because we have observed sharp features in the spectra of other ions created in the corona discharge source. Thus, the trapping does not give rise to unexpectedly large Doppler widths. One possibility is that the spectra are very congested. The internal temperature is quite sensitive to the field between the nozzle and the skimmer; it is possible that the field was still large enough to partially heat the ions. The large rotational constants, 3.2 cm^{-1} for H_5^+ and 1.2 cm^{-1} for H_7^+ , would indicate that the line density should be low; however, there are many low frequency modes which could contribute to the congestion, particularly if the molecules are internally hot. The larger clusters will also have overlapping bands at $\approx 4000\text{ cm}^{-1}$, since more than one H_2 will absorb. If the H_2 stretches are coupled, they will give rise to splittings which may congest the spectra. Precedence for such congestion at or near dissociation is seen in the highly congested spectrum of H_3^+ observed by Kennedy and Carrington.⁵⁴

Another possibility is that the spectrum consists of both sharp and broadened transitions. The spectrum might then appear as small lines on top of a continuous baseline, and would require more signal averaging to observe the structure. From the signal-to-noise in our experiment, we would conclude that the discrete spectrum must be at least ten times weaker than the continuous spectrum.

The peaks could also be at least partially homogeneously broadened. This would require that the linewidth be on the order of the rotational spacing of 2 to 7 cm^{-1} . If the mechanism were lifetime broadening, the corresponding lifetimes would be approximately 1 ps. Such linewidths have been observed in the predissociation of van der Waals complexes such as the ν_7 mode of the ethylene dimer.^{55,56} Attempts at observing H_3^+ spectra by velocity modulation absorption spectroscopy in a hydrogen discharge have thus far failed.⁸ This high resolution technique cannot detect significantly broadened transitions. The inability to detect any transitions can be explained if the transitions are homogeneously broadened. However, the high vibrational temperatures and low pressures may limit the concentration, and the negative result is therefore not conclusive.

The clusters H_7^+ and larger, as well as their products after loss of one H_2 , possess several low frequency vibrations and internal rotations. Therefore, these clusters will have very high densities of states at 4000 cm^{-1} . Furthermore, there will be many rovibrational dissociation channels available. The interaction between an H_2 at the corner of the H_3^+ is very anisotropic, so dissociation leading to loss of an H_2 occupying a corner site can proceed with transfer of excess energy into rotation.^{55,57} The large moments of inertia of H_2 and H_3^+ allow large energy transfer to rotation with very small changes in rotational quantum numbers. For these reasons, one might expect these clusters to dissociate efficiently.

C. The H_5^+ Ion

The high level *ab initio* calculations have found the H_5^+ potential to be very flat. The resulting difficulty in pinpointing the exact location of the equilibrium geometry has prompted theorists^{28,30,33,36,38} to conclude that among the hydrogen cluster ions, the H_5^+ ion deviates the most from the simple picture of an H_2 molecule weakly bound to an H_3^+ ion. Considered as $H_2 \cdots H^+ \cdots H_2$, it is the simplest of the proton bound complexes $A \cdots H^+ \cdots B$ such as $H_3O^+ \cdots H_2O$, $NH_4^+ \cdots NH_3$, and $H_3O^+ \cdots NH_3$. Theorists^{33,58} have investigated these complexes extensively. Experimental studies in the gas phase are far more limited. The location of the proton depends to a first approximation on the relative proton affinities of the two bases. At small separations, the potential well for the proton tends to be very flat; as the bases are pulled apart, the potential bifurcates and becomes a double minima well. At the equilibrium separation, the nature of the well, single or double, depends on the pair of bases A and B. In neutral hydrogen-bonded dimers such as $(HF)_2$ and $(NH_3)_2$, inversion of the dimer leading to exchange of the hydrogen bond is important, but there is no question of proton transfer.

In their exhaustive study of H_5^+ , Yamaguchi, Gaw, Remington, and Schaefer have computed the properties of ten stationary points, only one minimum at very high levels of theory. Their calculations show that there are three saddle points lying less than 0.6 kcal/mol above the energy minimum. The minimum energy geometry is the C_{2v} $H_3^+ \cdots H_2$, but the D_{2d} transition state for intramolecular proton transfer to $H_2 \cdots H_3^+$ is calculated to be only 0.08 kcal/mol or 30 cm^{-1} higher at the full CI level using an extended (larger than DZ+P) basis set. The calculated harmonic frequency is 478 cm^{-1} at the (DZ+P) full CI level. Thus, the zero point energy level is either at or just below the D_{2d} barrier. The zero point motion of the cluster therefore involves the central proton either tunneling or moving back and forth between the

two H_2 's, and undergoing the isomerization $H_3^+ \cdot H_2 \rightleftharpoons H_2 \cdot H_3^+$. As the intermolecular distance between the two H_2 is stretched, the barrier height will increase, and the proton, finding itself in a double well, must follow one of the H_2 .

Another low frequency motion is the torsional mode. This is the propeller-like rotation of the H_2 molecule about the C_2 axis. The C_{2v} barrier for this internal rotation at the extended basis set full CI level is only 128 cm^{-1} . At most, only two rotational levels could lie below this barrier. Thus, the internal rotation is only slightly hindered.

The third low lying stationary point, with D_{2h} symmetry, is the planar barrier for H_2 rotation from the symmetric D_{2d} configuration. The energy of this point is 178 cm^{-1} , very nearly the sum of the two previous barrier heights. Thus, the barrier for internal rotation is very low, and does not change as the central proton moves, and the two modes can be considered independent.

The H_5^+ oscillates between two wells because the D_{2d} barrier for isomerization is so low. The rovibrational energy levels are therefore doubled. Internal rotation of the H_2 about the C_2 axis is nearly unhindered, and rotation by π leads to a new framework (distinguishable permutation), so this internal rotation creates an additional doubling. The in-plane rotation of the H_3^+ about its own C_3 top axis has a much larger barrier, calculated by Yamaguchi *et al.* to be 4.8 kcal/mol (DZ+P full CI). This should further split the lines, although the splitting should be small in the ground state. It is readily seen that a combinations of the above isomerizations can lead to exchange of any pair of hydrogen atoms in H_5^+ . Thus, compared to the rigid structure, all five H atoms can be permuted, and the floppy H_5^+ can access $5! = 120$ potential minima! The proper group for treating the symmetry of this molecule⁵⁹ is then not C_{2v} , but the permutation inversion group G_{240} . In fact, a single C_{2v} level is not split into 120 levels; nuclear spin statistics place rather stringent

restrictions on the correlation between C_{2v} and G_{240} representations. Furthermore, the states in G_{240} are highly degenerate. Thus, a typical C_{2v} level is split into two to six very degenerate levels (some up to nine-fold degenerate), once all symmetry is accounted for. Thus, the large amplitude motions greatly increase the number of states, relative to a naive, rigid molecule assumption. This may result in a more congested spectrum than expected, as well as a significantly larger density of states at the dissociation energy.

What are the vibrational modes of such a nonrigid molecule? Can normal mode analysis properly predict the vibrational frequencies? As seen in Table II, the changes in the ν_1 and ν_2 vibrational frequencies on going from the C_{2v} geometry and to the D_{2d} geometry are over 200 cm^{-1} . The ν_3 through ν_6 modes change by 200 to 400 cm^{-1} , while the other three modes are almost unchanged. It is not clear that the observed frequencies should be interpreted as a means of choosing between two alternate equilibrium geometries. The large changes in vibrational frequencies with small changes in the stretching of the weak bond imply coupling of these higher vibrations with this coordinate. The anharmonic mixing of modes may be so strong that the harmonic frequencies predicted from the equilibrium geometry would be of limited use. The empirical scaling of the harmonic frequencies should only account for the anharmonicity inherent in the isolated molecule.

No vibrational calculation beyond the harmonic oscillator approach has been done yet. In the following paragraphs, we outline one possible approach based upon the reaction path⁶⁰ and reaction surface hamiltonian^{61,62} methods.

Yamaguchi and Schaefer have done DZ+P SCF calculations at different values of the intermolecular distance along the reaction path $H_3^+ + H_2 \rightarrow H_3^+ \cdot H_2 \rightarrow H_2 + H_3^+$. The points have been calculated⁶³ by fixing the distance from H_2 to the central H atom, and optimizing all other coordinates. The curve $V_e(R)$ shown in Fig. 12 is

a spline fit to their thirty points, and is plotted against R , the distance along the reaction path (treating the cluster as a collinear triatomic $\text{H}_2\text{—H}^+\text{—H}_2$ system). The point $R = 0$ is the D_{2d} saddlepoint. The double well for proton transfer is quite evident in Fig. 12. The potential deviates considerably from one obtained with higher level theory, because this calculation uses a small basis set and no correlation. At the C_{2v} minimum energy geometry, the intermolecular distance is 1.5 Å, not 1.2 Å. The D_{2d} saddlepoint is much higher in energy; 500 cm^{-1} instead of 30 cm^{-1} . The SCF dissociation energy is 1664 cm^{-1} , lower than the 2000 cm^{-1} obtained using the same basis set but with full CI. Despite these differences, we can at least qualitatively study some of the properties of the potential.

Yamaguchi and Schaefer⁶³ have also calculated force constants and harmonic frequencies at each point. Normal modes can be constructed from the remaining $3N - 7$ modes. The $V_i(R)$ potential, along with the vibrational information, can be used in a reaction path approach such as described by Miller, Handy, and Adams (related to the spectroscopic semi-rigid bender model)⁶⁰ to treat the dynamics of H_3^+ . The variations in vibrational frequencies as a function of R are treated, to a first approximation, with an adiabatic separation of the high frequency modes from the reaction path. The result is a set of effective potentials $V_i(R)$, one for every vibrational level i , i.e. the proton transfer motion and barrier height will vary for each vibrational state. For example, the relative changes in frequencies from C_{2v} to D_{2d} indicate that, compared to $V_e(R)$, the barrier for proton transfer is much lower in ν_1 and much higher in ν_2 . Such vibrational effects are the basis for dynamical resonances in reactive systems.⁶⁴

A two dimensional potential coordinate system for H_3^+ is shown in Fig. 13, where R_1 and R_2 are the distances from the central H atom to each H_2 in the collinear configuration. The curve $V_e(R)$ from Fig. 12 is the path of minimum energy shown

on this surface. The open boxes are the locations of the two DZ+P SCF C_{2v} equilibrium geometries. For reference purposes, the C_{2v} and D_{2d} configurations from the full CI calculations are also shown as open circles and as an X respectively. At the higher level of theory (DZ+P, full CI), the equilibrium bond length decreases, and the potential energy surface becomes shallower. The predicted C_{2v} minimum is below the D_{2d} saddlepoint by only 30 cm^{-1} at the full CI level. It is interesting to note that, while there is a large change in geometry when adding the effects of correlation, the change seems to be limited to one dimension, along the reaction path. The potential energy contours are not known, but one can guess that the reaction follows a steep walled "canyon" with a minimum near the saddlepoint.

If points on this surface are calculated, one can numerically integrate the potential. Carrington and Miller⁶¹ have developed the reaction surface hamiltonian approach to treat two coupled large amplitude coordinates. They have applied it to the problem of intramolecular H atom transfer in malonaldehyde,⁶² a problem similar to the proton transfer in H_5^+ . Again, vibrationally adiabatic surfaces can be constructed as a first approximation. Solution of the dynamical problem then gives the vibrational transition frequencies, as well as splittings due to the double well.

Examination of the reaction path in Fig. 13 reveals that this coordinate changes in character from a purely intermolecular stretch at large separations, to motion of the central proton at the saddlepoint. In the region near the potential energy minima, the reaction path has a large curvature. In other words, the intermolecular stretch, i.e. the dissociation coordinate, is strongly coupled to the higher frequency modes in H_5^+ , even in the ground vibrational state.

We have discussed, albeit qualitatively, some of the dynamical features of the H_5^+ cluster. This model provides an explanation for the large linewidths observed for the ν_1 and ν_2 modes. The calculations of Yamaguchi, Gaw, and Schaefer indicate

that these normal modes, although primarily high frequency H_2 stretches, include motion of the central proton. This coupling is not surprising, since the two H_2 bonds are coordinated directly with the proton. It is responsible for the observed intensity of the bands. Since the motion of the central proton is in turn strongly coupled to the intermolecular stretch, the ν_1 and ν_2 modes may be more strongly coupled to the dissociation channel than would normally be the case in neutral species such as the HF dimer. Vibrational predissociation of the high frequency modes would then be very fast. This IVR may be enhanced for the ν_1 mode, by coupling with the ν_2 mode at the D_{2d} geometry.

These assertions can be tested if a more accurate dynamical calculation is performed. Such a calculation would require many *ab initio* points of the potential energy surface, and a vibrational analysis such as the reaction surface hamiltonian.

D. Future Work

Most of the effort reported in this paper was expended searching the H_5^+ spectrum. Selected high resolution scans of the spectra of larger clusters H_7^+ and H_9^+ also revealed no structure, but the scans covered only a limited range. No scans using the F-center laser or the difference frequency laser were performed for the larger clusters created in the discharge source. A more detailed examination of the larger clusters therefore would be in order, although the ion intensity is rather low. The beam current might be increased, perhaps by different source conditions or better ion extraction optics. It might also be interesting to search for weak absorption by the outer H_2 molecules in the larger clusters.

A clear extension of this work would be to study the deuterated isotopes of H_5^+ . For mixed isotopes, we expect the spectra to be somewhat ambiguous, because several isomers would exist for a given parent mass. Interesting dynamical infor-

mation might be obtained, however, from studying the branching ratios to different products. Furthermore, in isotopically mixed clusters the relative vibrational frequencies would shift, possibly reducing problems such as broadening due to Fermi resonances. The fully deuterated species would also be interesting to study. The heavier nuclei might have a significant effect upon the rate of IVR and/or predissociation. Unfortunately, the vibrational frequency will be shifted to approximately 2800 cm^{-1} . The laser power in this region is an order of magnitude weaker, and spectra will be quite difficult to measure.

Other bands of H_5^+ can be accessed only by two photon experiments. Yamaguchi, Gaw and Schaefer predict that two bands, ν_3 and ν_4 , have transition strengths that are an order of magnitude larger than the bands studied here. The most useful lasers in this range are the tunable diode lasers (Spectra Physics/Laser Analytics) and difference frequency lasers. The typical power from these sources is quite low, milliwatts or less. There also appear to be modes with frequencies in the range of CO_2 lasers. Various two photon dissociation schemes can allow one to probe these states lying below the dissociation limit. These modes are prime candidates for study using the velocity modulation technique.

More exotic hydrogen clusters can also be studied. Although conventional ion sources yield only odd mass hydrogen cluster ions, Kirchner, Jarrold, and Bowers have reported the observation of H_4^+ . Theoretical work suggests that the geometry of this ion is $\text{H}_3^+ \cdots \text{H}$, with a dissociation energy comparable to that of H_5^+ . Such an ion should have a symmetric H_3^+ stretch mode at approximately 3500 cm^{-1} , similar to that of H_5^+ . Kirchner et al suggest that reaction to form H_4^+ cannot proceed along the ground state surface of $\text{H}_2^+ + \text{H}_2$. They believe that conventional sources of hydrogen cluster ions will not produce this species. They have developed a source which can create on the order of $10^6\text{ H}_4^+/\text{s}$, although the ions created

might be vibrationally hot. Design of a similar source should allow us to observe the spectrum of this ion as well. Vibrational bands of H_4^+ might give us more information on the structure and bonding in H_5^+ as well.

The negatively charged hydrogen cluster ions would also be worth studying. Recent calculations^{32,33} indicate that they are bound with energies roughly similar to H_n^+ , but their structures are quite different: The H_2 are solvated around a single H^- , and thus the octahedral H_{13}^- is predicted to be the ion with the completed inner shell.

V. SUMMARY

Using vibrational predissociation, we have observed the H_2 stretching mode in the ionic clusters H_n^+ , with $n = 5, 7, 9, 11, 13$, and 15 . We have also observed the H_3^+ symmetric stretch mode in H_5^+ . These spectra are an important first step in our investigation of the infrared spectroscopy of cluster ions. The H_2 stretch band positions we have observed for these clusters are consistent with the prediction that H_9^+ is a stable species, with a completed coordination shell of three H_2 at each corner of the H_3^+ ion. Spectra of all ions were scanned at 0.5 cm^{-1} resolution, but in no case were rovibrational lines observed. The spectrum of H_5^+ was searched at Doppler limited resolution ($<0.08\text{ cm}^{-1}$), but again no resolvable lines were seen, although the expected line spacing was 6 cm^{-1} . To eliminate hot bands and congestion, the ions were created in a high pressure corona discharge source to create thermalized ions. Only a change in the band contour was observed, including the emergence of a weak combination or overtone band. These results strongly suggest the possibility of homogeneous broadening. Calculations by *ab initio* theory suggest that H_5^+ has a very shallow potential surface. We have discussed possible implications, based on the theoretical information available. Calculations of the H_5^+ surface and dynamics

are eagerly awaited.

APPENDIX: SOURCES OF INTERNALLY COLD IONS

When we saw the need to create ions with little rotational or vibrational energy, we found several acceptable sources in the literature. In this appendix, I briefly discuss some of the alternatives, which fall into two categories: extraction from weak, high pressure discharges, and ionization of expanding jets.

Ionization typically leaves an ion internally hot; in high pressure discharges, the ions undergo many collisions and thermalize. Furthermore, in chemiionization sources, the cold ions can then react by charge transfer to gently ionize the molecule of interest. Many thermochemical studies of cluster ions have been performed by high pressure mass spectrometry. In experiments by Kebarle,³ the gas, at pressures of 0.1 to 10 torr, is ionized by a pulsed electron beam created outside the high pressure region. This source is carefully constructed to achieve thermal equilibrium of the ionic species. Jarrold, Illies, and Bowers⁶⁵ have built a similar chemiionization source for study of cluster ion photodissociation and metastable unimolecular decomposition.

An atmospheric pressure ionization source was originally built for this machine. This type of source, developed for analytical mass spectrometry, is particularly promising for the nondissociative ionization of large molecules.⁴⁸ A carrier gas such as He containing low concentrations of the molecule(s) of interest is ionized by low energy β particles emitted from a radioactive foil placed around the region immediately behind a small nozzle. The foil can be either ⁶³Ni or tritiated metal. These isotopes provide high activities of relatively low (63 KeV) energy β particles. At pressures of one atmosphere, the β particles would be quickly thermalized. The carrier gas is ionized; the molecule of interest would then be gently ionized by

charge exchange. This type of source is specifically designed to create the very low ion densities necessary for picogram analysis; total ion currents of 3×10^6 ions/s have been reported.⁶⁶ In preliminary experiments, the total current from our source apparently never exceeded 10^5 ions/s, close to the expected minimum usable current for a feasible experiment.

Analytical chemists have found that corona discharges provide a high current alternative to the β -ray source. Two types of corona discharge sources have been reported. The type used for this experiment has been described earlier. Many spectroscopic studies of radicals and ions have been reported using a very simple design by Engelking. In that source, a thin wire, often of tungsten is inserted behind a glass nozzle. A discharge is struck from the tip of the wire, through the nozzle, to an external electrode such as the skimmer. The plasma extends from the stagnation region through the nozzle and into the expansion region. Experiments indicate that the radicals and ions produced are rotationally cold, but possess substantial vibrational excitation. This condition is not surprising, since vibrations are not cooled efficiently in supersonic expansions. Furthermore, it is not clear that the ion distribution will be small. There will be a large electric field between the nozzle and the skimmer; the many collisions in this region will probably result in a wide dispersion of ion energies. The surface of the nozzle will charge up as well, influencing the field between nozzle and skimmer.

Flowing afterglows have been used extensively to study ion-molecule reactions and more recently to create positive ions for spectroscopic experiments. Weisshaar and co-workers^{67,68} have developed a flowing afterglow source to create small cluster ions for visible spectroscopy. Very recently, Leopold, Murray and Lineberger have developed a flowing afterglow source to study cold negative ions by photoelectron spectroscopy. These workers have reported negative ion beam currents of 1-100 pA.

This source provides a great deal of control over ion synthesis, albeit at a cost of greater construction complexity.

Ionization of gas in a supersonic expansion is also a relatively straightforward means of creating cluster ions. Johnson, Alexander and Lineberger^{70,71} have created ions by electron impact ionization of a pulsed supersonic jet immediately after the nozzle. The cluster ions are formed and cooled in the expansion; there have been no reports of the extent of vibrational cooling. Johnson *et al.*⁷² have observed rotational temperatures of 15 K and vibrational temperatures of 5000 K in diatomics from this source. The ions are extracted by pulsing a large field perpendicular to the jet, after the expansion. This technique allows extraction well after the high pressure regime, but also results in a wide (>100 eV) spread in ion energy. Posey, DeLuca, and Johnson⁷³ have reported creation of negative ions as well. Negative ion clusters with very low attachment thresholds have been produced by sending low energy electrons into a hard supersonic expansion.^{6,74,75} Typically, the electrons are from a heated filament(thoria coated iridium), creating several pA of ions.

Fenn and his co-workers have developed an electrospray ion source which does not fall into either category. Liquid (ionic solution) streams out of a capillary tube into a vacuum; by applying a voltage from the capillary to the opposing wall, the liquid will break up into fine microdroplets. By adjusting the voltage, ions ranging from small fragments to singly ionized solutes to large solvated clusters can be produced. This source provides a very promising means of obtaining gas phase ions of large, fragile molecules and clusters for analytic mass spectrometry. However, the technology is in an early stage, and at least one attempt to use it for spectroscopy experiments has failed⁷⁶ because the source was too unstable.

REFERENCES

1. T. D. Mark and A. W. Castleman, *Adv. At. Mol. Phys.* **20**, 65 (1985).
2. A. W. Castleman and R. G. Keesee, *Chem. Rev.* **86**, 589 (1986).
3. P. Kebarle, *Annu. Rev. Phys. Chem.* **28**, 445 (1977).
4. R. A. Kennedy and T. A. Miller, *J. Chem. Phys.* **85**, 2326 (1986).
5. P. J. Brucat, L.-S. Zhang, C. L. Pettiette, S. Yang, and R. E. Smalley, *J. Chem. Phys.* **84**, 3078 (1986).
6. J. V. Coe, J. T. Snodgrass, C. B. Freidhoff, K. M. McHugh, and K. H. Bowen, *J. Chem. Phys.* **83**, 3169 (1985).
7. R. J. Saykally and C. S. Gudeman, *Annu. Rev. Phys. Chem.* **35**, 387 (1984).
8. J. Owrutsky and R. J. Saykally, private communication.
9. R. E. Miller, *J. Phys. Chem.* **90**, 3301 (1986).
10. P. H. Dawson and A. W. Tickner, *J. Chem. Phys.* **37**, 672 (1962).
11. K. Buchheit and W. Henkes, *Z. Angew. Phys.* **24**, 191 (1968).
12. R. Clampitt and L. Gowland, *Nature* **223**, 816 (1969).
13. S. L. Anderson, T. Hirooka, P. W. Tiedemann, B. H. Mahan, and Y. T. Lee, *J. Chem. Phys.* **73**, 4779 (1980).
14. A. van Deursen, A. van Lumig, and J. Reuss, *Int. J. Mass Spectrom. Ion Phys.* **18**, 129 (1975).
15. A. van Lumig and J. Reuss, *Int. J. Mass Spectrom. Ion Phys.* **25**, 137 (1977).

15. A. van Lumig and J. Reuss, *Int. J. Mass Spectrom. Ion Phys.* **25**, 137 (1977).
16. A. van Lumig and J. Reuss, *Int. J. Mass Spectrom. Ion Phys.* **27**, 1197 (1978).
17. A. van Lumig, J. Reuss, A. Ding, J. Weise, and A. Rindtisch, *Mol. Phys.* **38**, 337 (1978).
18. T. Oka, *Molecular Ions: Spectroscopy, Structure, and Chemistry*, edited by T. A. Miller and V. E. Bondeybey, 73 (North Holland, Amsterdam, 1983).
19. S. G. Lias, J. F. Liebman, and R. D. Levin, *J. Phys. Chem. Ref. Data* **13**, 695 (1984).
20. U. A. Arifov, S. L. Pozharov, I. G. Chernov, and Z. A. Mukhamediev, *High Energy Chem. (USSR)* **5**, 69 (1971) ; *ibid.* p. 79.
21. S. L. Bennett and F. H. Field, *J. Am. Chem. Soc.* **94**, 8669 (1972).
22. M. T. Elford and H. B. Milloy, *Aust. J. Phys.* **27**, 795 (1974) ; *ibid.* 211.
23. K. Hiraoka and P. Kebarle, *J. Chem. Phys.* **62**, 2267 (1975).
24. R. Johnsen, C. M. Huang, and M. A. Biondi, *J. Chem. Phys.* **65**, 1539 (1976).
25. R. J. Beuhler, S. Ehrenson, and L. Friedman, *J. Chem. Phys.* **79**, 5982 (1983).
26. M. T. Elford, *J. Chem. Phys.* **79**, 5951 (1983).
27. R. A. Poshusta and F. A. Matsen, *J. Chem. Phys.* **47**, 4795 (1967).
28. R. Ahlrichs, *Theor. Chim. Acta* **39**, 149 (1975).
29. W. I. Salmon and R. D. Poshusta, *J. Chem. Phys.* **59**, 4867 (1973).
30. S. Yamabe, K. Hirao, and K. Kitaura, *Chem. Phys. Lett.* **56**, 546 (1978).

31. H. Huber, Chem. Phys. Lett. **70**, 353 (1980).
32. L. R. Wright and R. F. Borkman, J. Chem. Phys. **77**, 1938 (1982).
33. K. Hirao and S. Yamabe, Chem. Phys. **80**, 237 (1983).
34. H. Huber and D. Szekely, Theor. Chim. Acta **62**, 499 (1983).
35. S. Raynor and D. R. Hershbach, J. Phys. Chem. **87**, 289 (1983).
36. Y. Yamaguchi, J. Gaw, and H. F. Schaefer III, J. Chem. Phys. **78**, 4074 (1983).
37. H. Huber, J. Mol. Struct. **121**, 281 (1985).
38. Y. Yamaguchi, J. F. Gaw, R. B. Remington, and H. F. Schaefer III, preprint.
39. G. Herzberg, *Molecular Spectra and Molecular Structure: I. Spectra of Diatomic Molecules* (van Nostrand Reinhold, New York, 1950).
40. A. R. W. McKellar, Faraday Disc. Roy. Soc. **73**, 89 (1982).
41. S. A. Boggs, M. J. Cloutier, and H. L. Welsh, Can. J. Phys. **50**, 2064 (1972).
42. D. E. Bernholdt, S. Liu, and C. E. Dykstra, J. Chem. Phys. **85**, 5120 (1986).
43. T. Oka, Phys. Rev. Lett. **45**, 531 (1980).
44. W. Meyer, P. Botschwina, and P. Burton, J. Chem. Phys. **84**, 891 (1986).
45. J. Tennyson and B. T. Sutcliffe, Mol. Phys. **56**, 1175 (1985).
46. S. J. Brosnan and R. L. Byer, IEEE J. Quant. Electr. **15**, 415 (1979).
47. K. R. Jennings, in *Gas Phase Ion Chemistry, Vol. 2* edited by M. T. Bowers, Chap. 12 (Academic Press, New York, 1979).
48. M. W. Siegel and W. L. Fite, J. Phys. Chem. **80**, 2871 (1976).

49. H. Kambara and I. Kanomata, *Anal. Chem.* **49**, 270 (1977).
50. V. J. Caldecourt, D. Zakett, and J. C. Tou, *Int. J. Mass Spectrom. Ion Phys.* **49**, 233 (1983).
51. J. Q. Searcy and J. B. Fenn, *J. Chem. Phys.* **61**, 5282 (1974).
52. J. Q. Searcy, *J. Chem. Phys.* **63**, 411 (1975).
53. Y. Yamaguchi and H. F. Schaefer III, private communication.
54. A. Carrington and R. A. Kennedy, *J. Chem. Phys.* **81**, 91 (1984).
55. W. R. Gentry, *ACS Symp. Ser.* **263**, 289 (1984).
56. A. Mitchell, M. J. McAuliffe, C. F. Giese, and W. R. Gentry, *J. Chem. Phys.* **83**, 4271 (1985).
57. G. Ewing, *Farad. Disc. Chem Soc.* **73**, 325 (1982).
58. S. Scheiner, *Acct. Chem. Res.* **18**, 174 (1985).
59. J. T. Hougen, *J. Phys. Chem.* **90**, 562 (1986).
60. W. H. Miller, N. C. Handy, and J. E. Adams, *J. Chem. Phys.* **72**, 99 (1980).
61. T. Carrington Jr. and W. H. Miller, *J. Chem. Phys.* **81**, 3942 (1984).
62. T. Carrington Jr. and W. H. Miller, *J. Chem. Phys.* **84**, 4364 (1986).
63. Y. Yamaguchi and H. F. Schaefer III, unpublished results.
64. E. Pollack, *Comments At. Mol. Phys.* **15**, 73 (1984).
65. N. J. Kirchner, J. R. Gilbert, and M. T. Bowers, *Chem. Phys. Lett.* **102**, 7 (1984).

66. M. F. Jarrold, A. J. Illies, and M. T. Bowers, *Chem. Phys.* **65**, 19 (1982).
67. E. C. Horning, M. G. Horning, D. I. Carroll, I. Dzidic, and R. N. Stillwell, *Anal. Chem.* **45**, 936 (1973).
68. S. C. Ostrander and J. C. Weisshaar, *Chem. Phys. Lett.* **129**, 221 (1986).
69. S. C. Ostrander, L. Sanders, and J. C. Weisshaar, *J. Chem. Phys.* **84**, 529 (1986).
70. M. L. Alexander, M. A. Johnson, and W. C. Lineberger, *Chem. Phys. Lett.* **112**, 285 (1984).
71. M. L. Alexander, M. A. Johnson, and W. C. Lineberger, *J. Chem. Phys.* **82**, 5288 (1985).
72. M. A. Johnson, M. L. Alexander, I. Hertel, and W. C. Lineberger, *Chem. Phys. Lett.* **105**, 374 (1984).
73. L. A. Posey, M. J. DeLuca, and M. A. Johnson, *Chem. Phys. Lett.* **131**, 170 (1986).
74. H. Haberland, H.-G. Schindler, and D. R. Worsnop, *Ber. Bunsenges Phys. Chem.* **88**, 270 (1984).
75. M. Knapp, O. Echt, D. Kreisler, and E. Rehnagel, *J. Chem. Phys.* **85**, 636 (1986).
76. J. A. Lisy, private communication.

TABLE I. Experimental and theoretical dissociation energies and enthalpies for the hydrogen cluster ions H_n^+ .

Reference		5	7	9	11	13
Beuhler <i>et al.</i> ^a	ΔH_T°	6.6±0.3	3.1			
Elford ^b	ΔH_T°	5.8±1.1				
Elford and Milloy ^c	ΔH_T°	5.8±1.1				
Johnsen <i>et al.</i> ^d	ΔH_T°	8.1±0.7				
Hiraoka and Kebarle ^e	ΔH_T°	9.6	4.1	3.8	2.4	
Bennett and Field ^f	ΔH_T°	9.7±0.2	1.8±0.1			
Arifov <i>et al.</i> ^g	ΔH_T°	5.1±0.6				
Yamaguchi <i>et al.</i> ^h	$D_0(D_e)$, full CI	5.4(8.2)				
	$D_0(D_e)$, CISD	4.0(6.9)	2.6(3.4)	1.8(3.2)		
Hirao and Yamabe ⁱ	D_e , CISD	6.4	3.8	3.2	1.4	
	D_e , SCF	4.5	3.0	2.6	0.8	0.7
Huber ^j	D_e , SCF	5.7	3.8	3.0	1.2	1.2

^aRef. 25.

^bRef. 26.

^cRef. 22.

^dRef. 24.

^eRef. 23.

^fRef. 21.

^gRef. 20.

^hRef. 36 and 38.

ⁱRef. 30 and 33.

^jRef. 31, 34, and 37.

TABLE II. Theoretical scaled and experimental vibrational frequencies in cm^{-1} for the clusters H_n^+ , $n = 5, 7$, and 9 . Theoretical values in parentheses are unscaled harmonic frequencies. DZ+P basis set was used for all levels tabulated here. From Ref. 36 and 38.

		mode.	SCF	CISD	full CI	Experiment ^a
H_2			(4657)	(4533)	(4515)	4161 ^b
H_3^+	D_{3h}	A_1	(3566)	(3574)	(3604)	— ^c
		E	(2905)	(2826)	(2819)	2521 ^d
H_5^+	C_{3v}	A_1	(3663)	(3801)	(3824)	3532
	C_{2v}	A_1	3961(4434)	3887(4235)	3869(4198)	3910
	D_{2d}	B_2	(4088)	(4014)	(4000)	3532
	D_{2d}	A_1	3728(4173)	3748(4083)	3748(4067)	3910
H_7^+	C_{3v}	A_1	4012(4491)	4021(4380)		3980
		B_1	4010(4488)	4017(4376)		3980
H_9^+	C_{3v}	A_1	4035(4516)			4010
	C_{3v}	E	4030(4511)			4010

^aThis work, except as noted.

^bRef. 39.

^cNot observed. Best theoretical estimate 3178 cm^{-1} , Ref. 44.

^dRef. 18.

FIGURE CAPTIONS

FIG. 1 Sketch of H_n^+ clusters, $n = 5, 7$, and 9 , based on *ab initio* predicted geometries. See, for example Ref. 36.

FIG. 2 a) Mass spectrum of ions produced from electron impact ionization of neutral $(H_2)_n$ clusters. H_2^+ and H_3^+ peaks are clipped. b) Mass spectrum of ions produced from the corona discharge source at -20° C.

FIG. 3 Corona discharge source.

FIG. 4 Fragmentation ion branching ratios for photodissociation of H_n^+ created by electron impact ionization of neutral clusters. For each parent cluster, the laser was tuned to the absorption maximum of the H_2 stretch band.

FIG. 5 Low resolution OPO spectra of H_6^+ , H_7^+ , and H_9^+ (upper, middle, and lower panels respectively). For each cluster, the spectra obtained detecting the product ions from every dissociation channel are shown. The ions were created by electron impact ionization of neutral $(H_2)_m$ clusters. Typical laser resolution ranged from 5 to 20 cm^{-1} .

FIG. 6 Low resolution spectra taken with F-center laser of H_9^+ , H_{11}^+ , H_{13}^+ , and H_{15}^+ .

FIG. 7 Spectrum of the ν_2 mode of H_5^+ taken at 0.5 cm^{-1} resolution with an F-center laser.

FIG. 8 Comparison of OPO spectra of H_6^+ a) created by electron impact, and b) created in the corona discharge source.

FIG. 9 a) Spectrum of H_5^+ created in the corona discharge source, taken with difference frequency laser and a resolution of 1.3 cm^{-1} . b) Detail of spectrum in (a)

taken at 0.75 cm^{-1} , with higher signal-to-noise and smaller laser wavelength step size.

FIG. 10 Observed peak positions of the H_2 stretch as a function of cluster size.

FIG. 11 Artist's conception of larger ($n > 9$) hydrogen cluster ions, with the three H_2 at the corners of the H_3^+ in H_9^+ forming a complete inner solvation shell.

FIG. 12 H_3^+ potential energy curve $V_e(R)$ along the minimum energy path (reaction coordinate) R for the intermolecular stretch: $\text{H}_3^+ + \text{H}_2 \rightleftharpoons \text{H}_2 + \text{H}_3^+$. The curve is a spline fit to energies from DZ+P SCF calculations by Yamaguchi calculated at 15 points (Ref. 63). At each point the geometry is constrained to a C_{2v} symmetry, and the H_3^+ to H_2 distance is fixed. All other parameters are varied to minimize energy. Zero of the abscissa represents the D_{2d} $\text{H}_2 \cdots \text{H} \cdots \text{H}_2$ saddlepoint.

FIG. 13 H_3^+ potential energy surface. The two axes R_1 and R_2 are the distances between each H_2 molecule and the central H atom. The solid curve is the minimum energy reaction path described by V_e in Fig. 12, calculated with a DZ+P SCF level of theory. The dotted curve is the asymptotic limit $\text{H}_3^+ + \text{H}_2$ geometry. The open boxes mark the equilibrium geometry at the DZ+P SCF level, the open circles the equilibrium geometry at the DZ+P full CI level. The X marks the location of the D_{2d} saddlepoint at the DZ+P full CI level. *ab initio* points are from Ref. 38 and Ref. 63.

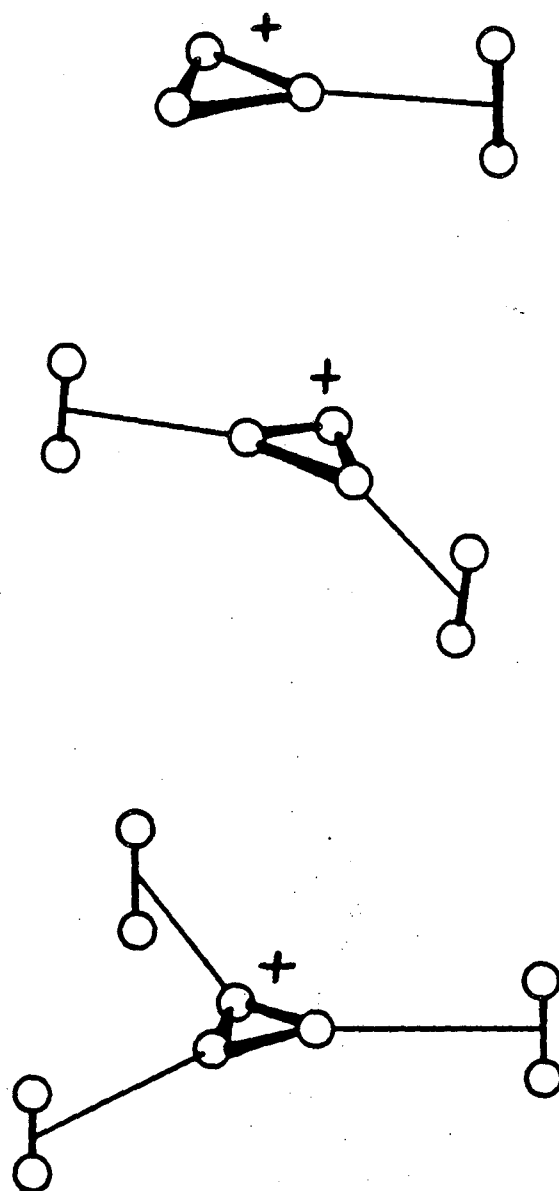


FIG. 1

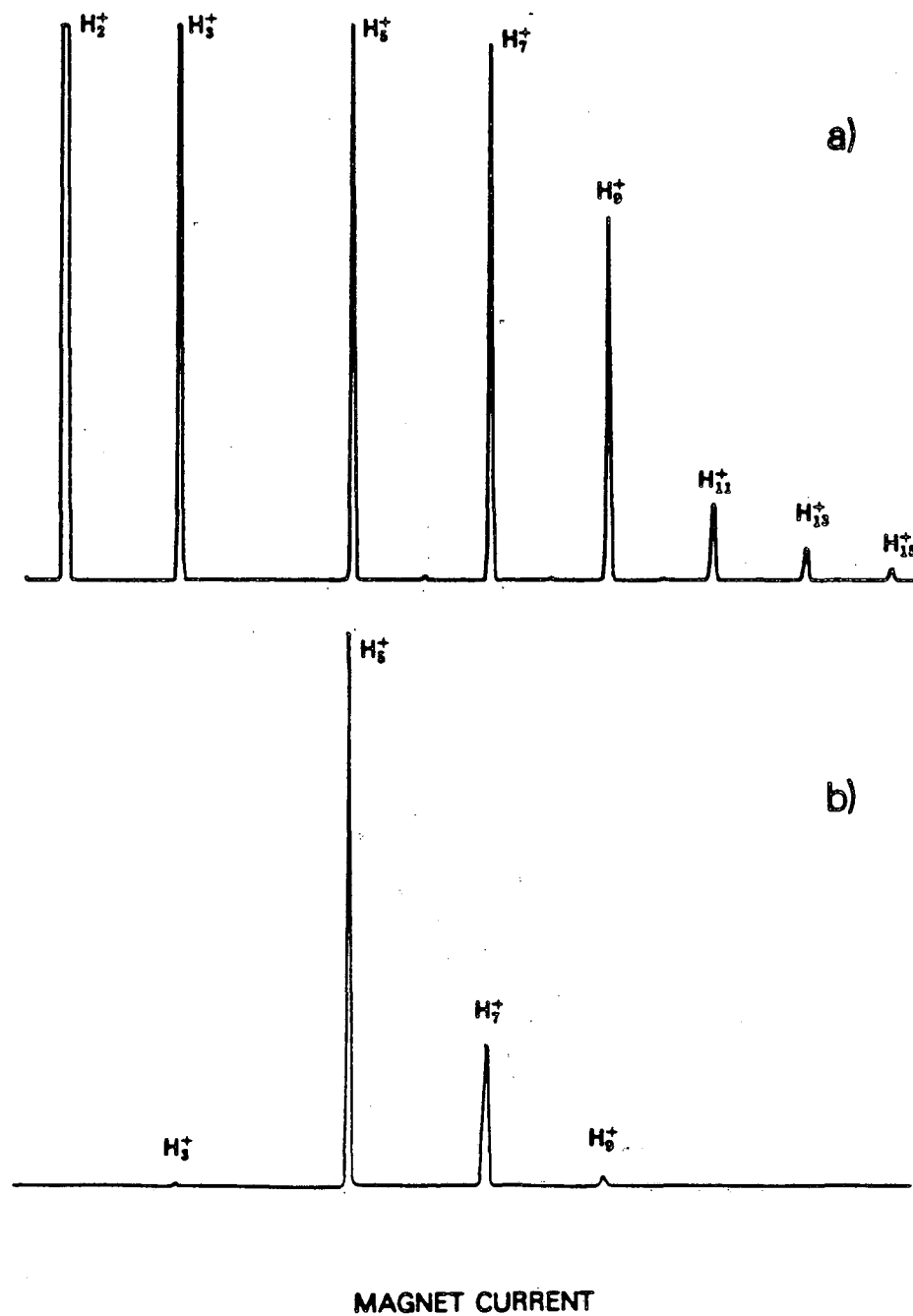


FIG. 2

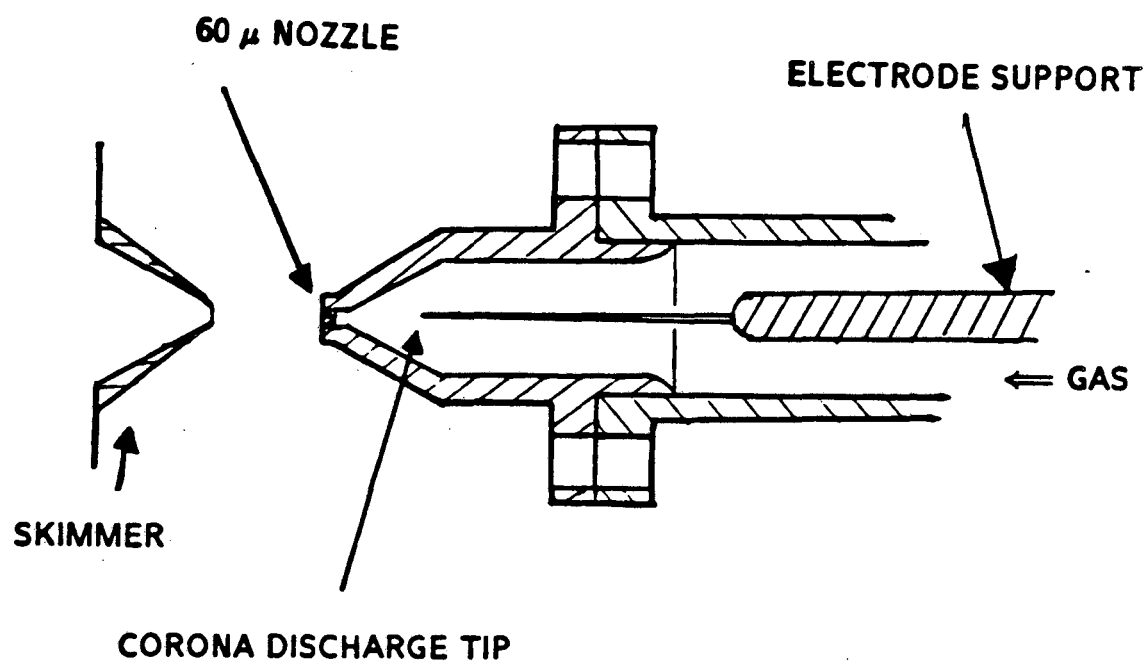


FIG. 3

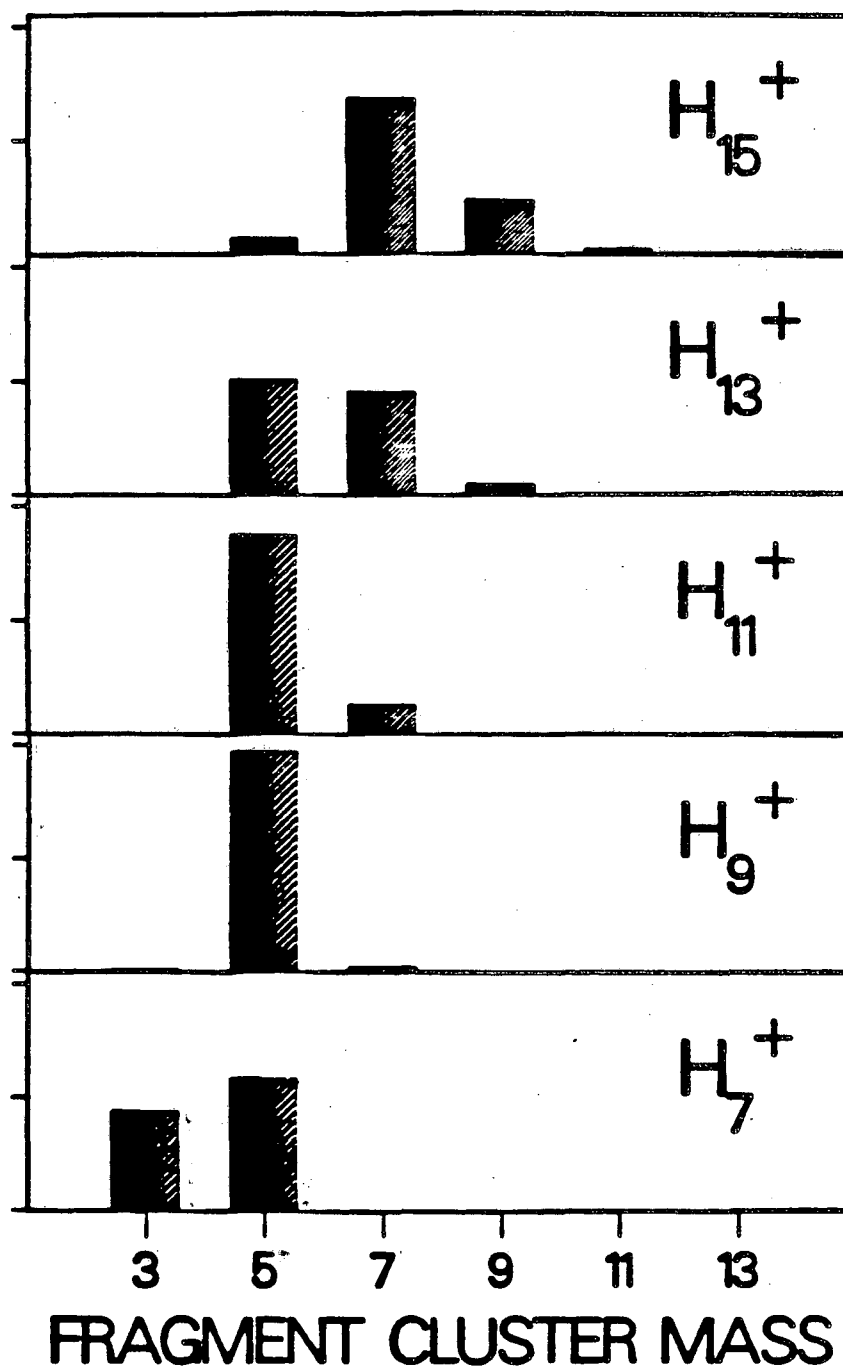


FIG. 4

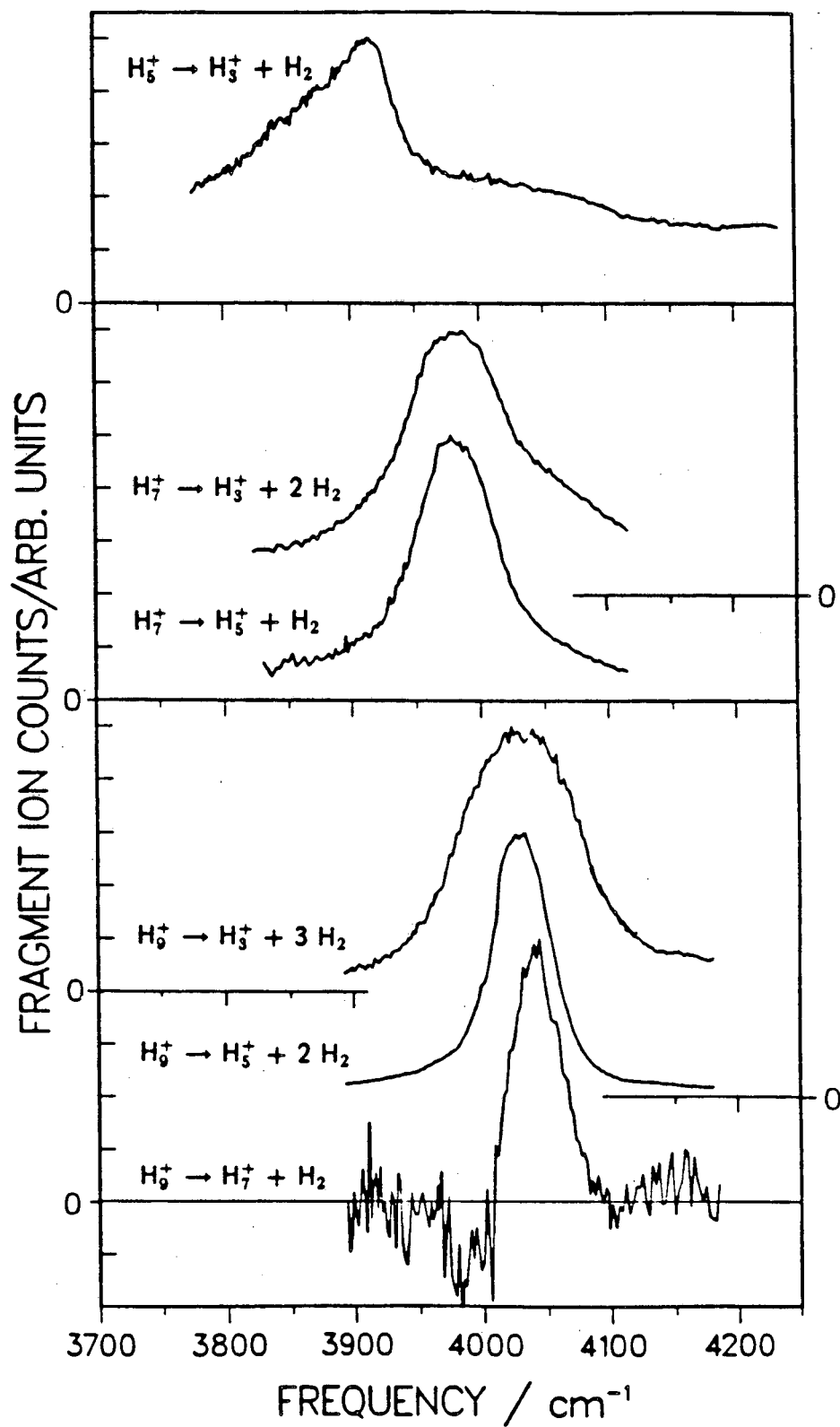


FIG. 5

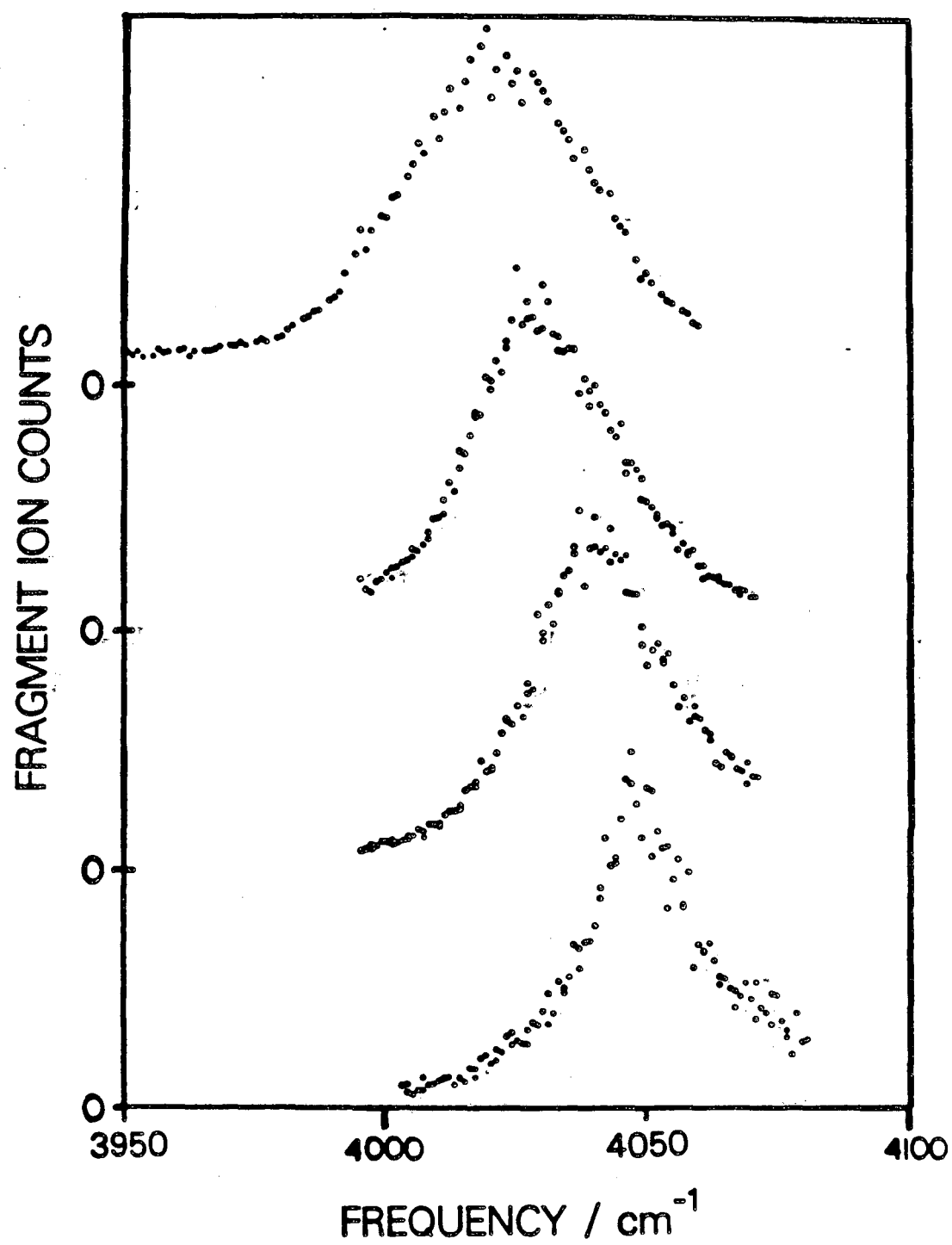


FIG. 6

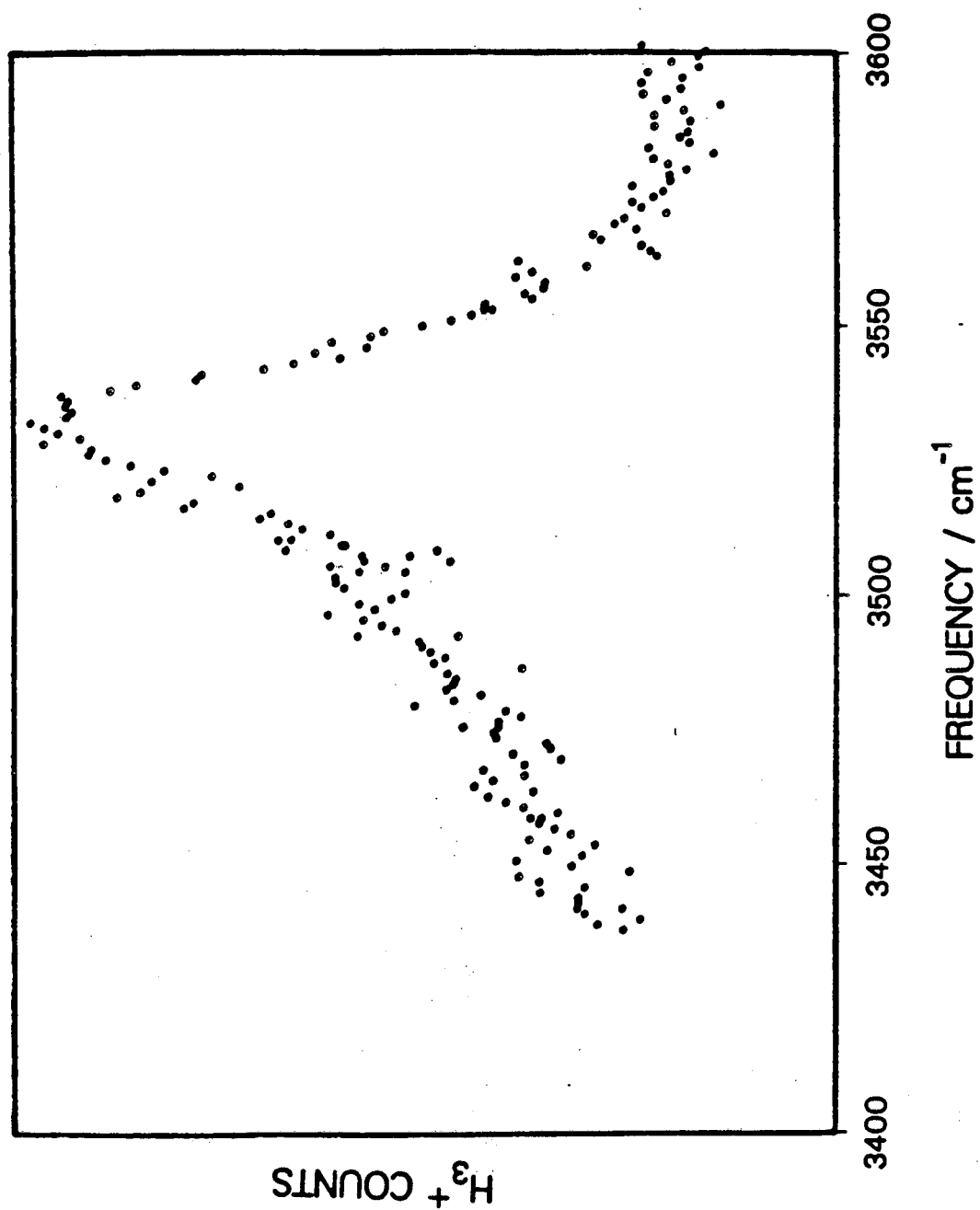


FIG. 7

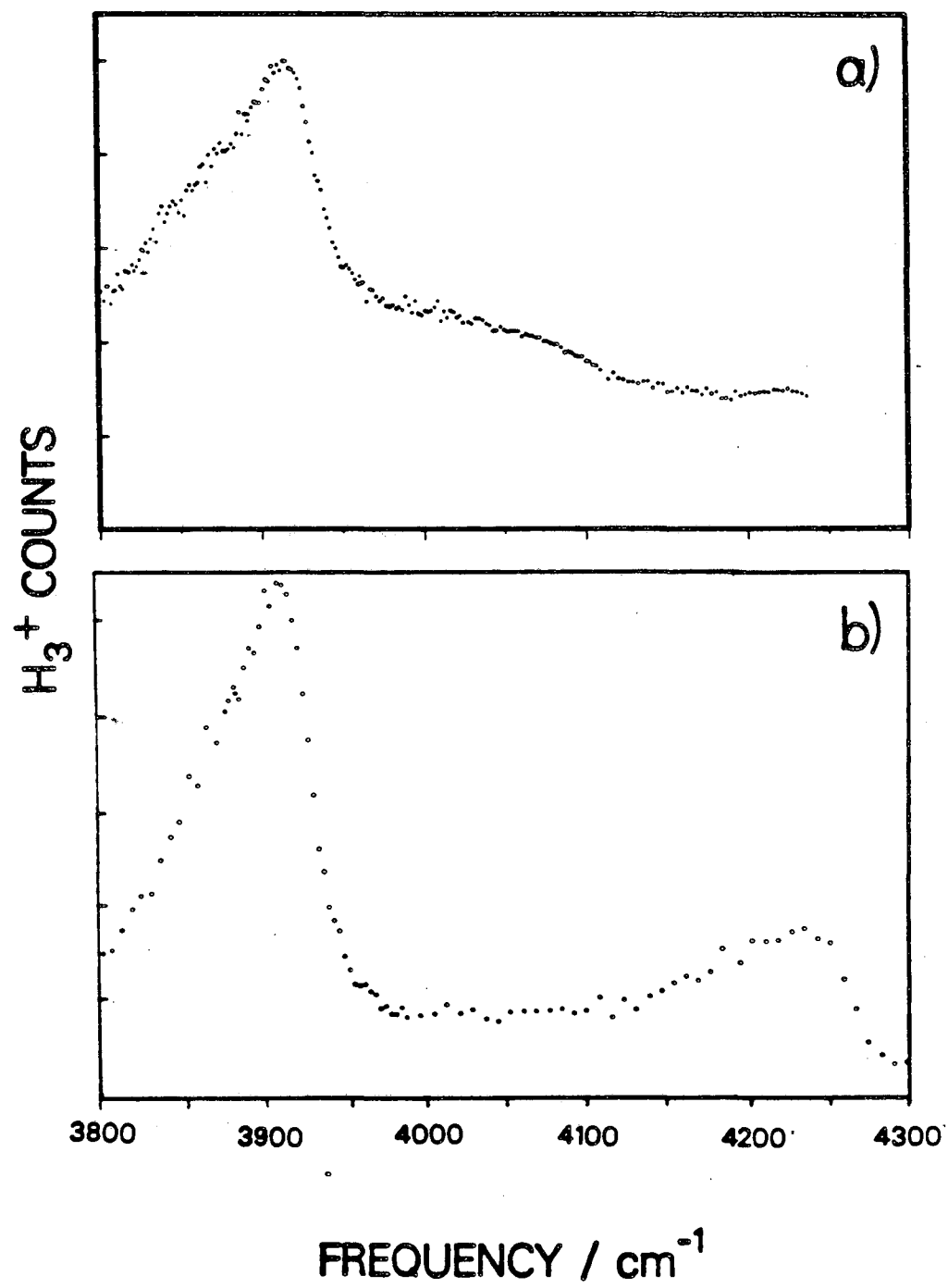


FIG. 8

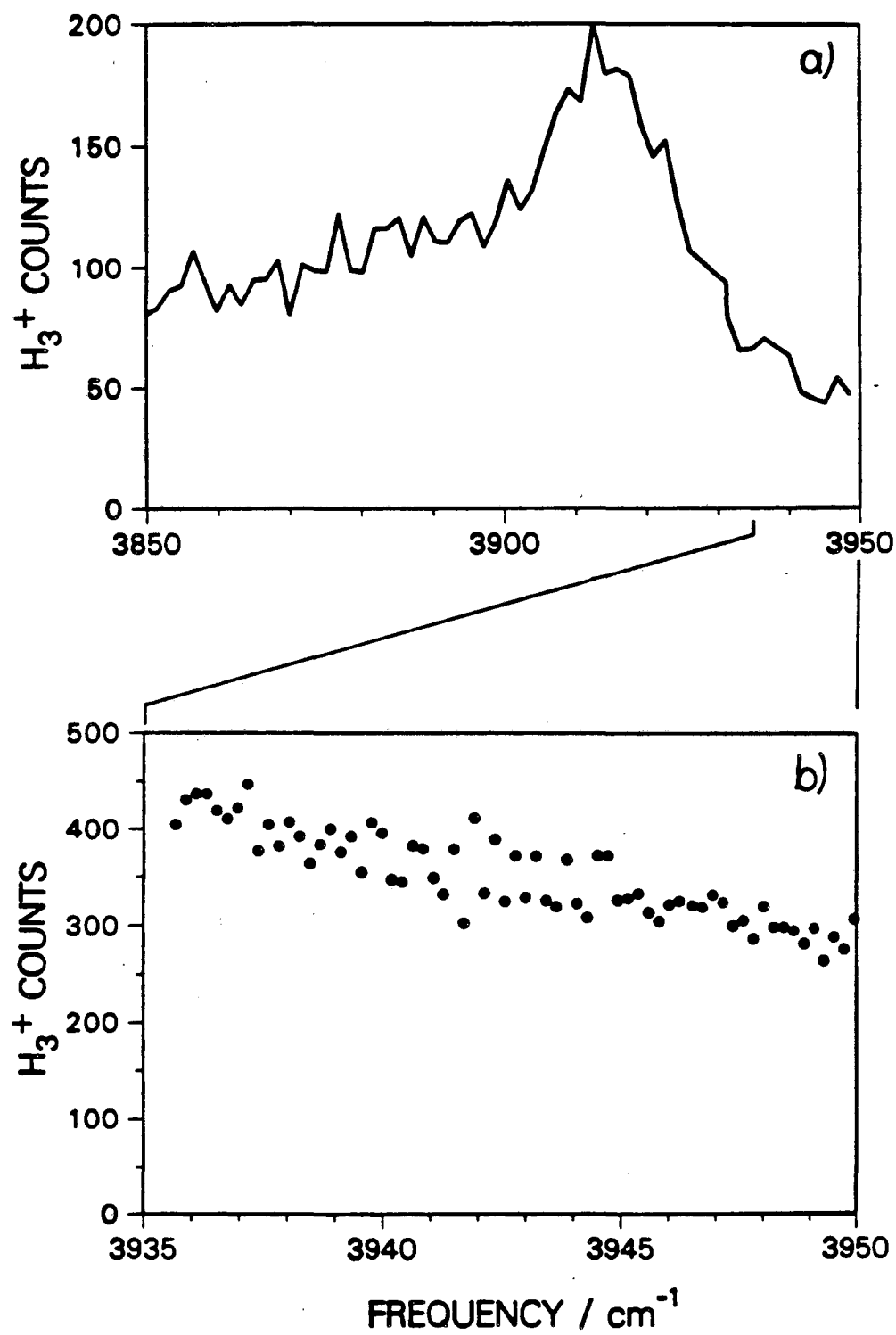
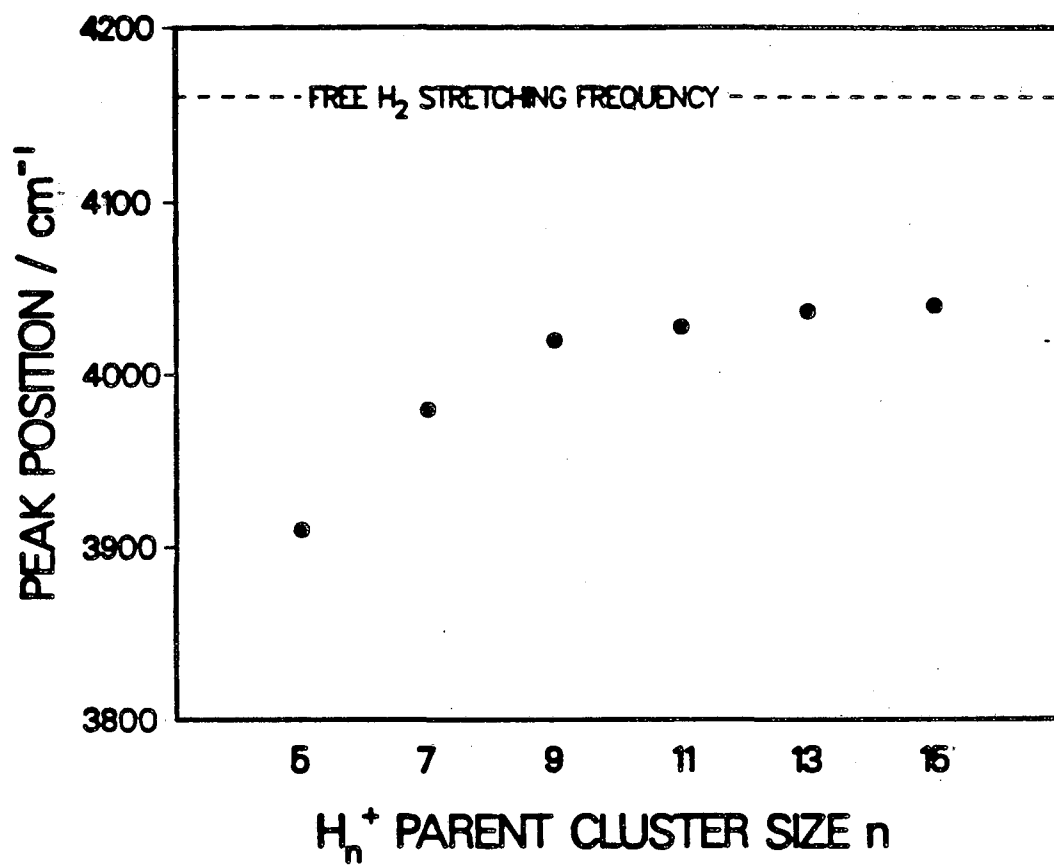


FIG. 9



XBL 856-2796

FIG. 10

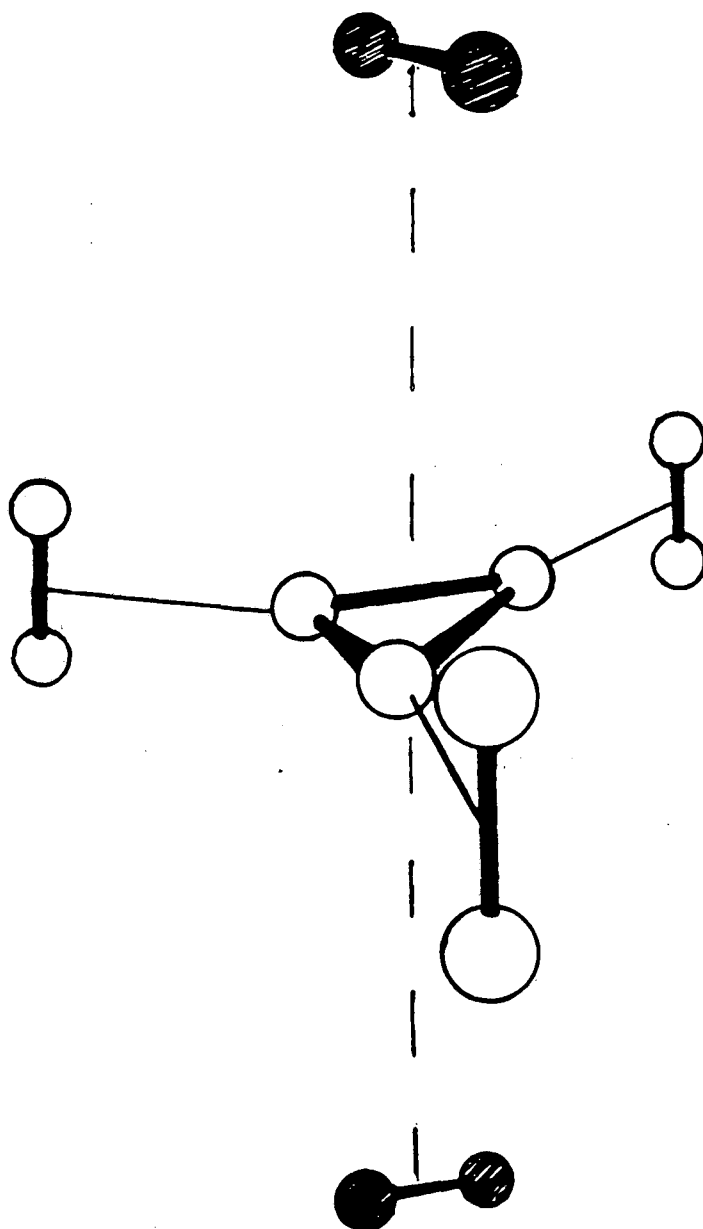
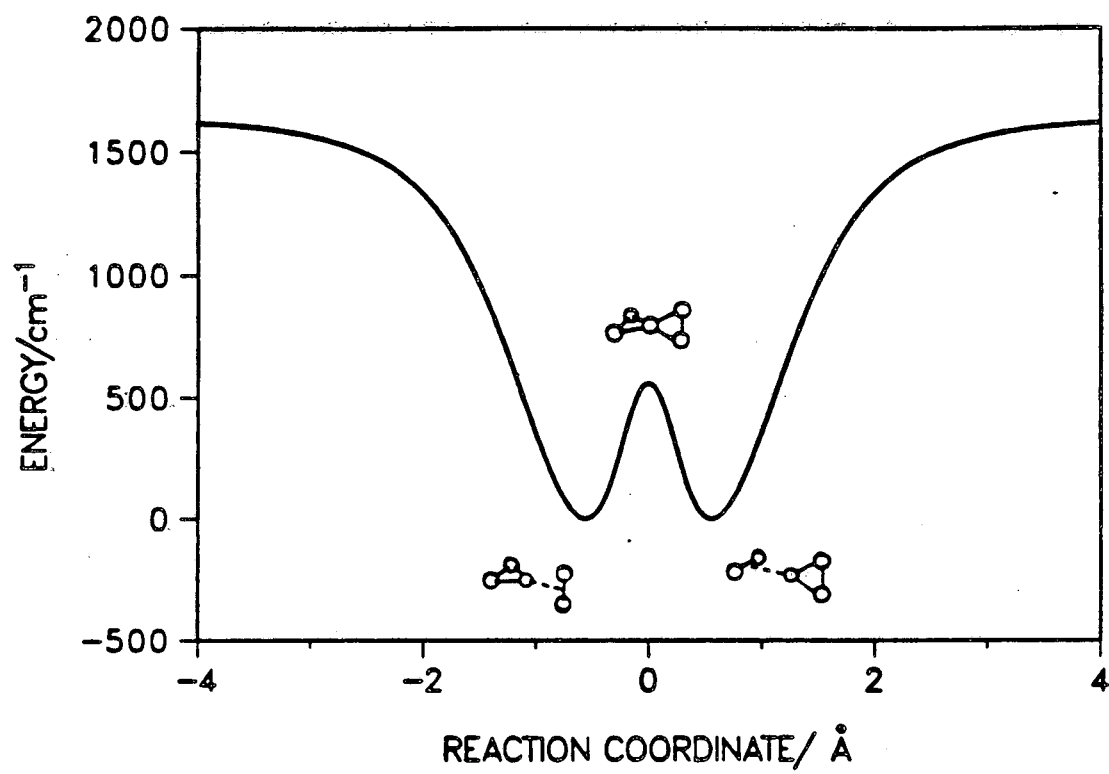


FIG. 11

**FIG. 12:**

Chapter 5

Molecular Espionage: The Vibrational Spectroscopy of the Solvated Hydronium Ion $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n \cdot (\text{H}_2)_m$

I. INTRODUCTION

The theory of ionic solutions was one of the triumphs of physical chemistry in the early 1900's. The Debye-Huckel theory, and related developments of Bjerrum, Born, Onsager and others, rely on the assumption of the solvent as a continuous dielectric medium. Ideally, a theory should be based on a microscopic model of ion-solvent interactions, but as Wolynes¹ has recently described, "molecular theories, in contrast to the maturity of continuum models, are still in their infancy." Perhaps the most ubiquitous ion in aqueous solution is the proton, which exists as the hydrated hydronium (or oxonium) ion $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n$. The generally accepted model² is an H_3O^+ ion with an inner solvation shell of three H_2O 's hydrogen-bonded to the ion, forming the H_9O_4^+ ion. The solvated proton is of fundamental importance to solution phase chemistry, and a detailed understanding of solvent effects on processes such as proton transfer is actively being pursued.^{3,4}

One approach for investigating ion-solvent interactions has been to study solvated ions in the gas phase.⁵ There, the properties of the ions can be studied as solvent molecules are added one by one to the ion. Gas phase investigations have also been motivated by the importance of these clusters in the upper atmosphere.^{6,7} Experiments have primarily explored their thermochemistry, association kinetics,

and dissociation dynamics.^{8,9} Our recent success with the IR vibrational predissociation spectroscopy of hydrogen cluster ions has led us to study the infrared spectra of the hydronium ion hydrates H_5O_2^+ , H_7O_3^+ , and H_9O_4^+ .

Vibrational spectroscopy has been an important technique for elucidating the nature of hydrogen bonded species in both the gas and condensed phases.¹⁰ There have been many studies of the infrared and Raman spectroscopy of the hydronium ion hydrates both in solution and in solids.^{11,12} The spectra however tend to be broadened and the analysis is often ambiguous. The positions and intensities of the bands assigned to $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ are often sensitive to the nature of the medium, e.g. a salt crystal or ionic solution.

In 1977, Schwarz¹³ obtained the first infrared absorption spectra of these clusters in the gas phase, recording low resolution (40 cm^{-1}) IR absorption spectra of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$, $n = 3, 4$, and 5 . These spectra are shown in Fig. 1. Schwarz created the ions in a static cell containing water vapor and Ar by pulsed radiolysis, which yielded a distribution of cluster sizes. The conventional direct absorption spectra were taken with a glowbar source and a monochromator, with a resolution of 40 cm^{-1} . To get the spectra of a given cluster, he took five spectra at different partial pressures of H_2O . He then assumed that the cluster distribution had reached equilibrium, and from the known gas phase values of ΔG° he estimated the contributions from every cluster at each pressure. The spectrum of each cluster was then determined by taking differences of the observed spectra.

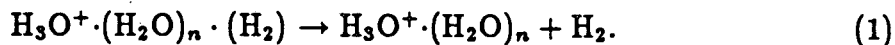
Soon after Schwarz's work, Newton published theoretical estimates of the vibrational frequencies of the hydrogen-bonded OH stretches in the H_9O_4^+ and larger clusters,¹⁴ based on *ab initio* calculations of the harmonic frequencies. This work, an extension of earlier *ab initio* calculations on the smaller hydrates,¹⁵ largely agreed with Schwarz's results. There have been many other *ab initio* studies of these clus-

ters with varying degrees of sophistication as well.¹⁶ The development of analytic derivative methods has facilitated *ab initio* calculations of vibrational frequencies. In unpublished work, Remington and Schaefer¹⁷ have recently calculated vibrational frequencies and intensities in the double harmonic approximation for all normal modes of the clusters H_5O_2^+ , H_7O_3^+ , and H_9O_4^+ . The structures they obtain are given in Fig. 2. Experimental tests of their results are important in the development of accurate potential surfaces for these clusters.

Since Schwarz's work, Saykally and co-workers obtained the first gas phase spectrum of the hydronium ion H_3O^+ using velocity modulation spectroscopy.^{18,19} Although three out of four vibrational bands of H_3O^+ have now been observed at high resolution,^{20,21,22} no further spectra of the larger clusters have been reported. The IR spectroscopy of weakly bound ions in the gas phase is a difficult experimental challenge. The approach developed in this thesis has been to obtain IR spectra of these ions by detecting their vibrational predissociation, to take advantage of the inherently high sensitivity of ion counting techniques. By using a tandem mass spectrometer, we can both mass select the parent ion prior to excitation and dissociation, and analyze the resulting product ions. We have previously observed vibrational spectra of the hydrogen cluster ions H_n^+ , where $n = 5, 7, 9, 11, 13$, and 15 . In these clusters, an H_3^+ ion is solvated by one or more H_2 molecules. In those experiments, ions from a mass-selected beam of clusters were trapped in a radio-frequency ion trap. There, they were excited with an infrared laser tuned to an H_2 vibration. After single photon excitation, the clusters had enough energy to predissociate, and by detecting the predissociation product ions as a function of laser frequency, we could indirectly observe the absorption spectrum of the parent cluster H_n^+ . Mass selection allows us to unambiguously identify the absorbing species and the photofragments.

This technique cannot be applied directly to the hydrated hydronium ions, which are bound far more strongly than the H_n^+ clusters. The dissociation energies of $H_3O^+ \cdot (H_2O)_n$ for loss of one H_2O are 31.6, 19.5, and 17.9 kcal/mol for $n = 1, 2$, and 3 respectively.^{23,24,25} A single infra-red photon exciting an OH stretching vibration cannot dissociate these clusters, and we therefore cannot observe their spectra. We overcome this problem by attaching an additional atom or molecule to the cluster. By choosing a "messenger" that is very weakly attached to the hydrate cluster, the vibrations of the hydrate itself will only be slightly perturbed. When we excite an OH stretch of the hydrate, the messenger atom will detach by vibrational predissociation. The messenger thus acts as a mass label, allowing us to use vibrational predissociation to probe the low resolution infrared spectra of a large variety of previously unobserved ions. Like a spy, its role is to gather information as unobtrusively as possible.

In this preliminary work, we have attached an H_2 molecule to the hydronium ion hydrates $H_3O^+ \cdot (H_2O)_n$, ($n = 0, 1, 2$, and 3) to search for spectra over the frequency range 2300 cm^{-1} to 4200 cm^{-1} , by detecting the process



We have sought to confirm Schwarz' gas phase spectrum of $H_9O_4^+$, as well as to obtain new spectra of the smaller clusters $H_5O_2^+$ and $H_7O_3^+$. In addition to spectra of the hydrated H_3O^+ ion, we have observed vibrational predissociation spectra of the clusters $H_3O^+ \cdot (H_2)_m$, with $m = 1$ to 3. These latter clusters can be more properly thought of as H_3O^+ solvated by H_2 ligands, and thus represent the strong bonding limit of the messenger technique. We expect these clusters to be similar in many respects to the hydrogen cluster ions. Furthermore, the infrared spectroscopy of the hydronium ion itself has been studied extensively at high resolution, providing a useful basis for understanding the solvation by H_2 ligands.

The "messenger" technique relies on the small influence of the H_2 . How does the H_2 bind to a large cluster ion? *ab initio* calculations have shown that H_2 molecules in $XH^+ \cdot H_2$ complexes form ionic hydrogen bonds with a number of small protonated molecules.^{26,27} The dissociation energies of several clusters $XH^+ \cdot H_2$ are listed in Table I. The binding strengths are quite strong, on the order of moderately strong hydrogen bonds in neutral species such as $(HF)_2$. We expect a similar binding energy for H_2 bonding to H_3O^+ alone, although the binding energy may be weaker, since the charge is dispersed among three protons. For the larger hydrates, we can expect that the messenger will be bound by much less energy, because the charge will be delocalized upon hydration: the larger the cluster, the smaller the perturbation by the H_2 . In ionic clusters, H_2 vibrations are perturbed and their transitions become IR allowed.²⁶ The H_2 stretch intensity and frequency shift, relative to the H_2 monomer, appear to be characteristic of the binding strength of the H_2 and thus can provide important clues to the perturbing influence of the H_2 ligand.

Finally, since completion of this work, spectra of the hydrated hydronium clusters alone (without messengers) have been obtained in our laboratory by Yeh and Myers using a new two color infra-red multiphoton dissociation scheme.²⁸ The messenger approach is not necessary, if an ion can absorb several photons to reach the dissociation limit. The new experiment is a two laser pump-probe arrangement in which a second laser, a CO_2 laser, is used for multiphoton dissociation of the clusters. Clusters, with their many low frequency vibrations, tend to have high vibrational state densities, and thus can readily undergo IR multiphoton dissociation (IRMPD). Beauchamp and co-workers²⁹ have shown, for example, that in the proton bound diethyl ether dimer, the quasi-continuum starts between 1000 cm^{-1} and 2000 cm^{-1} above the ground state. After the first tunable laser excites an OH stretch, the cluster can more easily absorb the several (and fewer) photons from the

CO₂ laser needed to dissociate. By setting the CO₂ laser fluence below the ground state MPD threshold, only ions excited by the F-center laser will dissociate. To date, they have successfully observed spectra of H₅O₂⁺, H₇O₃⁺, and H₉O₄⁺ in the region of free OH stretches. The results from the new experiment allow us to quantify the perturbations to the hydrate ion modes induced by the H₂ messenger.

II. EXPERIMENTAL

The apparatus has been described in detail in earlier chapters, and will be discussed briefly here.

The clusters H₃O⁺·(H₂O)_n·(H₂)_m were produced in a weak corona discharge of 200 to 300 torr of H₂ (Matheson ultra-high purity, 99.999%) further purified by passing through a liquid nitrogen cooled molecular sieve trap. The source was cooled to approximately 0°C and the discharge current was 30 to 60 μA. The plasma was then expanded through a 70 μ nozzle into vacuum. The electric field in the region between the nozzle and skimmer was minimized to prevent the acceleration of the ions with respect to the neutral gas. This was crucial in preventing collisional heating and dissociation of the clusters, as well as keeping the ion energy spread low. The expanded gas passed through a skimmer 7 mm from the nozzle. The ions were then accelerated to 350 eV, and hydrated ions H₃O⁺·(H₂O)_n·(H₂) of a given size *n* with an H₂ messenger attached were mass selected with a 60° sector magnet. The cluster ions were decelerated to about 0.5 eV or less, and then trapped in a radio frequency octopole ion trap. A tunable pulsed IR laser was fired into the trap after 1 ms. The ions were then released into a quadrupole mass spectrometer set to detect the dissociation product H₃O⁺·(H₂O)_n. The cycle was then repeated with the laser off, to measure the background dissociation which was subtracted from the signal of the laser on cycle. Spectra were taken by stepping the laser over

frequency ranges of 10 cm^{-1} to 200 cm^{-1} and normalizing for laser power. In these experiments, there was very little (laser off) background at the fragment masses, implying that the ions were internally cold, and that collisional dissociation in the trap was minimal.

In the current experiment, the primary function of the trap was to collect as many parent ions as possible prior to firing the laser. Trapping experiments indicated that the predissociation occurred faster than 1 ms, obviating the need to trap the ions after photolysis. The main disadvantages of trapping — the lower duty cycle and larger Doppler widths ($< 0.1\text{ cm}^{-1}$) — did not apply to this experiment, which used a pulsed, low resolution laser.

Under the source conditions described above, the hydrogen cluster ions H_n^+ were initially created. However, in such cold, high pressure discharges, the primary ions formed during initial ionization in the discharge could undergo many collisions and, through mechanisms such as charge exchange, proton transfer, and association, the most thermodynamically stable ions would be produced.³⁰ The proton affinity of water is 165 kcal/mol ,³¹ far greater than the 101 kcal/mol proton affinity of H_2 ; therefore, H_3^+ will transfer a proton readily to water. Because the ion density was on the order of 10^{10} less than the neutral density, the mass spectrum would be dominated by protonated water clusters $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n$ unless trace water impurities present in the H_2 were reduced below this level.

The hydrates were therefore easily generated by slightly heating the inlet line to desorb water from the walls, or bypassing the liquid nitrogen cooled sieve trap. These ions thermalized inside the source, especially in the narrow diameter transit region immediately prior to the nozzle. They were cooled further in the expansion. The additional H_2 most likely attached to the water cluster ions during the supersonic expansion as well. In the mass spectra, such as shown in Fig. 3, the hydrated

hydronium ions were the dominant ions. The small peaks were the hydrated ions with H_2 messengers bound to them, the $H_3O^+ \cdot (H_2O)_n \cdot (H_2)$. Only a small fraction of the hydrate ions had the H_2 messengers attached. As many as three H_2 were bound to H_3O^+ , and the $H_3O^+ \cdot (H_2)_n$ accounted for up to 90% of the hydronium ion counts, while H_2 attached to 5% or less of the larger water clusters.

The tunable infrared laser was a pulsed difference frequency laser, the Infrared Wavelength EXtender (IR-WEX) from Quanta Ray. The IR photons were produced by mixing the 1.06μ light from a Nd:YAG laser with the near IR from a dye laser in a $LiNbO_3$ crystal. The laser was focused through the machine with two 1 m lenses to a spot size of 0.5 cm in diameter inside the trap. The linewidths were 0.75 cm^{-1} or 1.2 cm^{-1} , depending on whether the YAG laser was operated with or without an intra-cavity etalon. We scanned the difference frequency laser over the range from 2200 cm^{-1} to 4200 cm^{-1} . The laser power was typically 2 to 8 mW at the higher frequency end of this range. The laser power was very low ($<1 \text{ mW}$) below 3200 cm^{-1} , due to a combination of poor dye laser power and lower difference frequency conversion efficiency. There was also a gap from 3540 cm^{-1} to 3580 cm^{-1} in which the laser power fell below 1 mW as well, arising from OH absorption in the $LiNbO_3$ crystal.

III. RESULTS

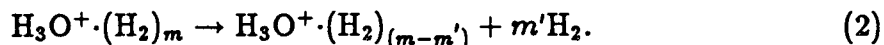
We searched for spectra of the hydrated cluster ions $H_5O_2^+ \cdot (H_2)$, $H_7O_3^+ \cdot (H_2)$, and $H_9O_4^+ \cdot (H_2)$ over the range from 3100 to 4200 cm^{-1} . For these clusters, the only dissociation channel monitored was loss of a single H_2 . In the region 3500 to 3800 cm^{-1} , characteristic of free OH stretching vibrations, the bands arise from the OH stretches of both the water ligands and the H_3O^+ ion. These spectra are shown in Fig. 4. In one case, $H_5O_2^+$, we also observed a spectrum of the hydrate with two

H_2 molecules bound to it. This spectrum is shown in Fig. 5. The ion count at mass 41 was about a factor of five lower than at mass 39 ($\text{H}_5\text{O}_2^+ \cdot (\text{H}_2)$), so the signal to noise was substantially poorer. All of the observed peaks were also scanned at 0.75 cm^{-1} resolution, with laser step sizes of 0.4 cm^{-1} or less. Although many of the peaks had irregular band contours, we found additional partially resolved peaks only in the 3720 and 3733 cm^{-1} bands of H_9O_4^+ . These peaks, spaced about 1 cm^{-1} apart, were most likely the resolution of rotational band contours, since the laser linewidth was much greater than the anticipated rotational spacing.

We searched for spectra of the H_2 stretch, in the region near 4100 cm^{-1} . We found very weak absorption bands in $\text{H}_5\text{O}_2^+ \cdot (\text{H}_2)_m$ and $\text{H}_7\text{O}_3^+ \cdot (\text{H}_2)$ at 4105 cm^{-1} and 4115 cm^{-1} respectively, but were unable to find any absorptions in this region by $\text{H}_9\text{O}_4^+ \cdot (\text{H}_2)$.

The vibrational frequencies of the hydrogen-bonded OH stretches should be red-shifted significantly from $3400\text{--}3500 \text{ cm}^{-1}$, where H_3O^+ absorbs. Schwarz observed a very strong band at 2660 cm^{-1} in the spectrum of H_9O_4^+ , as well as reporting absorption at 2300 cm^{-1} by H_7O_3^+ . The *ab initio* theory also predicted strong bands of the hydrogen-bonded OH below 3100 cm^{-1} for these two clusters, albeit at frequencies several hundred wavenumbers higher. To investigate the discrepancy between theory and experiment, we extended our spectra of H_9O_4^+ from 3100 cm^{-1} down to below 2600 cm^{-1} . The low laser power prevented us from observing all but the strongest absorptions. Despite the low power, we found a broad peak at 2670 cm^{-1} , shown in Fig. 6. We searched for spectra of H_7O_3^+ as well, but found no absorption above 2600 cm^{-1} . We continued the scan to 2350 cm^{-1} , and found a broad absorption beginning at 2500 cm^{-1} and increasing in intensity down to the limit of our scan. The laser power, less than 1 mW , was too low and we were unable to determine the band contour.

We observed spectra of the clusters $\text{H}_3\text{O}^+(\text{H}_2)_m$, with $m = 1, 2$, and 3 , over the frequency range from 3100 cm^{-1} to 4200 cm^{-1} from their vibrational predissociation



Composites of low resolution scans are shown in Fig. 7. For all three clusters, we have observed fundamental bands of the OH and H_2 stretches, as well as several weak combination or overtone bands. The power varied from 0.5 mW at 3100 cm^{-1} to $7\text{--}10\text{ mW}$ at 3800 cm^{-1} . Coincidentally, the strongest bands were at the region of low laser power, and power normalization lead to scaling up of these bands, along with their noise. The spikes seen in the bands below 3300 cm^{-1} are due primarily to noise, while the structure, for example in the 3500 cm^{-1} band of $\text{H}_3\text{O}^+(\text{H}_2)$ are real.

For the $\text{H}_3\text{O}^+(\text{H}_2)$ ion, we detected the H_3O^+ ion. For both the $\text{H}_3\text{O}^+(\text{H}_2)_2$ and the $\text{H}_3\text{O}^+(\text{H}_2)_3$ clusters, the major dissociation channel was loss of two H_2 molecules. The spectra of these two clusters were therefore obtained by detecting H_3O^+ and $\text{H}_3\text{O}^+(\text{H}_2)$ respectively. $\text{H}_3\text{O}^+(\text{H}_2)_2$ excited at the 3275 cm^{-1} band (9.4 kcal/mol) had a product branching ratio of $m'=2 : m'=1$ of $1 : 0.21$. Thus, loss of one hydrogen molecule was a very minor channel in the spectral range discussed here. For the larger cluster $\text{H}_3\text{O}^+(\text{H}_2)_3$ excited at 3296 cm^{-1} , the branching ratio $m'=3 : m'=2 : m'=1$ was $0.023 : 1.0 : 0.11$. At 4065 cm^{-1} (11.6 kcal/mol), however, the loss of all three H_2 made a much larger contribution, although the loss of two H_2 was still the dominant channel. The branching ratio was $0.47 : 1.0 : 0.11$. Assuming that the threshold for loss of the last H_2 occurs between these two bands, the average binding energy of an H_2 in $\text{H}_3\text{O}^+(\text{H}_2)_3$ is between 3.1 and 3.9 kcal/mol .

IV. SPECTRA OF THE CLUSTERS $\text{H}_3\text{O}^+(\text{H}_2)_m$

An investigation of the clusters $\text{H}_3\text{O}^+(\text{H}_2)_m$ should provide us with a better understanding of how H_2 binds to molecular ions. We therefore begin by examining the spectra of these ions, before considering the larger hydrated ions.

The σ bond in H_2 is not usually considered a Lewis base, but H_2 has a gas phase proton affinity of 101 kcal/mol, and upon protonation forms the H_3^+ ion.³² Theorists²⁷ have shown from *ab initio* calculations that the H_2 tends to form hydrogen bonds with small protonated molecules such as HNN^+ , with the H_2 perpendicular to and bisected by the weak $\text{X-H}^+ \cdots \text{H}_2$ bond. These proton bound dimers are the transition complexes for the proton transfer reactions $\text{X} + \text{H}_3^+ \rightleftharpoons \text{XH}^+ + \text{H}_2$. The three H atoms form an elongated isosceles triangle, and the rotation of the H_2 tends to be nearly unhindered. Other orientations of the H_2 appear to be significantly higher in energy.

The structure has not been determined directly by experiment for any of these species. The best evidence to date comes from the infrared spectra of the hydrogen cluster ions. Yamaguchi *et al.*²⁶ have found that the calculated vibrational frequencies change by hundreds of wavenumbers for different geometries of H_5^+ . The theoretical frequencies for the hydrogen cluster ions H_5^+ , H_7^+ , and H_9^+ agree well with experiment, and in conjunction with thermochemical measurements, provide indirect evidence in favor of the theoretical structures.

When possible, the H_2 will probably bind to one of the protons of the H_3O^+ ion. As in other hydrogen bonded species, the donor OH vibration of the H_3O^+ will be red-shifted, and will have an enhanced intensity. This is the band most likely to be perturbed by the presence of a messenger. In H_9O_4^+ , water molecules bind to all three OH bonds of the hydronium ion, so the H_2 should have a minimal effect.

No previous work, experimental or theoretical, has been published on the hy-

dronium ion solvated by H_2 molecules, but the theoretical studies on other $\text{XH}^+ \cdot \text{H}_2$ clusters provide an adequate guide. The proton affinity of H_2O is ~ 64 kcal/mol greater than that of H_2 .³¹ We expect that the H_2 will form a hydrogen bond with the H_3O^+ , with the proton in a single well bound closely to the O atom. The H_2 bond should be roughly perpendicular to the $\text{OH} \cdots \text{H}_2$ bond, and the H_2 should be a nearly free rotor.

Following our observation of the $\text{H}_3\text{O}^+ \cdot (\text{H}_2)$ spectrum, Remington and Schaefer performed a DZ+P SCF calculation¹⁷ on the $\text{H}_3\text{O}^+ \cdot (\text{H}_2)$ ion, and obtained a structure as we had anticipated, with the H_2 forming a hydrogen bond with one OH group. Their geometry is illustrated in Fig. 8. They have calculated a dissociation energy D_e of 3.2 kcal/mol, within our estimated bounds for D_0 obtained from the branching ratios in $\text{H}_3\text{O}^+ \cdot (\text{H}_2)_3$. They have also calculated vibrational frequencies and intensities which can be compared to our results. The dissociation energy corrected for zero point energy is D_0 of 1.1 kcal/mol. This is lower than our estimate based on the observed product branching ratios, but the use of *ab initio* harmonic frequencies in the estimate of the zero point correction can lead to a large error.

The high frequency stretching modes are readily understood. The H_2 stretch near 4000 cm^{-1} , will be red-shifted from the H_2 monomer value³³ at 4161 cm^{-1} . The free OH stretches will occur near the stretching frequencies of H_3O^+ , at approximately 3500 cm^{-1} , while the hydrogen-bonded $\text{OH} \cdots \text{H}_2$ intramolecular stretch will be red-shifted, intensified, and possibly broadened.

A. $\text{H}_3\text{O}^+ \cdot (\text{H}_2)$

The spectrum of this ion is characterized by four major bands and several weaker bands. The strongest ones are shown expanded in Fig. 9. From their proximity to the free monomer fundamental transitions, we assign the peak at 4046 cm^{-1} to the

H_2 stretch, and the peaks at 3480 cm^{-1} and $\sim 3560\text{ cm}^{-1}$ to OH stretches of the hydronium ion. The ν_1 symmetric stretch of the H_3O^+ monomer has not yet been observed, but *ab initio* calculations³⁴ put it near 3400 cm^{-1} . The strongest band we observe is located 300 cm^{-1} to the red, at 3110 cm^{-1} . This band is most likely the stretching mode of the hydrogen bonded $\text{O-H}\cdots\text{H}_2$.

The rovibrational absorption spectrum of the H_2 monomer is dipole-forbidden.³³ In $\text{H}_3\text{O}^+(\text{H}_2)$, this vibration is probably coupled to and borrows intensity from the motion of the hydrogen-bonded OH stretch. The large dipole moment of H_3O^+ will induce a small permanent moment in the H_2 as well. We observe a band at 4046 cm^{-1} , red-shifted from the monomer vibration by 115 cm^{-1} . The red-shift is slightly less than that observed in H_9^+ , which absorbs at 4020 cm^{-1} . For that cluster, the dissociation energy to $\text{H}_7^+ + \text{H}_2$ is 3.8 kcal/mol . The most striking aspect of this band is the clear resolution of the P, Q, and R branches, as well as partial resolution of rotational lines in the P and R branches. Prior to this spectrum, no rotational structure has been observed in the spectra of weakly bound cluster ions. We have therefore demonstrated that, as for neutral van der Waal's clusters,³⁵ rovibrational spectra of ionic clusters can be obtained from vibrational predissociation experiments.

The observation of an a type band is expected from a consideration of the geometry and approximate symmetry of the $\text{H}_3\text{O}^+(\text{H}_2)$ ion. From the geometry shown in Fig. 8, one can see that the complex will be a near prolate top with the smallest moment of inertia axis approximately along the $\text{OH}\cdots\text{H}_2$ axis. Remington and Schaefer's calculation¹⁷ predict rotational constants of $A=9.5\text{ cm}^{-1}$, $B=1.08\text{ cm}^{-1}$, and $C=1.03\text{ cm}^{-1}$. The molecule is close to a C_{2v} symmetry, with the symmetry axis along the weak $\text{OH}\cdots\text{H}_2$ bond, the a axis. The H_2 stretch then has A_1 symmetry. This is only an approximate symmetry but the H_3O^+ also undergoes inversion.

At the barrier for inversion the H_3O^+ is planar, and the complex as a whole has C_{2v} symmetry. This higher symmetry is the preferred point group when including the inversion.

Closer inspection of the R branch at a resolution of 0.75 cm^{-1} reveals a progression of doublets. Fig. 10 shows detail of this band. The splitting of a given doublet is approximately 0.6 to 0.8 cm^{-1} . The interval between doublets is 2.0 cm^{-1} , in fairly good agreement with the spacing expected from the *ab initio* results. Larger basis sets and inclusion of correlation often result in stronger and shorter hydrogen bonds, so a small discrepancy may not be unrealistic.

The source of the doubling is not clear. The molecule is so close to a symmetric top, that deviations from a pure symmetric rotor spectrum are unlikely to account for a doubling of this magnitude. One possibility is a splitting due to ortho and para H_2 . The normally small splitting due to coupling of vibration and internal rotation is somewhat larger for the light H_2 rotor. In the neutral H_2 dimer,³⁶ the vibrational origins of the $\nu=1$ fundamental for ortho and para hydrogen are split by approximately 5 cm^{-1} , similar to the difference in the monomer H_2 . Kenney, Roth and Levy³⁷ have observed an ortho/para splitting of about 1.5 wn in the laser induced fluorescence dispersed emission spectra of the $\text{I}_2\cdot\text{H}_2$ van der Waal's complex. Another possibility is a small inversion doubling²¹ arising from the umbrella motion of the H_3O^+ . The size of the splitting in such floppy molecules is generally mode-specific.³⁸ One would expect a small splitting for this vibration, because it would be only weakly coupled to the umbrella mode. Although these spectra bear more examination, at this resolution, the lines observed are almost certainly blends of many overlapping lines. An understanding of this spectrum, and specifically the source of the apparent doubling, probably requires a spectrum taken at much higher resolution. Such a spectrum can readily be taken using an F center laser, as was

done in the previous chapter.

We have also observed a strong cluster of lines over the region from 3450 to 3650 cm^{-1} , arising from absorption by the two free OH bonds of the H_3O^+ , seen in the middle panel of Fig. 9. From the approximate C_{2v} symmetry, we expect an a type band and a b type band, i.e., excitation of the A_1 and B_1 modes. The b type band gives rise to the strong Q sub-bands that are evident in the low resolution spectrum. The two strongest lines lie at 3550 cm^{-1} and 3560 cm^{-1} . The spacing between these strong lines is not very uniform, averaging approximately 10 cm^{-1} . The expected spacing based on a simple prolate top perpendicular band is much larger, with $2(A - B) \approx 17 \text{ cm}^{-1}$ from the *ab initio* predictions. Given the assumed geometry, it is unlikely that $2(A - B)$ would be significantly different. Again, inversion doubling may play a role. The absorption band of the degenerate ν_3 mode of the H_3O^+ observed at $\sim 3520 \text{ cm}^{-1}$ is split into $s-s$ and $a-a$ bands with origins at 3519 and 3533 cm^{-1} .¹⁹ The symmetry problem of $\text{H}_3\text{O}^+(\text{H}_2)$ is considerably different, but one does expect to see a sizable doubling arising from the inversion of the H_3O^+ moiety.

This absorption in the 3500 cm^{-1} region is very broad, covering over 200 cm^{-1} . At its red edge, there appears to be a band near 3490 cm^{-1} , but the low laser power in this region, due to the OH absorption in the LiNbO_3 crystal, makes it difficult to determine the band contour, although some structure is evident. We estimate that the maximum occurs near 3490 cm^{-1} . From its position relative to the series of Q branches, one would assign a band occurring here to the A_1 symmetric stretch mode of the free OH bonds. However, given the breadth of the overall absorption band and the inability to resolve structure, we cannot definitively place a band here. The band origin of an A_1 band could lie anywhere within the congested set of lines between 3450 and 3600 cm^{-1} .

The lowest band is the strongest band, approximately 40 cm^{-1} wide, centered at 3110 cm^{-1} , shown in the upper panel of Fig. 9. We assign this band to stretching of the donor OH bond. The band is irregularly shaped, with a dip near the center at 3107 cm^{-1} , suggesting two sub-bands at 3100 and 3115 cm^{-1} . No finer structure has been resolved at 0.75 cm^{-1} resolution. The observed frequency is approximately 400 cm^{-1} below the observed antisymmetric stretch (E mode) of H_3O^+ monomer and red-shifted 300 cm^{-1} from the theoretically predicted symmetric stretch at 3400 cm^{-1} .

We also searched for weaker bands, in the gaps between the major bands. This search was difficult below 3400 cm^{-1} , because the laser power dropped off, to 1 mW . We did however find a band at 3800 cm^{-1} , with some rotational structure evident. This band is shown in Fig. 11. The poor signal-to-noise made it difficult to find more than the strongest features. If this band is a combination band of the low frequency intermolecular stretch and the free OH stretch, the intermolecular stretch would have a frequency of 240 cm^{-1} . Another possible assignment is a combination band of the H_2 stretch with a $\Delta K = -2$ transition of the free rotation of the H_2 . Such a transition would be inactive, but the H_2 may have a large quadrupole moment induced by the large H_3O^+ dipole moment and charge. Remington and Schaefer calculate a respectable induced dipole moment of 0.064 D from their DZ+P SCF theory, but do not give enough parameters to estimate higher moments.

As seen in Fig. 7, there is an apparent band at 3280 cm^{-1} , appearing as a high frequency tail of the 3120 cm^{-1} band. This band was unnoticed in the preliminary scans, and thus no additional spectra were taken. Furthermore, there is a gap from 3240 cm^{-1} to 3260 cm^{-1} where a problem with the dye laser was encountered. A weak continuous absorption extends from the 3110 cm^{-1} band to this band. This 3280 cm^{-1} band may be a combination band of the OH stretch and the $\text{O}\cdots\text{H}_2$

stretch, or it may be an overtone of the H_3O^+ bend. In H_2O the first overtone of the bending mode lies nearby at 3151 cm^{-1} . The first overtone of the clusters mode correlated with the H_3O^+ ν_4 E mode is expected to occur at 3300 cm^{-1} from the DZ+P SCF calculations and scaling arguments.

Remington and Schaefer¹⁷ have made preliminary calculations for the vibrational frequencies, and intensities, of $\text{H}_3\text{O}^+(\text{H}_2)$ at the DZ+P SCF level. With one exception, their scaled frequencies, as seen in Fig. 7, are in excellent agreement with the results of our experiment, given the relatively low level of theory (DZ+P SCF). The theory specifically supports our assignment of the possible 3490 cm^{-1} band as the symmetric stretch of the free OH groups. The worst agreement is for the donor OH stretching mode at 3110 cm^{-1} . The theory predicts a scaled frequency of 3304 cm^{-1} , off by over 180 cm^{-1} . The frequency of this mode is quite sensitive to the strength of the hydrogen bond, and the geometry of the complex. It is not clear that the level of theory is adequate for describing this particular mode; however, the calculation is preliminary, and further theoretical investigations have not yet been carried out. They also predict a harmonic frequency of 322 cm^{-1} for the intermolecular stretch. After taking into account anharmonicity, we cannot rule out that possibility that the 3800 cm^{-1} band is a combination band of this mode and the 3560 cm^{-1} mode.

B. $\text{H}_3\text{O}^+(\text{H}_2)_2$

Details of the $\text{H}_3\text{O}^+(\text{H}_2)_2$ bands are shown in Fig. 12. The frequency of the H_2 stretching modes are shifted slightly from the 4046 cm^{-1} band origin seen in $\text{H}_3\text{O}^+(\text{H}_2)$ to 4055 cm^{-1} . Although the band contour is suggestive of P , Q , and R sub-bands, no individual rotational lines are resolvable. The only fine features are peaks at 4050 cm^{-1} , 4055 cm^{-1} , and 4062 cm^{-1} . We can estimate the rotational

constants from the structural parameters given in the *ab initio* calculation¹⁷ for $\text{H}_3\text{O}^+(\text{H}_2)$, assuming that the second H_2 binds similarly to the hydronium ion. The estimated constants are $A = 1.76 \text{ cm}^{-1}$, $B = 0.72 \text{ cm}^{-1}$, and $C = 0.54 \text{ cm}^{-1}$. The rotational spacing is roughly comparable to the laser linewidth and the observed peaks are probably maxima in the *P*, *Q*, and *R* branches. Furthermore, both H_2 ligands will absorb, so overlapping bands, one *a* type and the other *b* type, are possible.

The free OH stretch of the H_3O^+ ion gives rise to a band at approximately 3550 cm^{-1} . This band also has a shoulder at 3620 cm^{-1} . The two strongest bands at lower frequency are assigned to donor OH stretches, the symmetric stretch at 3180 cm^{-1} , and the antisymmetric stretch at 3275 cm^{-1} . Without rotationally resolved spectra, we cannot definitively assign these bands. The best we can do is suggest that, because a perpendicular band for a somewhat prolate top will have a broader band contour, the wider peak at higher frequency is the B_1 antisymmetric stretch.

C. $\text{H}_3\text{O}^+(\text{H}_2)_3$

In this cluster, all three OH bonds of the hydronium ion are coordinated with an H_2 molecule. The cluster most likely is an oblate symmetric top with a three-fold symmetry axis, and, because the H_3O^+ ion remains pyramidal (as in H_3O_4^+), the point group will be C_{3v} , with a saddle point geometry of D_{3h} for the barrier to inversion. By assuming this geometry, and fixing the intermolecular coordinates to mimic those shown in Fig. 8, we estimate the rotational constants to be $B = 0.65 \text{ cm}^{-1}$ and $C = 0.37 \text{ cm}^{-1}$.

The H_2 stretch, at 4065 cm^{-1} , is again close to the H_2 stretch frequencies observed in the smaller clusters. The band contour is irregular, as seen in Fig. 13.

From an assumed symmetry of C_{3v} , we deduce that there will be two normal modes, an A_1 mode and a double degenerate E mode, but the resolution is too poor to observe any distinct structure.

A very weak peak is observed at 3635 cm^{-1} , as well as a broad, weak absorption between 3450 and 3550 cm^{-1} . These are shown in Fig. 9, although their intensity should be obtained from Fig. 7. There were, however, no strong peaks present, giving clear evidence that all three OH bonds of the hydronium ion are involved in hydrogen bonding. The hydrogen bonded OH stretches themselves lie at 3200 cm^{-1} and 3290 cm^{-1} . The latter band is significantly broader, as might be expected of a b type band. These two bands are close to the absorption bands for the donor OH stretches in $\text{H}_3\text{O}^+(\text{H}_2)_2$. The symmetric stretch, with A_1 symmetry, gives rise to a parallel band, while the antisymmetric stretch, an E mode, will give rise to a perpendicular band. The width of the 3290 cm^{-1} band suggests that it is the E mode, but other broadening mechanisms may be involved. One possibility, as described above, is a Fermi resonance with an HOH bend. Resolved rotational spectra are needed for a definite assignment. The relative order of the symmetric and antisymmetric stretches of H_3O^+ are reversed in H_9O_4^+ .^{14,39} Our tentative assignment here, with the E mode higher in frequency than the A_1 mode, implies that the hydronium ion in the $\text{H}_3\text{O}^+(\text{H}_2)_3$ cluster is not perturbed enough to change the ordering of the frequencies of these two modes.

V. SPECTRA OF THE LARGER HYDRATES $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n \cdot (\text{H}_2)$

The H_2 clearly has a pronounced effect on the spectrum of H_3O^+ and we must therefore consider the effects of the H_2 carefully in trying to extract the $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ spectrum from the spectrum of the messenger-bound cluster. We have concluded that the H_2 forms a weak ionic hydrogen bond with the hydronium

ion, having a binding energy of approximately 3-4 kcal/mol. There is predicted to be a large partial charge on the protons in H_3O^+ ,^{17,34} and it is this charge with which the H_2 interacts. Stabilization of the charge upon hydration leads us to expect that the effect of H_2 on $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ will be less than on the lone H_3O^+ . We can therefore anticipate that the H_2 will bind by energies less than 3 kcal/mol, and will shift specific OH bond frequencies by less than 200 cm^{-1} .

In terms of solvation, the H_2 acts as a weaker cousin of H_2O , which binds with energies of 18 kcal/mol or more. The H_2 is most likely to bind to a given cluster $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ at the same location as the next additional H_2O would bind. The expected structures are shown in Fig. 14. In H_5O_2^+ and H_7O_3^+ , it should form a hydrogen bond with a free H atom on the H_3O^+ ion. In H_9O_4^+ , all three OH bonds are hydrogen-bonded to water molecules, so as in $\text{H}_{11}\text{O}_5^+$, the H_2 should be in an outer shell, coordinating to one of the three H_2O . In the following sections, we will interpret the observed spectra given this picture of the clusters.

A. H_5O_2^+

The structure of the H_5O_2^+ ion is still controversial. Although it is nominally the singly hydrated species $\text{H}_3\text{O}^+(\text{H}_2\text{O})$, many studies^{16,17,40,41,42} indicate that the central proton lies symmetrically between the two H_2O groups, to form the symmetric ion $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$. Although several condensed phase experiments, such as X-ray diffraction studies,⁴³ have addressed this question, there has always been an uncertainty resulting from the perturbing influence of the surrounding environment. Theoretical studies indicate that the symmetric structure is the most stable. A recent *ab initio* result obtained at the CISD (configuration interaction with all single and double excitations) level has determined that the symmetric structure is stable by only 0.2 kcal/mol.^{17,42} The basis set size and effect of correlation have

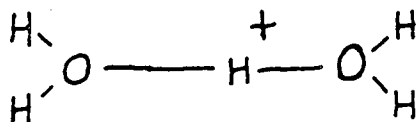
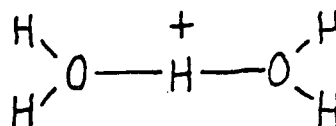
been found to be very important, and lower level theory does not yield the correct structures and energies in this and other loosely bound molecules. These studies indicate that the potential energy surface for the proton is very flat; therefore, the proton undergoes very large amplitude motion. Furthermore, the potential for the central proton becomes a double well if the $\text{O}\cdots\text{O}$ distance is stretched a small amount.

We have observed four bands in the OH stretching region, shown in Fig. 4. Two, at 3617 cm^{-1} and 3693 cm^{-1} roughly match the spacing seen in H_2O , and are assigned as red-shifted H_2O symmetric and asymmetric stretches. The red shifts are 40 cm^{-1} and 63 cm^{-1} respectively. The other two bands can be assigned as free OH stretches of the H_3O^+ . In fact, all of the frequencies of the OH stretches may be quite close, and there is probably substantial mixing in the normal modes. A search of these bands at 0.75 cm^{-1} resolution yielded little additional structure. Higher resolution scans of two of the peaks in the spectrum of the OH bands of $\text{H}_5\text{O}_2^+ \cdot (\text{H}_2)$ are shown in Fig. 15. Most of the fine structure is noise; some broad structure appears in the 3660 cm^{-1} and 3693 cm^{-1} bands. There are no previous gas phase spectra of H_5O_2^+ alone. Schwarz¹³ observed a transient absorption at 3170 cm^{-1} , which he assigned to H_5O_2^+ . We found no absorption from 3100 cm^{-1} to 3500 cm^{-1} . The dye laser output in this region was weak, so our experiment does not rule out the possibility of absorptions weaker than the H_5O_2^+ peaks around 3600 cm^{-1} . Two of the bands lie close to the vibrational bands of the H_2O monomer, and are red-shifted by 42 cm^{-1} and 61 cm^{-1} . The lowest frequency mode is therefore clearly the $\text{OH}\cdots\text{H}_2$ stretch. The relative positions and intensities of the bands in this spectrum agree well with the calculated results of Remington *et al.* for the asymmetric C_s structure. For the symmetric C_2 structure of H_5O_2^+ , the calculations give two absorption bands, as one would expect if the two H_2O groups were identical by sym-

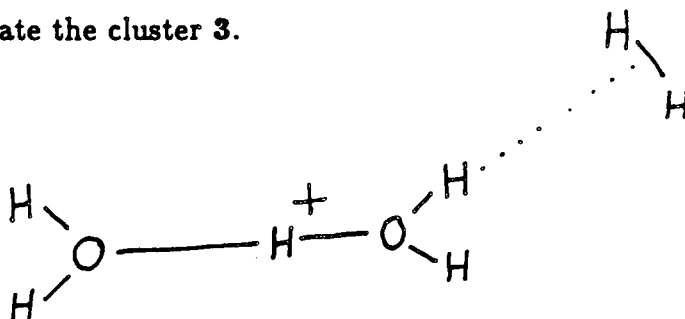
metry. These bands are close to the two H_2O bands observed in the C_s structure. All of the observed peaks are somewhat higher in frequency than predicted, but one peak, the 3528 cm^{-1} band, is shifted to the red, and has a higher than predicted intensity. If the pattern of lines predicted by theory is correct, these signs indicate that this band is perturbed by the H_2 .

The spectrum of the $\text{H}_5\text{O}_2^+ \cdot (\text{H}_2)_2$ cluster is shown in Fig. 5 plotted along with the $\text{H}_5\text{O}_2^+ \cdot (\text{H}_2)$ spectrum. The major change upon adding a second H_2 is to increase slightly the frequency of the 3528 cm^{-1} band by 37 cm^{-1} , and to double its intensity. The peak at 3660 cm^{-1} also appears a bit broader and weaker, but the signal to noise is too poor to say anything conclusive. Remington and Schaefer's results show that this band is a normal mode containing some H_3O^+ stretching character, and so should also be perturbed by the H_2 , although perhaps to a lesser extent.

A comparison with the theoretical predictions leads us to conclude that the H_5O_2^+ ion possesses the asymmetric $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})$ structure when bound to an H_2 . One expects that the H_2 will bind to an OH and stabilize the H_3O^+ ion, forming the asymmetric ion. As seen in Table I, the H_2 can bind to various protonated species with energies of 0.5 to 10 kcal/mol. The energetics of the $\text{H}_3\text{O}^+ \cdot (\text{H}_2)_3$ dissociation indicates that the binding energy of H_2 to H_3O^+ is approximately 3 to 4 kcal. These binding strengths are far larger than the calculated energy differences between the asymmetric structure **1** and the symmetric **2** structure of 0.2 kcal/mol.

**1****2**

Because the potential energy surface is so flat, attaching the H_2 should skew the potential to create the cluster 3.



3

As a result, spectra obtained using H_2 as a messenger cannot unambiguously yield the correct structure of the $H_5O_2^+$ cluster.

The spectrum of the $H_5O_2^+$ ion without messenger obtained in the two color IRMPD experiment²⁸ is strikingly different. That spectrum appears to consist of two major bands, one at 3610 cm^{-1} and a stronger band at 3697 cm^{-1} . The first of these is relatively broad, with an apparent width of 12 cm^{-1} . The 3697 cm^{-1} band is a series of sharp lines spread out over 100 cm^{-1} . It appears to be a perpendicular band, with the sharp lines as Q sub-branches, but the spectrum has not yet been analyzed. There is therefore some uncertainty both in the band origin and in the possibility of another absorption band nearby. The observed frequencies agree well with the vibrational frequencies predicted by the *ab initio* calculations for the symmetric $H_2O \cdot H \cdot OH_2^+$ structure. These preliminary low resolution spectra therefore provide definitive evidence that the unperturbed $H_5O_2^+$ ion is symmetric. The dramatic change in the spectrum with the H_2 messenger reveals the small energy difference between the symmetric and asymmetric structures.

B. H_7O_3^+

In $\text{H}_3\text{O}^+(\text{H}_2\text{O})_2$, water molecules hydrogen bond to two of the OH bonds of H_3O^+ , as shown in Fig. 2. The third OH group on the hydronium ion is thus "free," and is the most likely site at which the H_2 messenger would bind, as seen in Fig. 14.

We have observed three bands in the spectral region of OH absorption, from 3000 cm^{-1} to 4000 cm^{-1} , shown in Fig. 4. Again, two bands, at 3644 and 3725 cm^{-1} , are red-shifted slightly (13 cm^{-1} and 31 cm^{-1}) from the two absorption bands of the H_2O monomer. As the hydration number increases, the perturbation to the H_2O groups can be clearly seen to decrease. These are the symmetric and antisymmetric stretch modes of the solvating H_2O moieties. A third band, at a lower frequency (3589 cm^{-1}), we assign to the OH stretch of the H_3O^+ ion. The H_2 messenger will bind to this OH group, decreasing the OH vibrational frequency and enhancing its intensity. Thus, the observed frequency of 3589 cm^{-1} is a lower limit to the true frequency of this mode. We have scanned all of the observed bands at 0.74 cm^{-1} resolution without observing any new features.

The *ab initio* transitions, shown as stick spectra in Fig. 4, do not completely agree with the observed peaks. The two H_2O stretching bands are in fairly good agreement, but instead of a weak peak above 3640 , we observe our intense 3589 cm^{-1} band. Remington *et al.* predict that the free OH of the H_3O^+ mixes with the symmetric stretch of the H_2O 's near 3620 to 3640 cm^{-1} . The theory thus indicates that the frequency of the free OH stretch on the hydronium ion is close to 3640 cm^{-1} . We can conclude from our spectrum that the H_2 thus appears to shift the OH stretch by approximately 50 cm^{-1} .

In this case, the *ab initio* results are in good agreement with the spectrum of the H_7O_3^+ ion recorded by the IRMPD technique. Three bands have been observed, two

that are close to the H_2O stretch bands observed in the $\text{H}_7\text{O}_3^+ \cdot (\text{H}_2)$ spectrum and one weak band at 3670 cm^{-1} , approximately 30 cm^{-1} above the H_2O symmetric stretch. If we assign this band as the stretching vibration of the unperturbed "free" OH of the H_3O^+ , then the H_2 messenger shifts the frequency by 80 cm^{-1} .

We have also scanned the region from 2200 cm^{-1} up to 3000 cm^{-1} , to search for absorption by the hydrogen-bonded (donor) OH bonds. Schwarz¹³ has observed absorption near 2300 cm^{-1} , which from the time dependence he attributed to H_7O_3^+ . We have found a broad absorption in the region below 2500 cm^{-1} , but the low laser power, generally less than 1 mW, prevented us from getting good signal-to-noise. From the scaled *ab initio* frequencies, one expects a strong vibrational band near 2650 cm^{-1} . We have found no absorption in the region near $2600\text{--}2700 \text{ cm}^{-1}$, although the laser power is far stronger.

C. H_9O_4^+

With the addition of another H_2O to form H_9O_4^+ , the H_3O^+ ion has a complete inner coordination shell, i.e. one water molecule on each OH bond. From the three-fold symmetry, we see that the H_2O -type vibrations will be triply degenerate. These will combine to form the A_1 and E normal modes of the cluster, defined by the relative phases of the vibrations on each H_2O ligand. With all OH bonds participating in hydrogen bonds, the hydronium ion OH stretches will all be significantly red-shifted.

The spectrum of $\text{H}_9\text{O}_4^+ \cdot (\text{H}_2)$ shown in Fig. 16 consists of two doublets, as well as two weaker bands at 3803 cm^{-1} and 3824 cm^{-1} . The two strongest peaks at 3648 cm^{-1} and 3733 cm^{-1} lie 9 and 23 cm^{-1} to the red of their nearest water monomer bands. These two doublets can be assigned as the symmetric and anti-symmetric stretches of the solvent H_2O groups. In each doublet, the lower frequency

component is about half the intensity of its higher frequency mate. A higher resolution scan at 0.75 cm^{-1} shown in Fig. 16 reveals a partially resolved triplet structure in the strongest band at 3733 cm^{-1} . The splitting of the triplet is approximately 1 cm^{-1} , and may be partially resolved P, Q, and R branches of a parallel band, or partially resolved Q branches of a perpendicular transition.

Schwarz's spectrum¹³ of H_9O_4^+ has a partially resolved pair of bands at 3620 cm^{-1} and 3710 cm^{-1} , as seen in the dotted curve in Fig. 16. The resolution of the monochromator used in that experiment is 40 cm^{-1} , so the agreement is the best that can be expected. Furthermore, as seen in Fig. 1, all of the large hydrated ions absorb in this region. Given the resolution used and the need to separate contributions from every cluster, it would be too difficult to obtain clear spectra of the H_2O stretch absorption bands for each cluster in Schwarz's experiment.

Remington *et al.* predict that the H_9O_4^+ cluster will have two bands in this region.¹⁷ The frequencies scaled to the H_3O^+ frequencies agree to within five cm^{-1} of the high frequency peaks in each doublet. The frequencies scaled to the H_2O frequencies are below the lower frequency components by 5 and 10 cm^{-1} . The rules for scaling require that the latter (H_2O) scaling be used, because these vibrations are essentially vibrations of the solvating H_2O groups. The theory predicts that the a_1 and e modes have approximately the same intensity ratios that we have observed in the $\text{H}_9\text{O}_4^+ \cdot (\text{H}_2)$ cluster. However, the predicted splitting is effectively zero, indicating that there is no harmonic coupling of the H_2O stretches.

The splitting is absent as well in the H_9O_4^+ spectra without the messenger. The bands observed in the two color IRMPD spectra coincide, to within 2 cm^{-1} , with the higher frequency band in each doublet.²⁸

We believe that the H_2 messenger is responsible for the lower frequency component of the doublets. If the H_2 binds to one of the outer H_2O moieties, the

vibrational frequencies will be red-shifted. The H_2 will form either a single hydrogen bond to one OH, or perhaps a bifurcated hydrogen bond bridging both OH bonds of the water. The 2:1 intensity ratio provides further support that one water molecule is involved.

Perturbations induced by H_2 should be similar in magnitude to those seen in a neutral $H_2O \cdot H_2$ complex. To the best of our knowledge, no work on this complex has been done; however, Bernholdt, Liu, and Dykstra have recently calculated the vibrational shifts and other properties of the complex $HF \cdot H_2$ at a relatively high level of theory (including correlation).⁴⁴ As in complexes with protonated species, the H_2 forms a hydrogen bond with the HF. The cluster dissociation energy D_e is calculated to be 0.86 kcal/mol, somewhat less than the binding energies found for the ionic clusters. These authors find that the donor HF stretch is lowered in frequency by 15 cm^{-1} . This shift is close to the red-shifts of 10 and 12 cm^{-1} of the OH stretches observed in $H_9O_4^+$. The H_2 stretching frequency in the $HF \cdot H_2$ complex is predicted to shift by 20 cm^{-1} . We were unable to observe any band between 3850 cm^{-1} and 4200 cm^{-1} . If we assume that the H_2 binds more weakly to $H_9O_4^+$ than to $H_7O_3^+$, we can set an upper bound to the shift of 45 cm^{-1} . Furthermore, the weaker $H_2O \cdot H_2$ interaction will substantially decrease the H_2 stretching intensity. In summary, the results of the calculations on $HF \cdot H_2$ support our hypothesis that the H_2 forms a hydrogen bond with a solvent H_2O , and thus gives rise to the observed splitting of the water bands.

In H_3O^+ , the *ab initio* calculations indicate that each proton carries a partial charge of about +0.5.^{17,34} As the hydration number increases, the charge becomes delocalized, and the strength of a given hydrogen bond decreases. This effect is manifested as an increase in the vibrational frequency of the donor OH. We have found a strong, broad band at 2670 cm^{-1} seen in Fig. 6. As seen in Fig. 1, Schwarz

observed a very strong band in H_9O_4^+ at 2660 cm^{-1} , as well as a shoulder at approximately 3000 cm^{-1} . These he assigned to the symmetric and antisymmetric stretching modes of the hydrogen bonded OH's. The scaled theoretical frequencies place these modes at 3020 and 2997 cm^{-1} . We have also observed a weak shoulder at higher frequencies, but the low laser power prevented us from observing any structure. Our results show that Schwarz's initial assignment of the 2660 cm^{-1} band to H_9O_4^+ is correct, and indicate that his deconvolution of the spectra is probably sound for the strongest, most distinguishable peaks.

The spectral region from 2800 cm^{-1} to 3100 cm^{-1} lies in a gap in the coverage between two dyes. Thus, the laser power was particularly low, and we were unable to confirm the existence of the shoulder at 3000 cm^{-1} that Schwarz assigned to the symmetric hydrogen-bonded stretch. Schaefer's calculations predict a very small splitting of 33 cm^{-1} between the symmetric and antisymmetric stretches. On the other hand, they predict a sizable (120 cm^{-1}) splitting between these modes in the H_3O^+ monomer. Since to a first order approximation, the splitting will be induced by harmonic terms in the Hamiltonian, either the calculation did poorly in estimating the harmonic coupling, or the splitting is due primarily to large anharmonic or kinetic terms, or Schwarz misassigned the band. The larger clusters have strong absorption maxima in this range, so once again the question of contamination of spectra must be raised. Our results do not give any insight into this problem.

An interesting feature of the 2670 cm^{-1} band is its large width. The width is 100 cm^{-1} , less than the approximately 200 cm^{-1} FWHM of the peak in Schwarz's spectrum, but greater than the 8 cm^{-1} width of the H_2O stretching modes at 3731 cm^{-1} and 3644 cm^{-1} . Since the H_2 messenger is bound to an H_2O ligand, it is unlikely that exciting the hydrogen-bonded OH of the H_3O^+ ion would result in faster energy transfer. Such large widths are found in many ionic and neutral

hydrogen-bonded complexes, even in the gas phase, where inhomogeneous broadening due to the environment cannot occur. The broadening in neutral species such as $\text{HF}\cdot\text{X}$ appear to arise from combination bands and hot bands with low frequency intermolecular stretch and bend modes, with some possible contribution from Fermi resonances.

There are several possible assignments for the identity of the weak bands at 3802 and 3825 cm^{-1} , shown in more detail in Fig. 17. They could be a combination band of one of the OH stretches with a low frequency mode such as an intermolecular stretch, or an overtone of a lower frequency mode, e.g. a bending mode. These bands are observed at the same positions in the IR-MPD spectra of the H_3O_4^+ ion without the H_2 ; therefore, they are directly attributable to the hydrated cluster alone. If these bands are combination bands arising from the asymmetric stretch at 3733 cm^{-1} , why is no similar band observed in combination with the lower H_2O mode? Such a combination band with the symmetric 3644 cm^{-1} mode might overlap with the 3733 cm^{-1} band and thus be obscured. If we assign these lines as combinations with the stretching of the hydrogen bond, the intermolecular stretching frequency would be either $70\text{--}90\text{ cm}^{-1}$, or $158\text{--}178\text{ cm}^{-1}$. In contrast, Remington and Schaefer¹⁷ predict harmonic, unscaled frequencies of 247 and 319 cm^{-1} . A final possibility is the asymmetric H_2O stretch in combination with the $\Delta K_1 = +1$ internal rotation of the H_2O ligand about the intermolecular band. The expected rotational spacing is $\approx 55\text{ cm}^{-1}$.

VI. DISCUSSION

A. Hydronium ion hydrates

Schwarz¹³ reported spectra from 2000 cm^{-1} to 4000 cm^{-1} for the large hydronium ion clusters H_9O_4^+ , $\text{H}_{11}\text{O}_5^+$, and $\text{H}_{13}\text{O}_6^+$, at a resolution of 40 cm^{-1} . Questions were raised⁴⁵ due to the necessity of deconvoluting the observed spectra in order to obtain spectra of the individual ions. Of these ions, only the H_9O_4^+ ion has been studied in this work. Our spectrum of H_9O_4^+ agrees qualitatively with his results, particularly with regard to his assignment of the 2660 cm^{-1} peak to H_9O_4^+ . Schwarz was also able to observe transient absorptions at short times after the electron pulse, which he assigned to the smaller clusters, albeit with some ambiguity.

Most of our spectra have been of bands in the region from 3500 to 3800 cm^{-1} , due to absorption by the free OH stretching modes of the H_2O solvent molecules and partially solvated H_3O^+ . In this region, Schwarz was unable to obtain distinct bands for the different clusters, because all hydronium ion clusters, as well as background H_2O monomers, contributed to the absorption. We have found relatively sharp, well defined bands arising from absorption by the solvent H_2O 's and free OH groups of the H_3O^+ ion. Table II summarizes the observed bands and their assignments. The positions and intensities of the vibrational bands in this region for differing cluster sizes are quite distinct, and are thus useful in testing the theoretical predictions.

B. Messengers

This experiment has provided preliminary $\approx 1\text{ cm}^{-1}$ resolution spectra of the hydrated hydronium cluster ions. The messenger technique in principle is very general, and can be used to locate the infra-red absorption bands of many molecular ions, but we must first understand the perturbing influence of attaching a messenger.

In this respect, the messenger technique can be thought of as matrix isolation spectroscopy (in the limit of a very small matrix), because the two techniques suffer from a common limitation, namely uncertainty concerning effects induced by the "environment."

From the true vibrational origins of the hydronium ion hydrates recently obtained from the two color multiphoton dissociation spectra we can directly determine the effect of H_2 on the vibrational frequencies of the clusters. Our results show that the interaction between the H_2 molecule and a hydronium ion cluster can be relatively large and specific. The H_2 forms hydrogen bonds with ionic OH bonds, shifts the vibrational frequencies of those bonds by 10 to 90 cm^{-1} , and intensifies the transitions. Other bands are generally not perturbed (with one exception). The frequency shifts observed in the higher hydrated clusters are much smaller than the 200 cm^{-1} to 300 cm^{-1} shift seen in the $H_3O^+ \cdot (H_2)_m$ clusters. The 3-4 kcal/mol binding energy of H_2 and H_3O^+ is undoubtedly an upper limit to the binding energy of H_2 to the larger hydrates.

In all but $H_5O_2^+ \cdot (H_2)$, only vibrational bands directly involved in bonding to H_2 are perturbed. The changes in the $H_5O_2^+$ spectrum reveal the ability of the weak $OH \cdots H_2$ interaction to stabilize the H_3O^+ in $H_5O_2^+$. For ions like $H_5O_2^+$ with flat potentials near their equilibrium geometry, even a weak solvent interaction can drastically alter the geometry and observed spectrum. Clearly, care must be taken in applying the messenger technique to an ion which can be so easily perturbed. In particular, it raises questions concerning the validity of structural measurements of $H_5O_2^+$ in the condensed phase, where the interactions and external perturbations are surely stronger.

Formation of the ionic hydrogen bond also perturbs the H_2 vibration, shifting the vibrational frequency and making the vibration IR active. In many respects, the

strength of the interaction can be judged by how the H_2 messenger itself is changed, because the bonding electrons are directly perturbed by the interaction. We have observed the H_2 stretching bands in a number of $\text{XH}^+\cdot\text{H}_2$ complexes. Their peak locations are plotted in Fig. 18. The hydrogen cluster ions, which are bound by 3.8 to 6 kcal/mol have the largest red shifts relative to the H_2 monomer. H_9^+ , with a dissociation energy of 3.8 kcal/mol, absorbs at 4020 cm^{-1} , 140 cm^{-1} below H_2 . The $\text{H}_3\text{O}^+\cdot(\text{H}_2)_m$ clusters have red-shifts of 120 to 100 cm^{-1} . Remington and Schaefer predict a value of 3.2 kcal/mol for D_e of $\text{H}_3\text{O}^+\cdot(\text{H}_2)$. The H_2 bound to the hydrated H_3O^+ have red shifts of only 55 and 45 cm^{-1} , and in H_9O_4^+ , the H_2 absorption is too weak to be seen.

The significantly smaller red-shifts of the OH and H_2 stretches observed in the complexes hydrated ions, and the weaker H_2 vibrational transitions, support the idea that hydration as delocalizes the charge, it reduces the strength of the interaction between the ion and the H_2 molecule.

It is logical to extend this work to other messengers which would have a smaller perturbing effect on the ion of interest. The best candidates are the rare gas atoms, the few species with proton affinities less than that of H_2 . He, Ne, Ar, and Kr have proton affinities of 42.5, 48.1, 88.6, and 101.6 kcal/mol, compared to the 101.3 kcal/mol proton affinity of H_2 .⁴⁶ He and Ne have ionization potentials above 20 eV, as well. A series of spectra of a given ion bound to different atoms would provide a useful diagnostic for determining which modes are perturbed in the ion-messenger complex. The H_5O_2^+ ion would be particularly sensitive to the binding strengths of different messengers, and would provide an important test.

There are few experiments investigating ionic complexes involving the light rare gas atoms, beyond simple rare gas dimers, and protonated XH^+ . Miller and co-workers⁴⁷ have begun work on the optical spectroscopy of the $\text{C}_6\text{F}_6^+\cdot\text{X}$ complexes,

with $X = \text{He, Ne, and Ar}$. They have found that in $\text{C}_6\text{F}_6^+\cdot\text{He}$, the He is bound by approximately 100 cm^{-1} , and lies $2.43\text{ \AA}$ above the plane of the ring.

Wilson and his collaborators^{48,49} have performed *ab initio* calculations on a number of complexes of He with cations forming closed shell molecules. They have found that some species are very weakly bound. $\text{CH}_3^+\cdot\text{He}$ and $\text{NH}_2^+\cdot\text{He}$, for example, are bound by 0.14 kcal/mol and 0.7 kcal/mol , respectively. On the other hand, HeCN^+ and HeCCH^+ , which are isoelectronic with HCN and HCCH, are bound by 14 kcal/mol and 31.5 kcal/mol . These calculations imply that closed shell He complexes, particularly with ions possessing saturated bonds, may be fairly strongly bound. However, this problem should not arise if the He binds to a closed shell species, such as the hydronium ion. For example, Dykstra has calculated that He binds to HCNH^+ with a dissociation energy D_0 of only 0.24 kcal/mol .⁵⁰

As seen in the mass spectra in Fig. 3, the complexes $\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})_n\cdot(\text{H}_2)$ represent a small fraction of the ions. The more weakly bound clusters with a rare gas atom will be far more difficult to create. The source will have to be operated at a lower temperature and higher stagnation pressure. He will clearly present the greatest problems; furthermore, there will be ambiguities if H_2 and He are mixed, due to the possibilities of two H_2 or a D_2 binding to an ion. Ne may therefore prove to be the best messenger. Initial attempts with a H_2/Ne mixture failed to produce ions. The nature of a corona discharge depends in part on the dominant gas, and discharge conditions may need to be carefully selected to yield a usable beam of the desired cluster.

C. *Ab initio* calculations

The scaled *ab initio* results of the highest frequency modes¹⁷ are in reasonable agreement with experiment. Deviations for the free OH stretching vibrations of

the H_2O ligands, as well as the H_2 stretch of the $\text{H}_3\text{O}^+(\text{H}_2)$ cluster, were less than 30 cm^{-1} . Curiously, applying the H_3O^+ scaling factor gave almost perfect agreement for the H_2O frequencies in all three hydrates, although the "rules" require using the H_2O scaling factor. Given the empirical nature of scaling, we probably cannot interpret this result as more than coincidence. Newton¹⁴ was able to predict the OH stretching frequencies of a number of hydrated hydronium ions by using a function $\nu_i = a(F_i G_i) + b$, where the a and b parameters were derived from a fit to six known OH stretching frequencies. The use of an empirical offset b as well as a scaling parameter a gave good scaled frequencies, but there was no apparent justification for this ansatz.

That the relative positions and intensities of the free OH stretches match the data well is not unexpected, because these vibrations are only slightly perturbed upon forming the complex. On the other hand, theory fares poorly in predicting the frequencies of the hydrogen bonded donor OH stretches. For H_9O_4^+ , the scaled *ab initio* value of the antisymmetric stretch is 3020 cm^{-1} , about 350 cm^{-1} above the experimental value, while for $\text{H}_3\text{O}^+(\text{H}_2)$, the scaled theoretical frequency is 3304 cm^{-1} , 200 cm^{-1} above the experimental result.

We can play the scaling game with a new twist, by scaling the hydrogen-bonded stretch in H_9O_4^+ with the correction factor from a known hydrogen-bonded stretch. If we use the experimental hydrogen bonded OH stretch in $\text{H}_3\text{O}^+(\text{H}_2)$ at 3110 cm^{-1} to obtain a scaling factor, we arrive at a scaled value of 2827 cm^{-1} for the hydrogen bonded antisymmetric stretch in H_9O_4^+ , in better agreement with Schwarz's result.

There are several possible reasons for the failure of theory. First, the level of theory, DZ+P SCF, is quite low, and may not be adequate for such a loosely bound species. The calculation tends to overestimate the force constant, but it is not clear that scaling will be correctly estimate the error for such a perturbed vibration.

Furthermore, the donor OH frequency can be particularly sensitive to the length of the weak hydrogen bond. Small changes in geometry may therefore lead to relatively large changes in frequency of this vibration. It is clear that the potential energy surface is fairly shallow, and as has been demonstrated in calculations for H_5O_2^+ and H_6^+ , DZ+P SCF may be inadequate to obtain the correct geometry.

In addition to the electronic structure calculation, the nuclear part of the calculation may also be at fault. The current calculation is simply a normal mode model using the *ab initio* force constants and geometry, empirically scaled to account for systematic deviations and anharmonicity. It is unreasonable to assume that the OH anharmonicity will be reduced proportionately with the harmonic frequency as the hydrogen bond is formed. Many theorists suggest that anharmonic coupling of the modes involved in the hydrogen bond is strong,¹⁰ suggesting that a more sophisticated treatment of the vibrational problem is necessary. Perhaps even a mean field approach such as vibrational SCF may be inadequate. An accurate theory would also require several high level *ab initio* calculations to describe the potential energy surface. These are problems which theorists are now addressing.

The observed shifts of OH frequencies upon binding of an H_2 are all relatively small, with the largest being 10% for $\text{H}_3\text{O}^+(\text{H}_2)$. The expected dominance of electrostatic interactions leads one to expect that the red shifts might be estimated from a relatively simple theory. Recently, Liu and Dykstra⁵¹ have developed a perturbation theory approach for predicting vibrational shifts in neutral hydrogen bonded complexes from the electrostatic properties of the isolated monomers. At first glance, this theory seems readily applicable to ionic complexes; however, charge transfer cannot be treated well from a strictly electrostatic model. It remains to be seen if a modified version of the theory can succeed.

D. Linewidths

We have observed a wide range of linewidths, from the 100 cm^{-1} FWHM of the hydrogen bonded OH absorption in $\text{H}_9\text{O}_4^+ \cdot (\text{H}_2)$, to the laser limited widths of the rotational transitions seen in $\text{H}_3\text{O}^+ \cdot (\text{H}_2)$. Many other bands had contours suggesting unresolved rotational sub-bands.

The well resolved structure in the free OH and H_2 stretching modes of $\text{H}_3\text{O}^+ \cdot (\text{H}_2)$ contrast sharply with the broad absorption by the hydrogen-bonded $\text{OH} \cdots \text{H}_2$ in the same cluster. In every cluster studied, when H_2 has hydrogen-bonded to the H_3O^+ ion, the band of the donor OH has been intensified, red-shifted and broadened. The exact broadening mechanism is unclear. Because the donor OH is coupled to the dissociation channel, lifetime broadening or rapid intramolecular relaxation (IVR) may be important. Some workers have also suggested that a progression of combination bands causes similar broadening seen in neutral hydrogen-bonded clusters such as the dimethyl ether/HCl complex.⁵²

The absorption band of the asymmetric $\text{O-H} \cdots \text{O}$ bond in H_9O_4^+ is the widest band observed in this experiment. This mode, however, is unlikely to be coupled strongly to the dissociative channel. The band is, however, over an order of magnitude wider than the free OH stretches of H_9O_4^+ near 3700 cm^{-1} . The H_2O bands shifted due to bonding with the H_2 are less than 10 cm^{-1} FWHM. The broad peak is therefore intrinsic to the H_9O_4^+ cluster. The question left open is whether the broadening is due to IVR, or to an unresolved progression of combination bands.

E. Future work

An underlying goal of this apparatus⁵³ has been to develop a general technique for observing infrared spectra of ions. A primary example has been the study of carbonium ions such as CH_5^+ and C_2H_7^+ , ions which exhibit nonclassical structures

with three center, two electron bonds. These ions tend to have shallow potential energy surfaces at their equilibrium configuration, and messenger-induced perturbations of the size observed in this experiment may cause problems. In the case of carbonium ions, the absence of a hydrogen bond to form a proton bound pair may result in a very weak $\text{H}_2 \cdots \text{CH}_5^+$ bond, but such a result is not certain. As discussed above, experiments using alternate messengers, namely the smaller rare gas atoms, will determine if the messenger approach is a viable method for obtaining vibrational spectra of molecular ions.

Another important extension of the $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n$ spectroscopy will be to study the larger clusters H_9O_6^+ and $\text{H}_{11}\text{O}_6^+$. Low resolution spectra of the H_2O bands should yield evidence for the beginning of a second solvation shell. Furthermore, the hydrogen-bonded OH stretch should increase in frequency, into a range of higher laser power. Finally, as the number of water molecules increases, more unusual effects become possible, such as intra-cluster proton transfer and cyclic hydrogen bonds.

The spectra reported here were preliminary scans taken with a moderate resolution laser. An F-center laser was used in the previous study of hydrogen cluster spectroscopy, and could be similarly used here. Higher resolution scans might be worthwhile for a number of these clusters. For the larger clusters, higher resolution scans are not necessary, given the success of the IR MPD experiment, except as a means of probing the H_2/ion interaction. The most rewarding subject of such a scan would be the H_5O_2^+ cluster. The relatively large rotational constants for this molecule should make rotational structure easily resolvable. Important insights about the H_5O_2^+ solvation can be gained from understanding exactly how the H_2 distorts the H_5O_2^+ structure. The partially resolved rotational structure of $\text{H}_3\text{O}^+ \cdot (\text{H}_2)$ make this ion a prime candidate for further investigation. Information

about the inversion doubling extracted from high resolution spectra would provide new information on the effect of solvation on such large amplitude motion. Besides a high resolution look at the H_2 and free OH stretching modes, scans of the 3110 cm^{-1} band to examine the nature of the apparent broadening would be interesting, and might shed light on the general problem of broadening in hydrogen-bonded OH modes. The current spectra indicate that bands of the other $\text{H}_3\text{O}^+(\text{H}_2)_m$ clusters may also have resolvable rotational structure.

REFERENCES

1. P. G. Wolynes, *Annu. Rev. Phys. Chem.* **31**, 345 (1980).
2. M. Eigen, *Angew. Chim. (English edition)* **3**, 1 (1964).
3. G. W. Robinson, P. J. Thistlethwaite, and J. Lee, *J. Phys. Chem.* **90**, 4224 (1986).
4. J. Lee, G. W. Robinson, S. P. Webb, L. A. Phillips, and J. H. Clark, *J. Am. Chem. Soc.* **108**, 6538 (1986).
5. P. Kebarle, *Annu. Rev. Phys. Chem.* **28**, 445 (1977).
6. F. Arnold, H. Bohringer, and G. Henschen, *J. Geophys. Res.* **L5**, 653 (1978).
7. E. E. Ferguson, F. C. Fehsenfeld, and D. L. Albritton, in *Gas Phase Ion Chemistry, Vol I* (edited by M. T. Bowers) 45 (Academic Press, New York, 1979).
8. T. D. Mark and A. W. Castleman, *Adv. At. Mol. Phys.* **20**, 65 (1985).
9. A. W. Castleman and R. G. Keesee, *Chem. Rev.* **86**, 589 (1986).
10. P. Schuster, G. Zundel, and C. Sandorfy, *The Hydrogen Bond. Recent Developments in Theory and Experiments*, Vol. 1 to 3 (North Holland, Amsterdam, 1976).
11. M. H. Brooker, preprint.
12. G. Zundel and J. Fritsch, preprint.
13. H. A. Schwarz, *J. Chem. Phys.* **67**, 5525 (1977).
14. M. D. Newton, *J. Chem. Phys.* **67**, 5535 (1977).

15. M. D. Newton and S. Ehrenson, *J. Am. Chem. Soc.* **93**, 4971 (1971).
16. S. Yamabe, T. Minato, and K. Hirao, *J. Chem. Phys.* **80**, 1576 (1984).
17. R. Remington, M. E. Colvin, G. P. Raine, and H. F. Schaefer III, unpublished.
18. M. H. Begemann, C. S. Gudeman, J. Pfaff, and R. J. Saykally, *Phys. Rev. Lett.* **51**, 554 (1983).
19. M. H. Begemann and R. J. Saykally, *J. Chem. Phys.* **82**, 3570 (1985).
20. D. J. Liu and T. Oka, *Phys. Rev. Lett.* **54**, 1787 (1985).
21. D. J. Liu, T. Oka, and T. J. Sears, *J. Chem. Phys.* **84**, 923 (1986).
22. P. B. Davies, S. A. Johnson, P. A. Hamilton, and T. J. Sears, *Chem. Phys.* **108**, 335 (1986).
23. A. J. Cunningham, J. D. Payzant, and P. Kebarle, *J. Am. Chem. Soc.* **94**, 7627 (1972).
24. K. Y. Lau, P. P. S. Saluja, and P. Kebarle, *J. Am. Chem. Soc.* **102**, 7429 (1980).
25. Y. K. Lau, S. Ikuta, and P. Kebarle, *J. Am. Chem. Soc.* **104**, 1462 (1982).
26. Y. Yamaguchi, J. Gaw, and H. F. Schaefer III, *J. Chem. Phys.* **78**, 4074 (1983);
R. J. Beuhler, S. Ehrenson, and L. Friedman, *J. Chem. Phys.* **79**, 5982 (1983).
27. K. Hirao and S. Yamabe, *Chem. Phys. Lett.* **79**, 279 (1981).
28. L. I. Yeh and J. D. Myers, unpublished results; L. I. Yeh, Ph. D. Thesis, in progress.

29. D. S. Bomse, R. L. Woodin, and J. L. Beauchamp, *J. Am. Chem. Soc.* **101**, 5503 (1979).
30. K. R. Jennings, in *Gas Phase Ion Chemistry, Vol. 2* (edited by M. T Bowers) Chap. 12 (Academic Press, New York, 1979).
31. S. G. Lias, J. F. Liebman, and R. D. Levin, *J. Phys. Chem. Ref. Data* **13**, 695 (1984).
32. T. Oka, "Molecular ions: spectroscopy, structure, and chemistry," 73 (North Holland, Amsterdam, 1983).
33. G. Herzberg, *Molecular Spectra and Molecular Structure: I. Spectra of Diatomic Molecules* (van Nostrand Reinhold, New York, 1950).
34. M. E. Colvin, G. P. Raine, and H. F. Schaefer III, *J. Chem. Phys.* **79**, 1551 (1983).
35. K. D. Kolenbrander and J. M. Lisy, *J. Chem. Phys.* **85**, 2463 (1986).
36. A. R. W. McKellar and H. L. Welsh, *Can. J. Phys.* **52**, 1082 (1974).
37. J. E. Kenney, T. D. Roth, and D. H. Levy, *J. Chem. Phys.* **78**, 3607 (1980).
38. G. Herzberg, *Molecular Spectra and Molecular Structure: II. and Raman Spectra of Polyatomic Molecules* (van Nostrand Reinhold, New York, 1945).
39. M. DePaz, G. Giardini, and L. Friedman, *J. Chem. Phys.* **52**, 687 (1970).
40. G. H. F. Diercksen, W. Von Niessen, and W. P. Kraemer, *Theor. Chim. Acta* **31**, 205 (1973).
41. J. E. DelBene, M. J. Frisch, and J. A. Pople, *J. Phys. Chem.* **89**, 3669 (1985).

42. G. E. Scuseria, A. C. Scheiner, T. J. Lee, and H. F. Schaefer III , preprint.
43. I. Olovsson and P. G. Jonsson, in *The Hydrogen Bond. Recent Developments in Theory and Experiments*, vol. 2, edited by P. Schuster, G. Zundel, and C. Sandorfy, 693 (North Holland, Amsterdam, 1976).
44. D. E. Bernholdt, S. Liu, and C. E. Dykstra, *J. Chem. Phys.* **85**, 5120 (1986).
45. R. J. Saykally and C. S. Gudeman, *Annu. Rev. Phys. Chem.* **35**, 387 (1984).
46. C. R. Moylan and J. I. Brauman, *Annu. Rev. Phys. Chem.* **34**, 187 (1983).
47. R. A. Kennedy and T. A. Miller, *J. Chem. Phys.* **85**, 2326 (1986).
48. S. Wilson and S. Green, *J. Chem. Phys.* **73**, 419 (1980).
49. D. L. Cooper and S. Wilson, *Mol. Phys.* **44**, 161 (1981).
50. C. E. Dykstra, *Chem. Phys. Lett.* **111**, 405 (1984).
51. S. Liu and C. E. Dykstra, *J. Phys. Chem.* **90**, 3097 (1986).
52. M. J. Wojciak, *Int. J. Quant. Chem.* **29**, 855 (1986).
53. S. W. Bustamente, PhD thesis, University of California, Berkeley, California, 1983.

TABLE I. Dissociation energies of several $\text{XH}^+ \cdot n\text{H}_2$ clusters in kcal/mol. Theoretical values from Hirao and Yamabe, Ref. 27. Experimental values from Kebarle, Ref. 5, except as noted.

XH^+		P.A. of X^a	$\text{XH}^+ \cdots \text{H}_2$	$\text{XH}^+ \cdot \text{H}_2 \cdots \text{H}_2$
H_3^+	exp. ^b	101	6.6	3.1
	DZP CI		4.0	2.0
HN_2^+	exp.	118.2	7.2	1.5
	DZP CI		5.2	0.6
HO_2^+	exp.	100.9	12.5	
	DZP SCF		4.7	
HCO^+	exp.	141.9	3.9	
	DZP CI		3.1	0.75

^aLias *et al.*, Ref. 31 and Moylan and Brauman, Ref. 46.

^bBeuhler *et al.*, Ref. 26.

TABLE II. Vibrational frequencies in cm^{-1} of the hydrated hydronium ion clusters.

Cluster ion	Experiment			Theory ^a		Assignment
	M ⁺ ·H ₂ ^b	2 color ^c	Schwarz ^d	(Scaled)		
	MPD			H ₃ O ⁺	H ₂ O	
H ₅ O ₂ ⁺	3528			3549		H ₃ O ⁺ ·H ₂ stretch
	(3565)					H ₅ O ₂ ⁺ ·2H ₂
	3617	3610		3607	3594	H ₂ O sym stretch
	3662			3633		H ₃ O ⁺ stretch
	3693	3697(?) ^e		3692	3678	H ₂ O asym stretch
	4105					H ₂ stretch
H ₇ O ₃ ⁺	~2300		2200	2655		H-bonded H ₃ O ⁺ stretch
				2722		
	3587	3670		3622	3617	H ₃ O ⁺ ·H ₂ OH stretch
					3619	
	3642	3640	3620	3631	3627	H ₂ O sym stretch
			3632			
	3726	3725	3710	3717	3702	H ₂ O asym stretch
	4115					H ₂ stretch
H ₉ O ₄ ⁺	2670		2660	2997		H-bonded H ₃ O ⁺ stretch
				3020		
	3636					H ₂ O·H ₂ sym stretch
	3648	3648	3620	3643	3629	H ₂ O sym stretch
				3645	3630	
	3723					H ₂ O·H ₂ asym stretch
	3733	3731	3710	3728	3713	H ₂ O asym stretch
				3629	3614	
	3803	3798				weak combination bands
	3824	3825				or overtones

^aDZ+P SCF calculations from Ref. —17.^bThis work.^cRef. 28.^dDirect absorption, Ref. 13.^eApparent origin of perpendicular band

FIGURE CAPTIONS

FIG. 1 Infrared absorption spectra of the clusters $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ with $n = 3, 4$, and 5 at a resolution of 40 cm^{-1} from ref. 13. The clusters were formed by pulsed radiolysis of a room temperature Ar/ H_2O mixture in a gas cell. The spectra were direct absorption of broad band IR from a glow bar discharge, dispersed by a monochromator. Reproduced with permission.

FIG. 2 *ab initio* predicted geometries of the hydrated hydronium ion clusters from DZ+P SCF and CI calculations by Remington and Schaefer. Unpublished, Ref. 17

FIG. 3 Mass spectrum of the hydrated hydronium ion clusters produced from the supersonic expansion of a weak plasma. The plasma was formed in a corona discharge of 200 torr of pure H_2 at 0°C with a discharge current of $30 \mu\text{A}$. The water clusters were produced from trace impurities in the gas.

FIG. 4 Infrared spectra of $\text{H}_5\text{O}_2^+(\text{H}_2)$, $\text{H}_7\text{O}_3^+(\text{H}_2)$, and $\text{H}_9\text{O}_4^+(\text{H}_2)$. The laser linewidth was 1.2 cm^{-1} . The arrows at the top indicate the band origins of transitions to the symmetric (3657 cm^{-1}) and antisymmetric (3756 cm^{-1}) vibrations for the H_2O monomer. The dashed stick spectra are *ab initio* predictions of the vibrational frequencies and intensities of the respective $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ clusters, made by Remington and Schaefer at the DZ+P SCF level. See Ref. 17. Calculations are in the double harmonic approximation, with the vibrational frequencies subsequently scaled. The theoretical calculations for the H_5O_2^+ ion are at the asymmetric C_s geometry, the minimum energy configuration predicted at this level.

FIG. 5 Comparison of the infrared spectra of $\text{H}_5\text{O}_2^+(\text{H}_2)$ and $\text{H}_5\text{O}_2^+(\text{H}_2)_2$. The

relative intensities of the two molecules are correct only to within 20%. In both cases, the H_5O_2^+ daughter ion was detected.

FIG. 6 Infrared spectrum of the $\text{H}_5\text{O}_4^+ \cdot (\text{H}_2)$ antisymmetric stretch of the hydrogen-bonded $\text{O-H} \cdots \text{O}$.

FIG. 7 Infrared spectra of the clusters $\text{H}_3\text{O}^+ \cdot (\text{H}_2)_m$, with $m = 1, 2$, and 3 . The fragment ions detected were H_3O^+ , H_3O^+ , and $\text{H}_3\text{O}^+ \cdot (\text{H}_2)$, respectively. Laser resolution was 1.2 cm^{-1} . The arrows at the top indicate the origins of fundamental bands in the H_3O^+ and H_2 monomers. The ν_1 mode of H_3O^+ has not yet been observed in the gas phase. The indicated value is from an *ab initio* calculation (Ref. 34).

FIG. 8 Geometry of $\text{H}_3\text{O}^+ \cdot (\text{H}_2)$ predicted by *ab initio* calculations of Remington and Schaefer with the DZ+P SCF theory. See Ref. 17.

FIG. 9 Details of the vibrational predissociation spectrum of the $\text{H}_3\text{O}^+ \cdot (\text{H}_2)$ cluster, detecting the $\text{H}_3\text{O}^+ \cdot (\text{H}_2)$ product ion. Partially resolved rotational structure can be seen in the 3560 cm^{-1} and the 4046 cm^{-1} bands.

FIG. 10 A segment of the 4046 cm^{-1} band, taken at a resolution of 0.75 cm^{-1} , with laser frequency step size of 0.2 cm^{-1} . This spectrum shows details of the *Q* and *R* branches.

FIG. 11 Weak combination or overtone band of $\text{H}_3\text{O}^+ \cdot (\text{H}_2)$ at 0.75 cm^{-1} resolution.

FIG. 12 Details of the vibrational predissociation spectrum of the $\text{H}_3\text{O}^+ \cdot (\text{H}_2)_2$ cluster, detecting the H_3O^+ product ion.

FIG. 13 Details of the vibrational predissociation spectrum of the $\text{H}_3\text{O}^+ \cdot (\text{H}_2)_3$ cluster, detecting the $\text{H}_3\text{O}^+ \cdot (\text{H}_2)$ product ion.

FIG. 14 Postulated location of H_2 binding to larger hydronium ion hydrates.

FIG. 15 Vibrational bands of $\text{H}_5\text{O}_2^+ \cdot (\text{H}_2)$ at a resolution of 0.75 cm^{-1} .

FIG. 16 Vibrational bands of $\text{H}_9\text{O}_4^+ \cdot (\text{H}_2)$ at a resolution of 0.75 cm^{-1} .

FIG. 17 Weak combination or overtone vibrational bands of $\text{H}_9\text{O}_4^+ \cdot (\text{H}_2)$ at a resolution of 1.2 cm^{-1} .

FIG. 18 Observed peak frequencies of vibrational bands assigned to H_2 stretches in various $\text{XH}^+ \cdot \text{H}_2$ clusters.

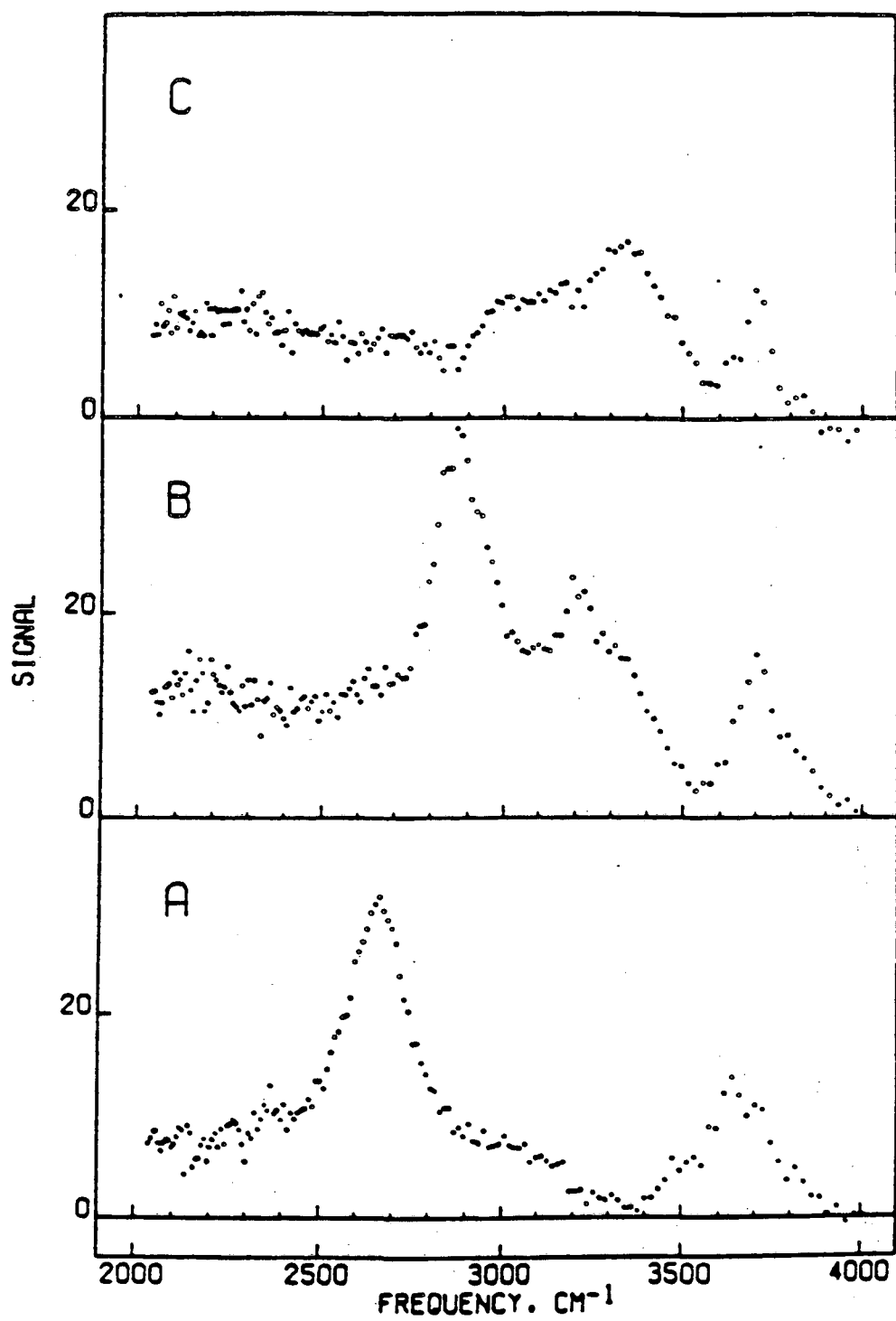


FIG. 1

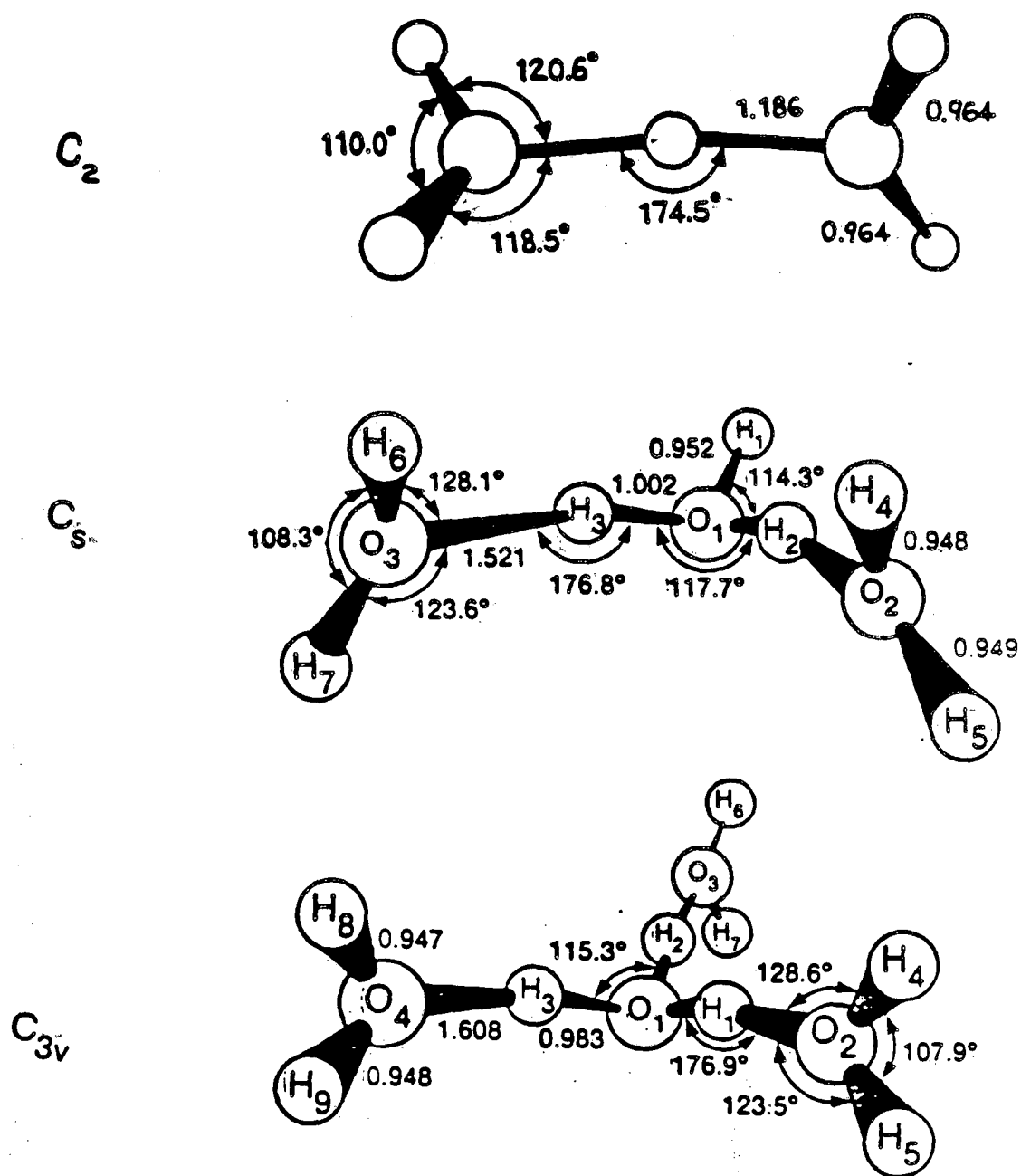
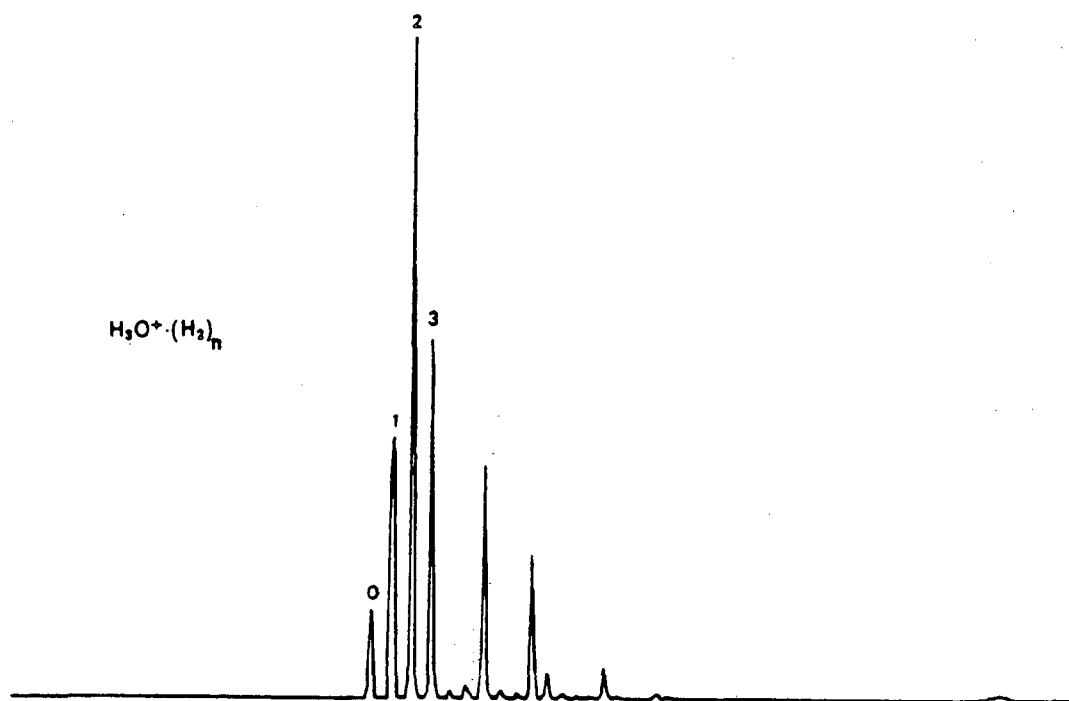
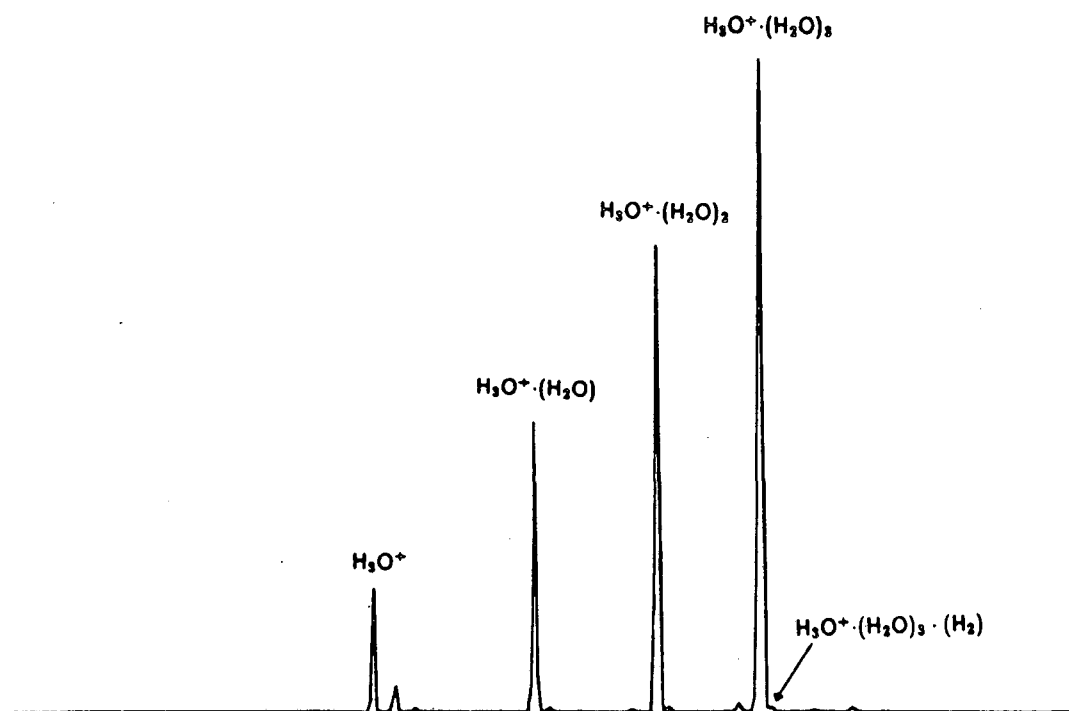


FIG. 2



MAGNET CURRENT

FIG. 3

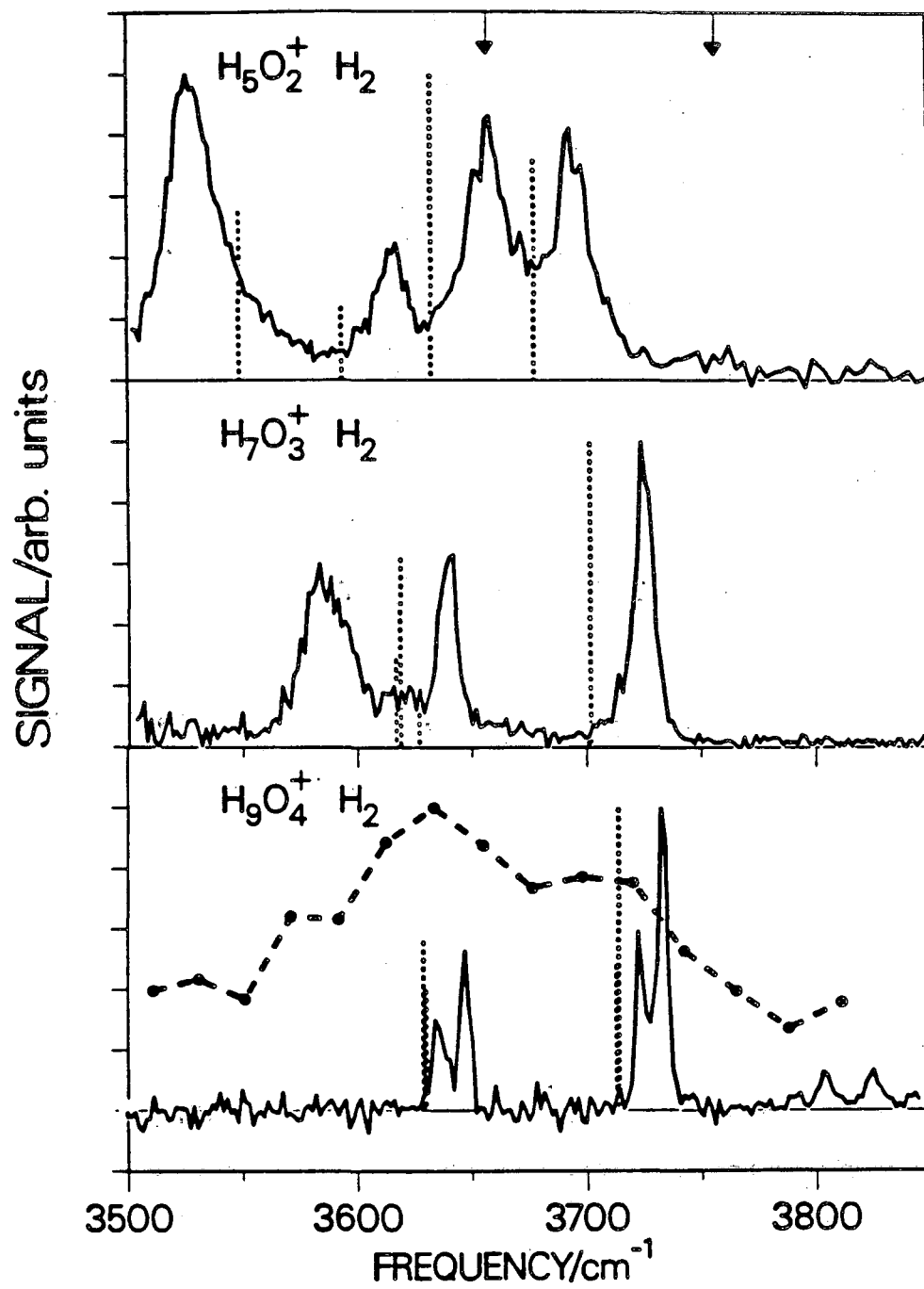


FIG. 4

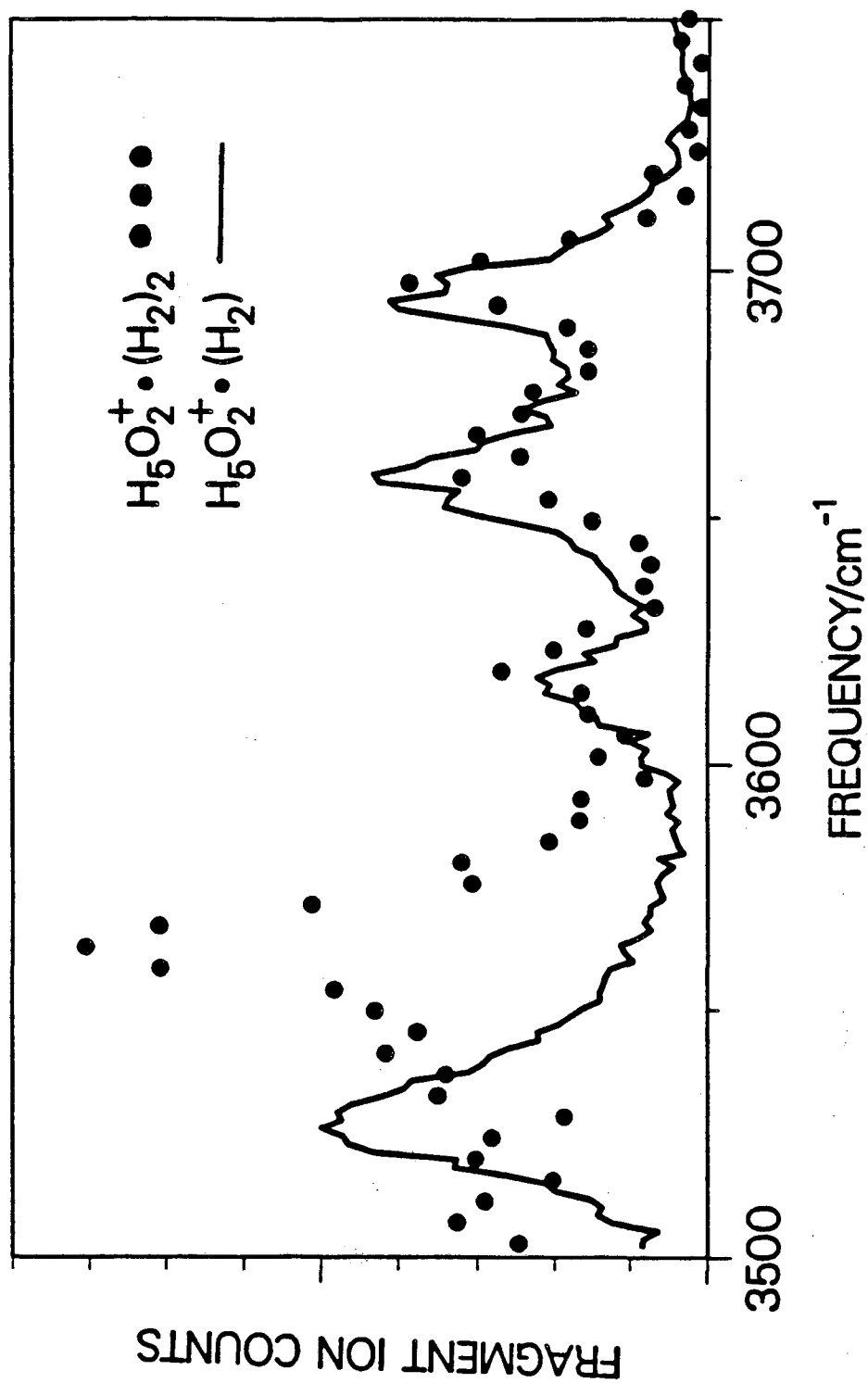


FIG. 5

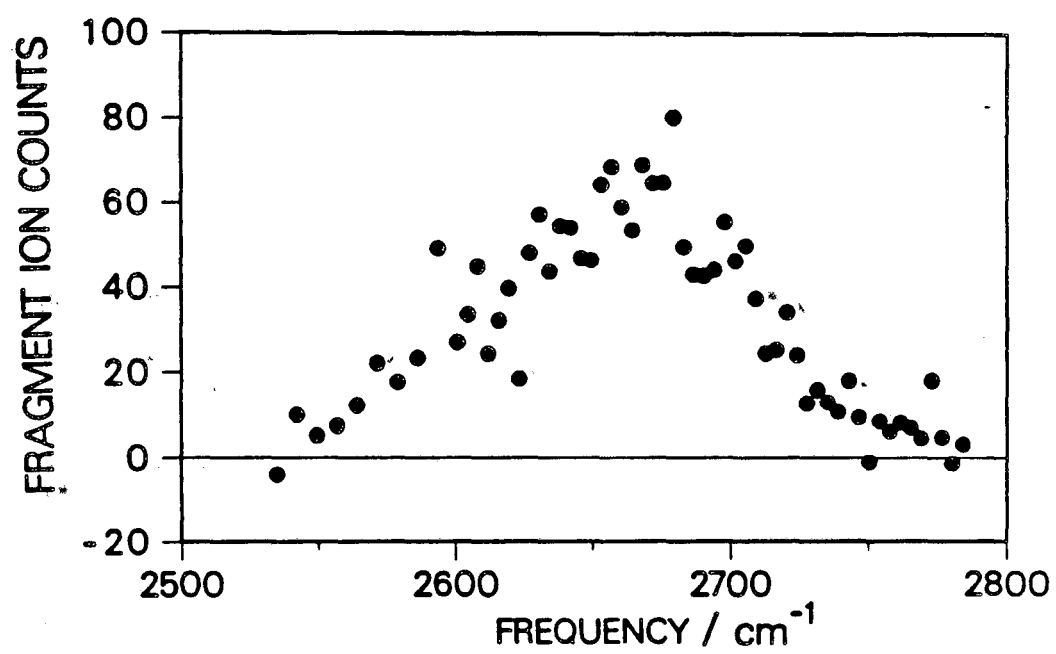


FIG. 6

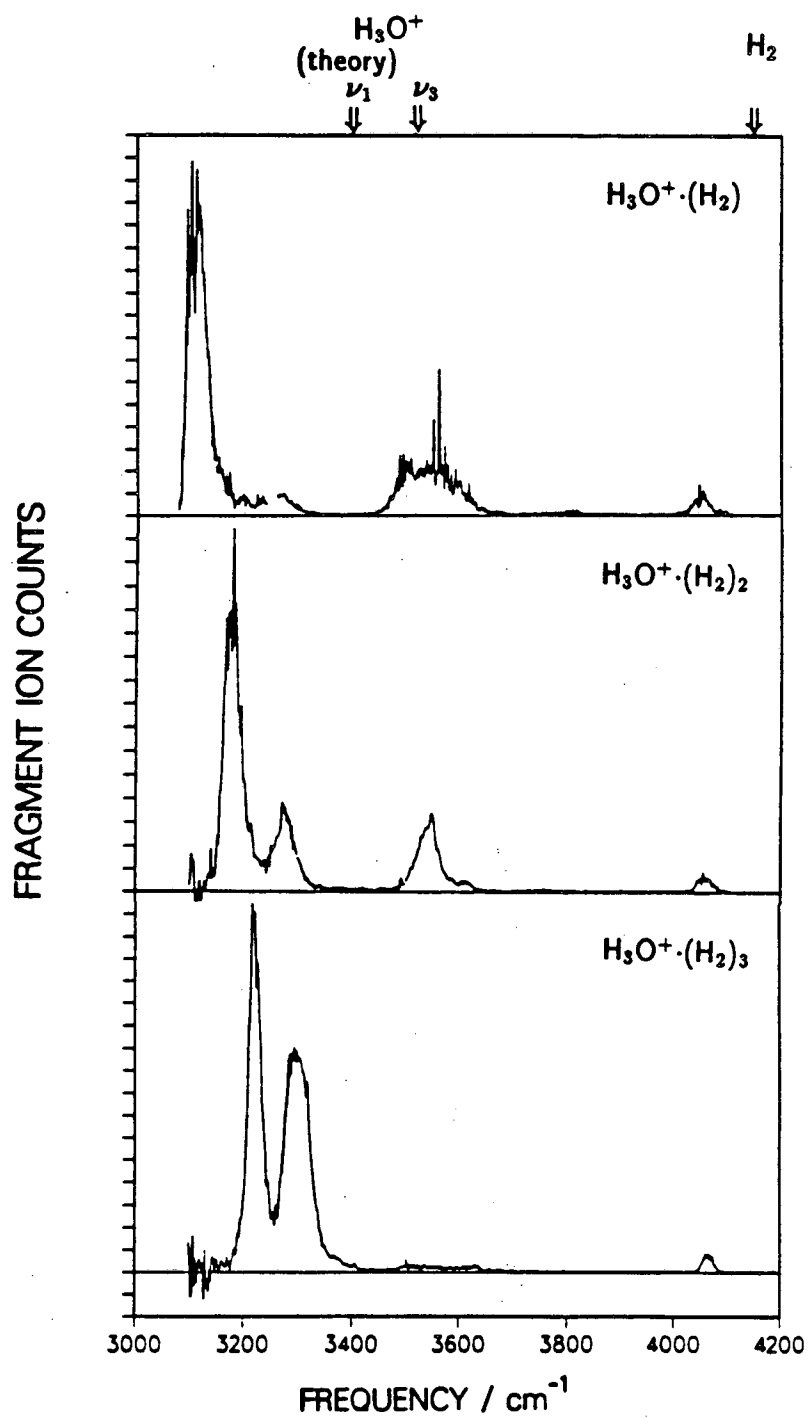


FIG. 7

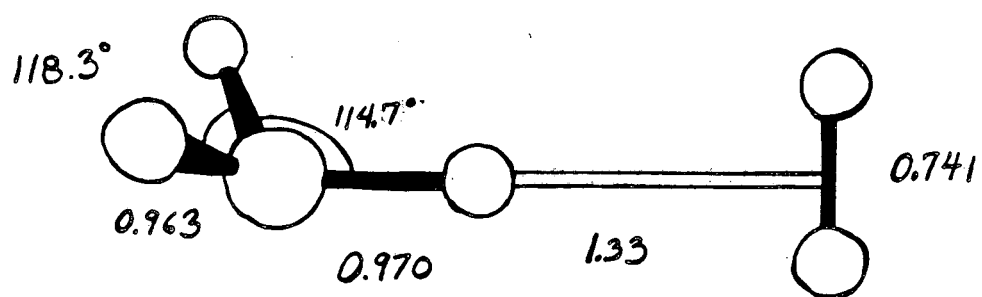


FIG. 8

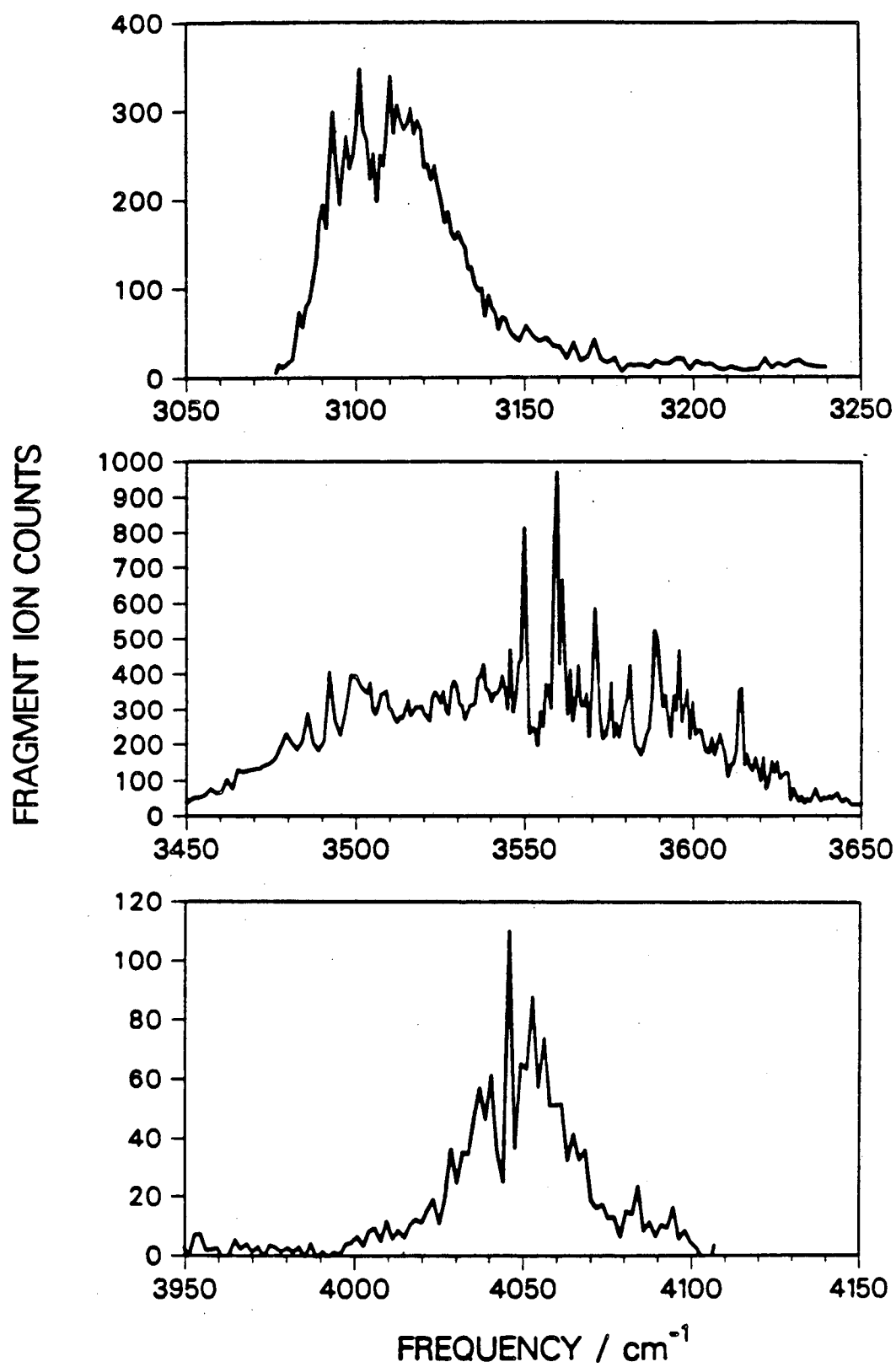


FIG. 9

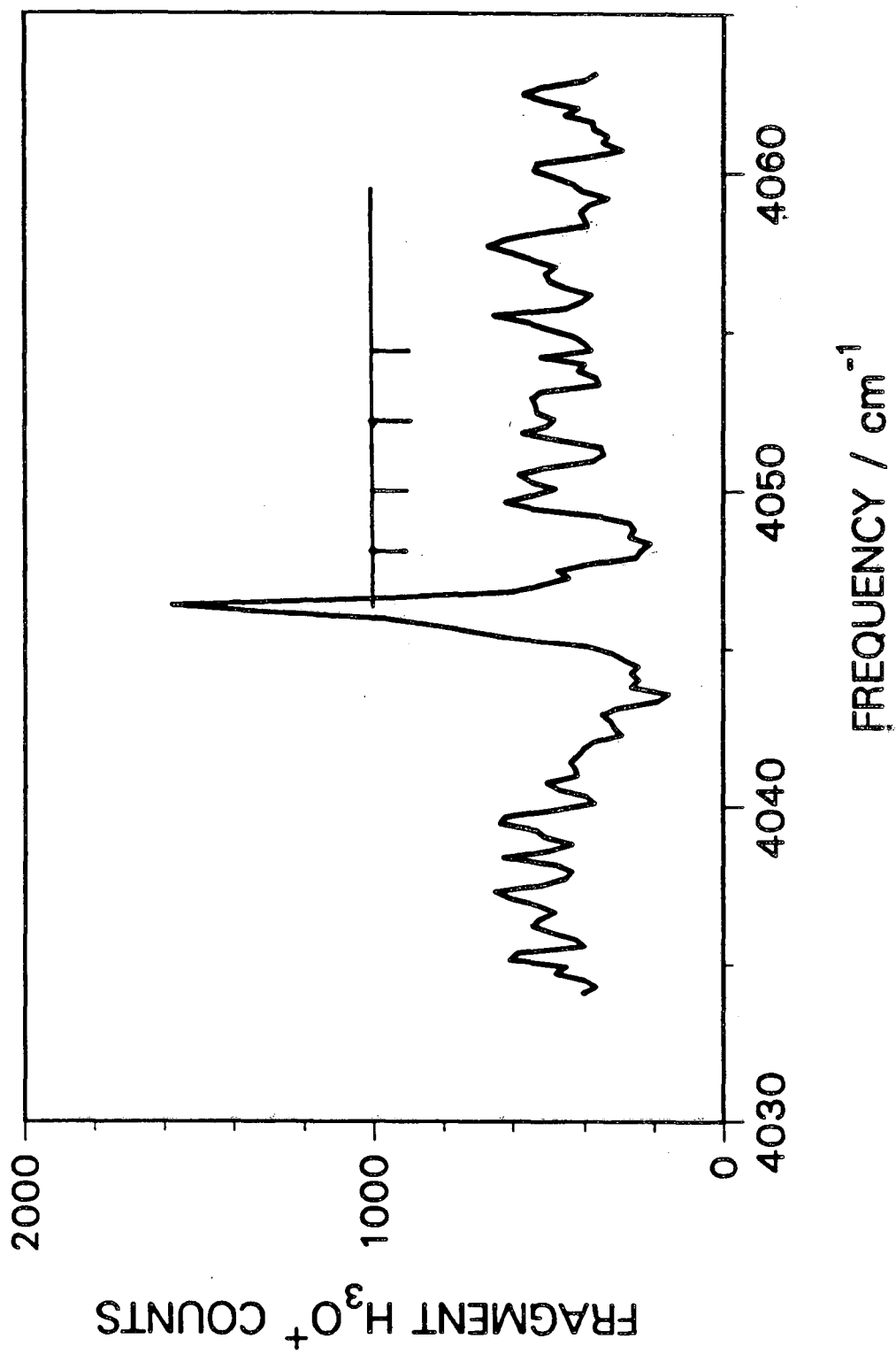


FIG. 10

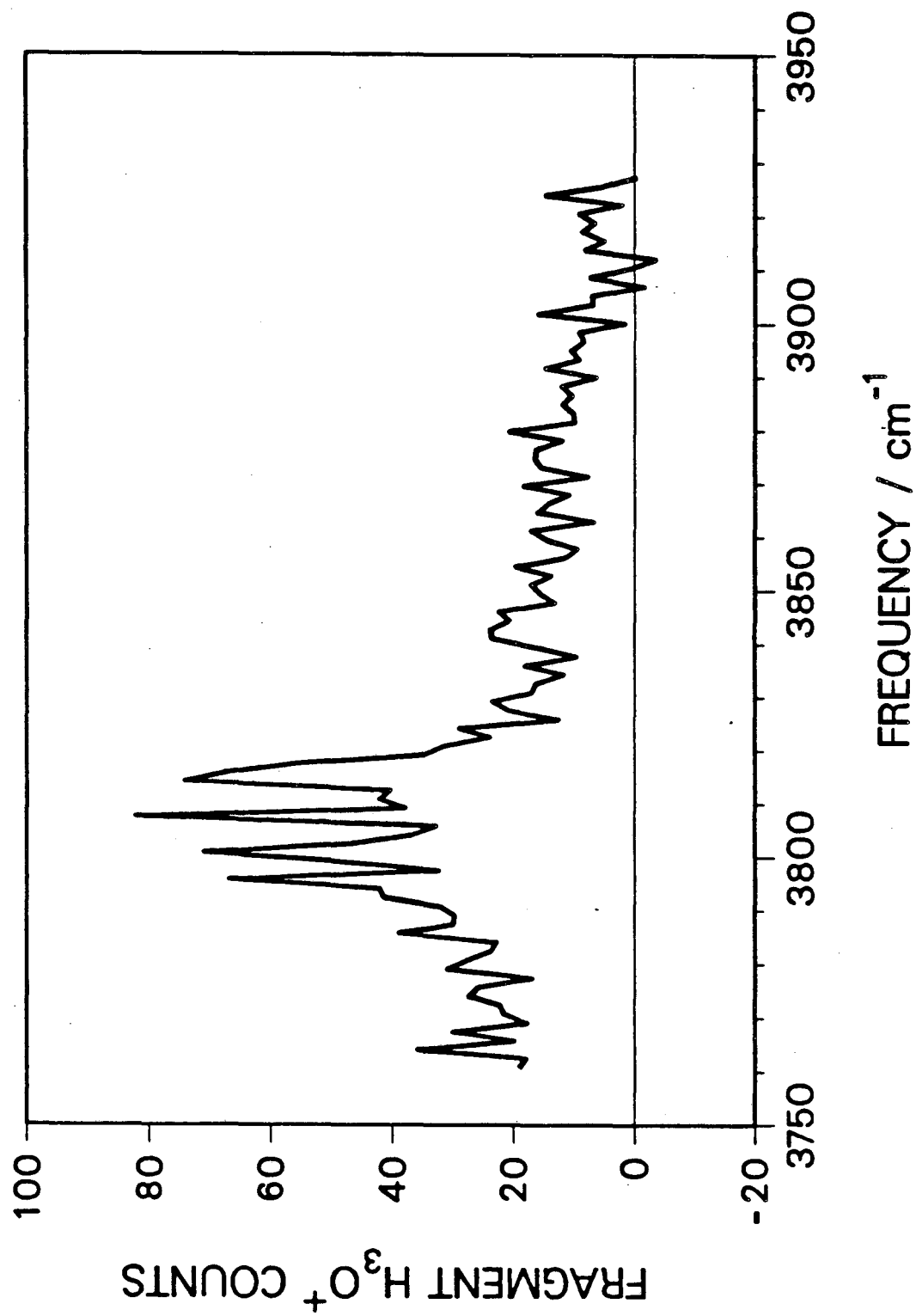
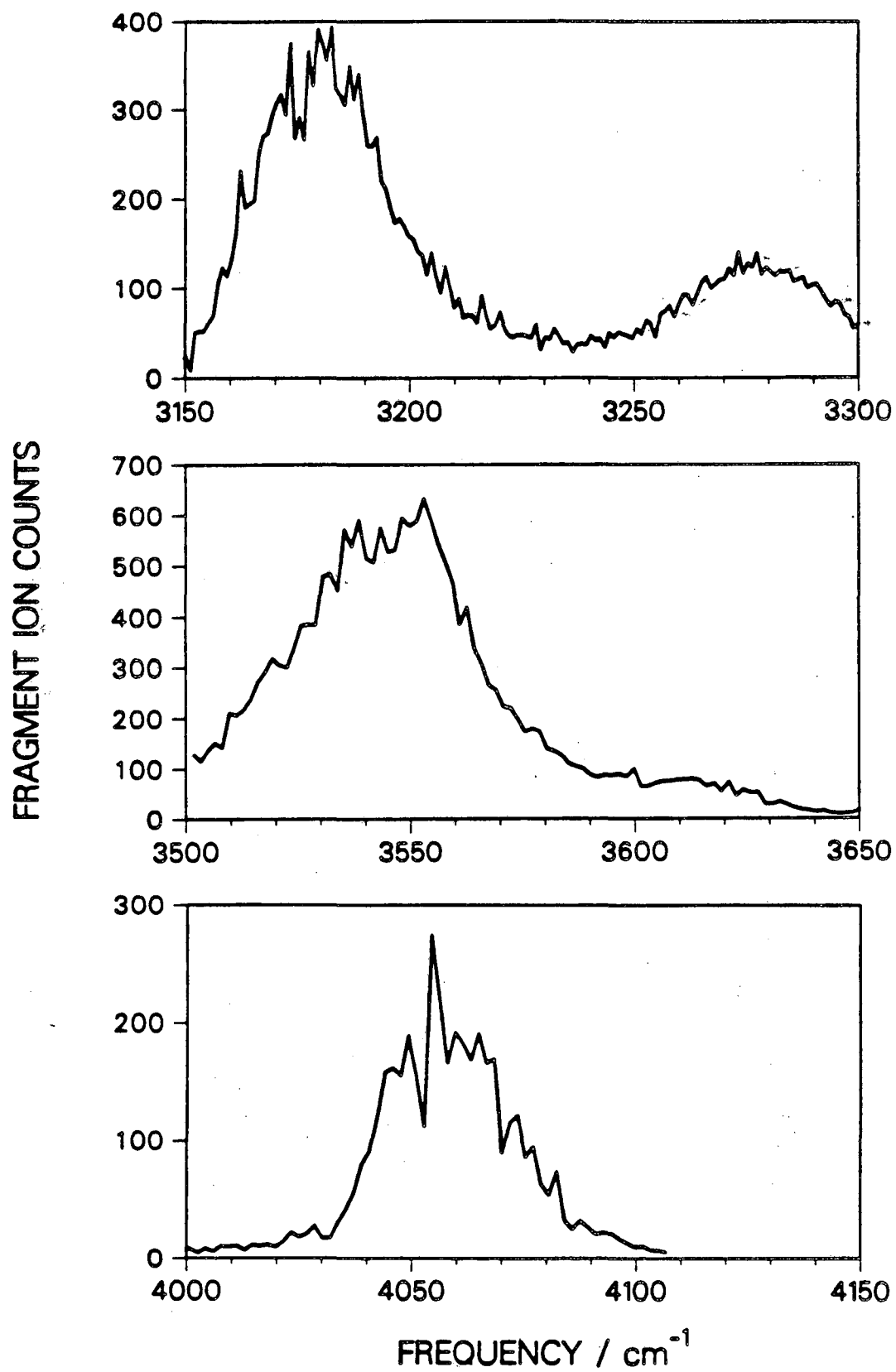


FIG. 11

**FIG. 12**

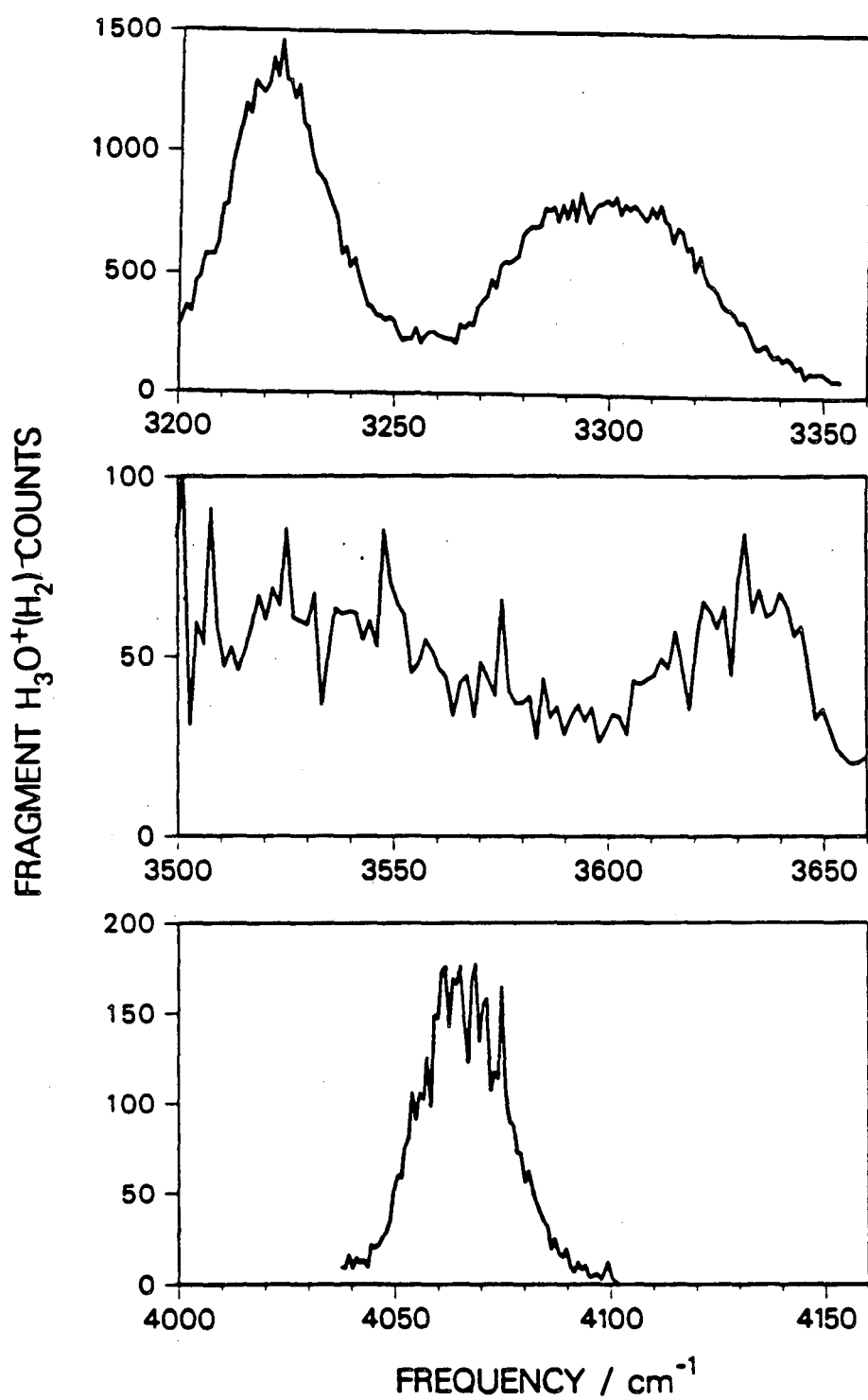


FIG. 13

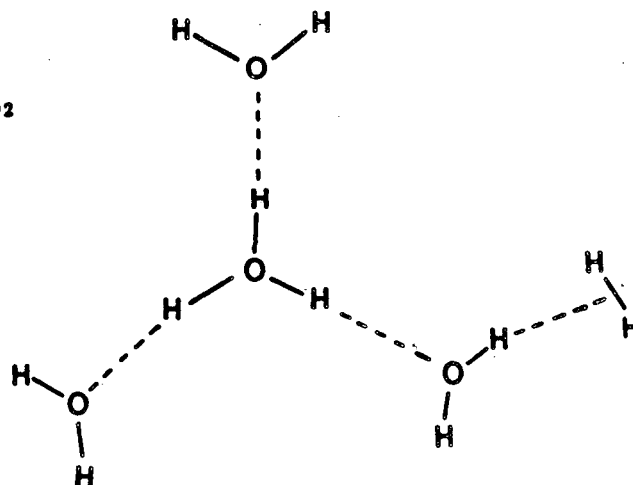
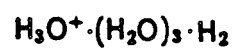
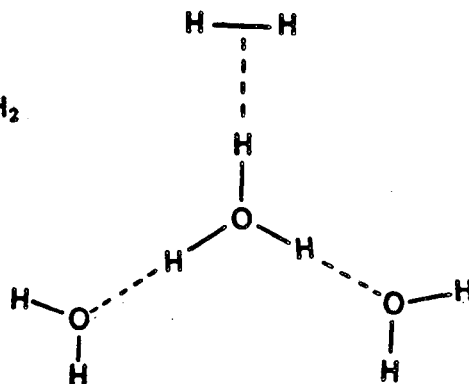
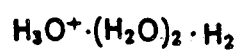
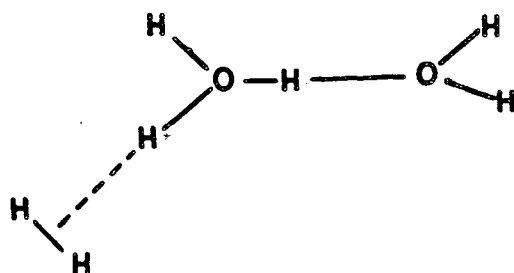
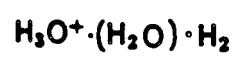


FIG. 14.

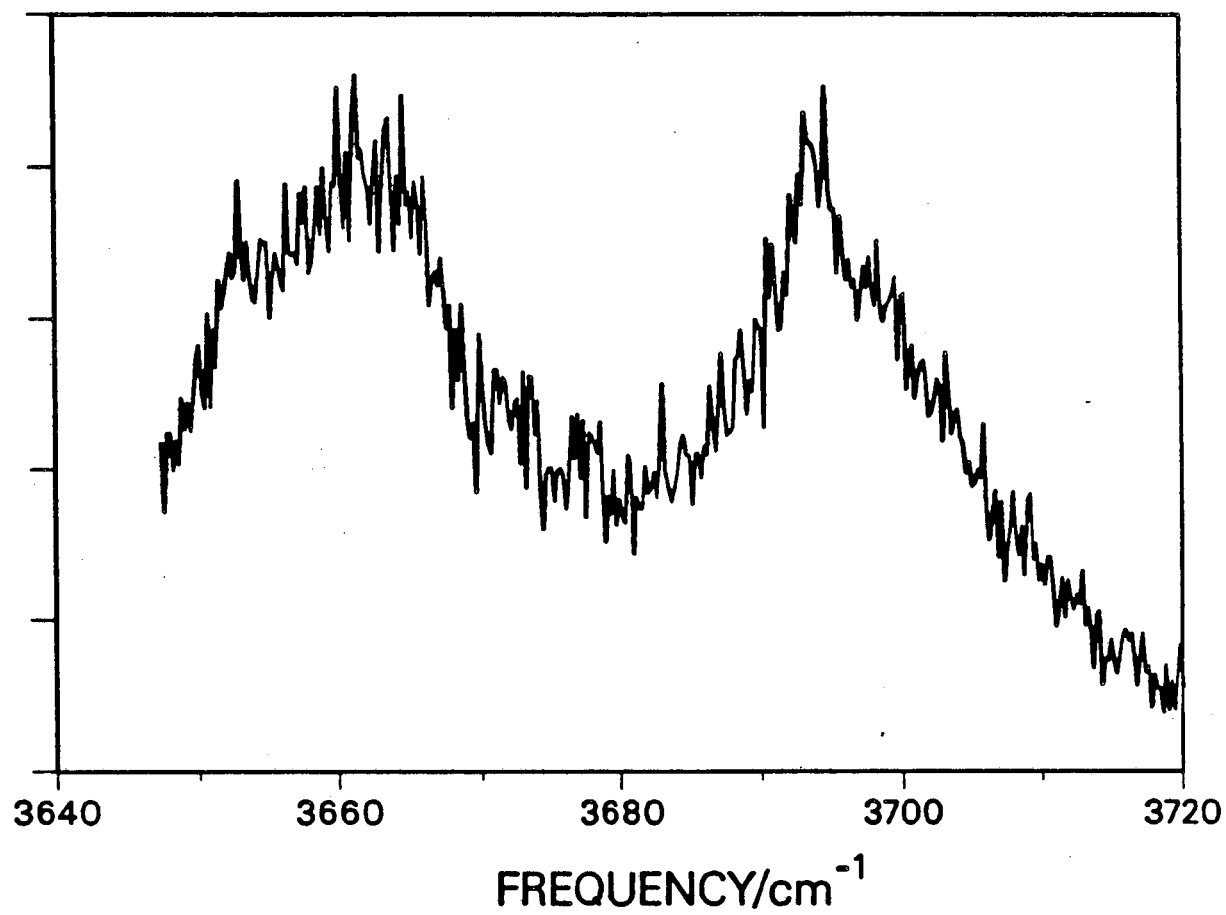


FIG. 15

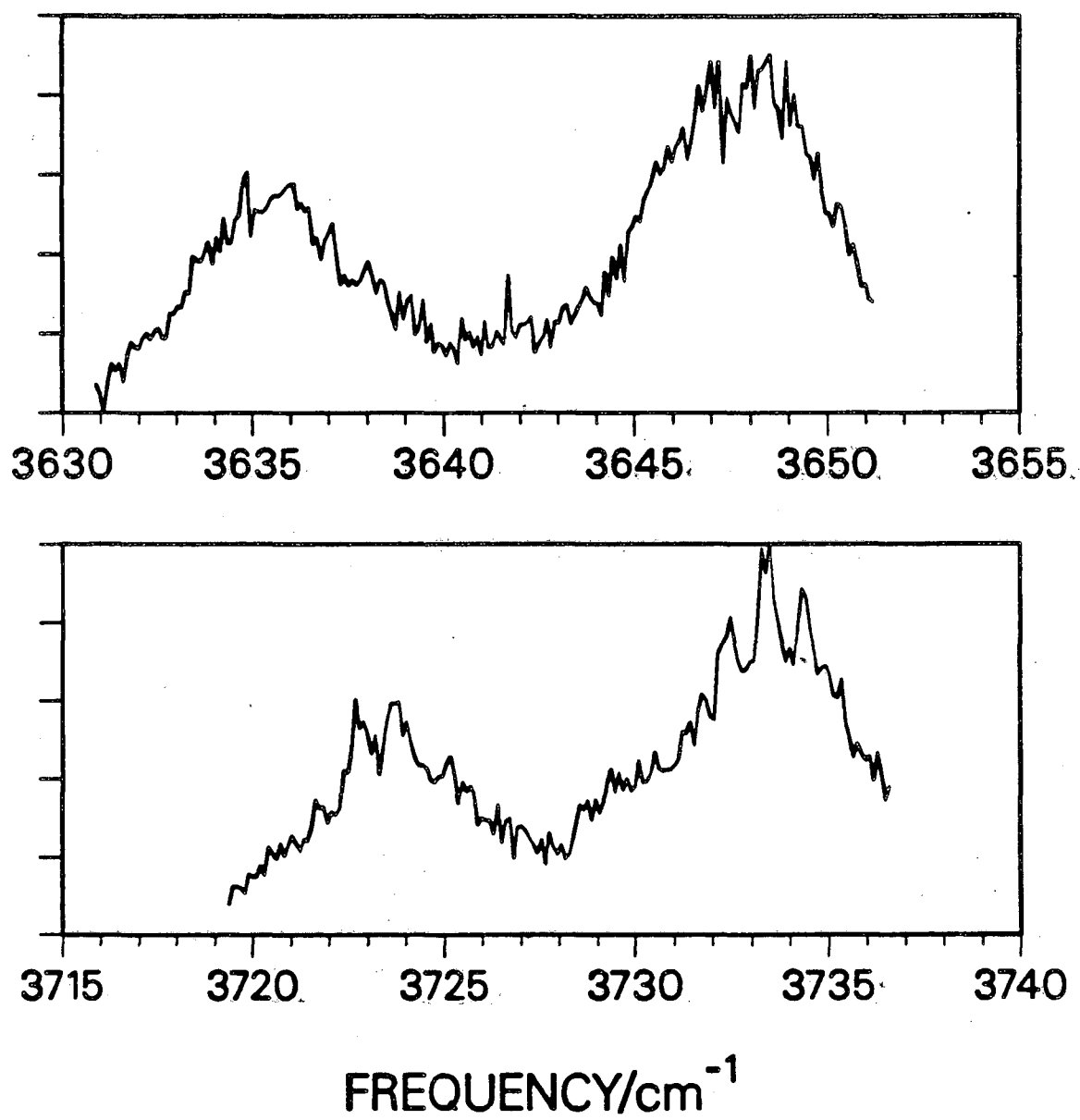


FIG. 16

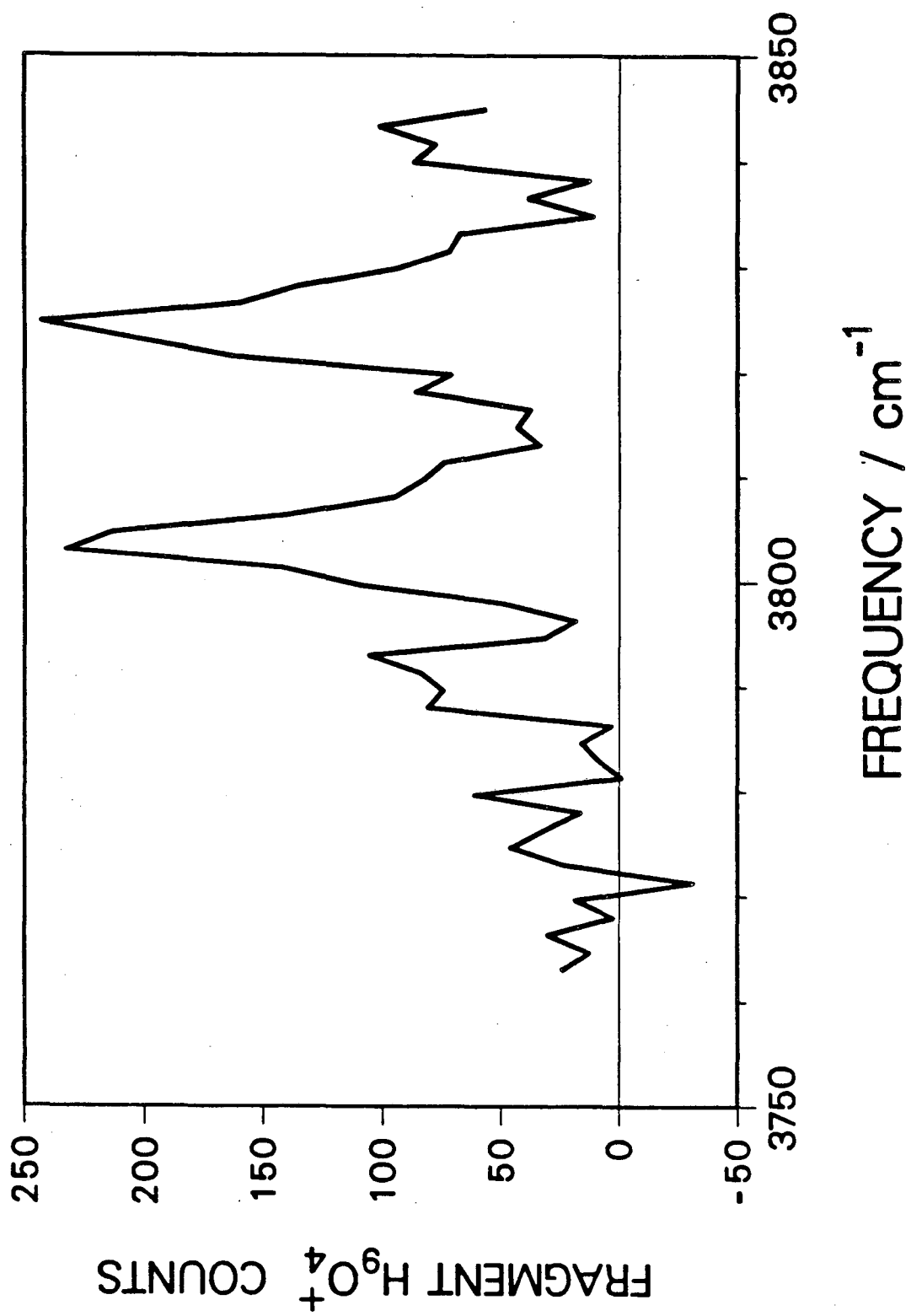


FIG. 17

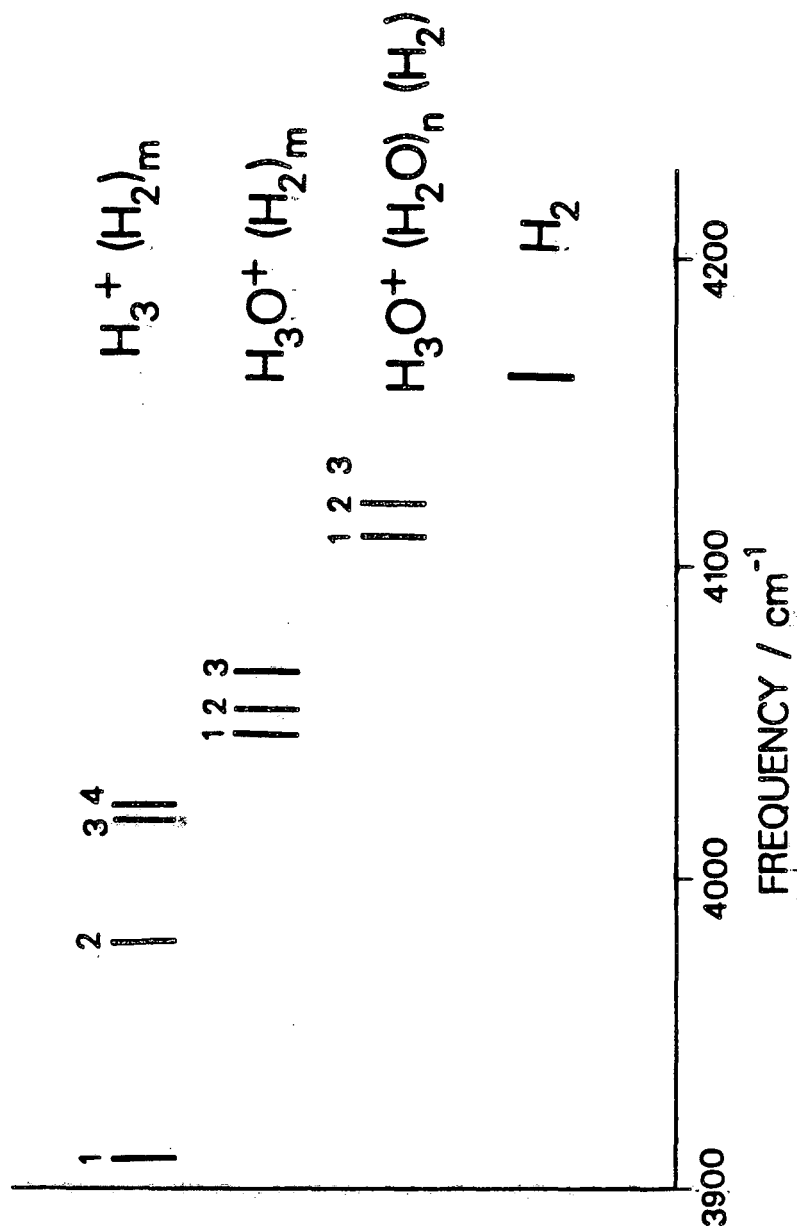


FIG. 18

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