Title
PHOTOIONIZATION OF (H2)2 AND THE CLUSTERS OF O2 MOLECULES

Author
Anderson, S.L.

Publication Date
1980-06-01

LBL-11033
Preprint C.2

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

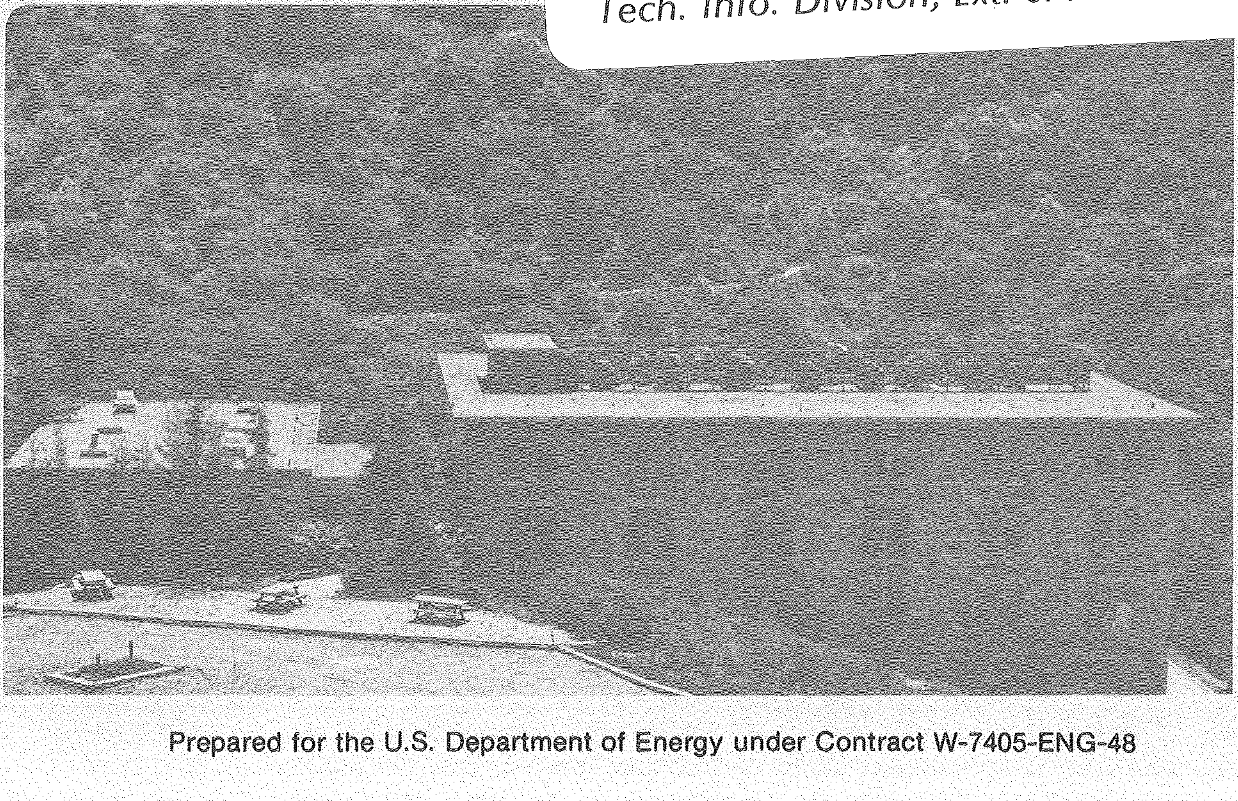
Submitted to the Journal of Chemical Physics

PHOTOIONIZATION OF $(H_2)_2$ AND THE CLUSTERS OF O_2 MOLECULES

S. L. Anderson, T. Hirooka, P. W. Tiedemann,
B. H. Mahan, and Y. T. Lee

June 1980

LBL-11033 C.2



Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

DISCLAIMER

LBL-11033

PHOTOIONIZATION OF $(H_2)_2$ AND THE CLUSTERS OF O_2 MOLECULES

S. L. Anderson[a], T. Hirooka[b], P. W. Tiedemann[c],
B. H. Mahan and Y. T. Lee

Materials and Molecular Research Division
Lawrence Berkeley Laboratory

and

Department of Chemistry
University of California
Berkeley, California 94720

JUNE 1980

ABSTRACT

Photoionization of $(H_2)_2$ and clusters of O_2 are investigated in a molecular beam experiment. No evidence was found for the existence of stable $(H_2)_2^+$. Photoionization spectra of $(H_2)_2 \overset{h\nu}{\rightarrow} H_3^+ + H + e$ is quite similar to that of $H_2 \overset{h\nu}{\rightarrow} H_2^+ + e$, yet the appreciable differences in some features of spectra suggests that there is a competition between the autoionization and vibrational predissociation of vibronically excited $(H_2)_2$. From the photoionization thresholds of $(O_2)_n$, n = 1-5, it is concluded that $(O_2)_2^+$ is bound by 0.26 ± 0.02 eV, but the additional binding energies for higher clusters of O_2^+ are much smaller; just about what one would expect from a charge induced dipole interaction.

---

[a] National Science Foundation Fellow.

[b] Permanent address: Department of Chemistry, Faculty of Science,
The University of Tokyo, Hono, Tokyo 113, Japan.

[c] Permanent address: Instituto de Química, Universidade de São Paulo,
C.P. 20780, São Paulo, Brazil.

INTRODUCTION

The molecular beam photoionization technique has been shown to provide many advantages over the photoionization study using a bulk gas. The rotational and vibrational cooling of molecules during the isentropic expansion removes the complication of hot bands in the determination of the ionization threshold and the possibility of handling corrosive, exotic, sensitive molecules and radicals under strictly collision free conditions in the ionization region are two of the most obvious strengths of this method. But, the most exciting aspect of the molecular beam photoionization method is the possibility of using weakly bound van der Waals molecules, which are formed in the supersonic expansion, as the starting materials for the investigation of the energetics and dynamics of molecule ions. In previous experiments we have been able to determine the binding energies of such weakly bound dimers as $(NO)_2^+$,[1] $(H_2O)_2^+$,[2] $(NH_3)_2^+$,[3] $(C_2H_4)_2^+$,[4] $(HCl)_2^+$, $(HBr)_2^+$, and $(HF)_2^+$,[5] and further derived the proton affinities of H_2O,[2] NH_3,[3] HCl, and HBr[5] directly from the threshold energies of the production of protonated molecules from the molecular dimers.

In this paper, we report photionization studies of $(H_2)_2$ and molecular clusters of O_2 molecules. The possible existence of $(H_2)_2^+$, the binding energies of $(O_2)_n^+$ (n = 2 to 5) and the competition between the vibrational predissociation and the autoionization processes in the photoexcited hydrogen molecule dimers are among the subjects of investigation.

EXPERIMENTAL

The apparatus and experimental method have been described in detail in previous reports,[1-6] and will only be touched on here. Van der Waals dimers and clusters are formed by adiabatic cooling in a high pressure supersonic expansion through a nozzle. The nozzle temperature, pressure, diameter, and seeding ratio are varied to maximize the formation of the cluster of interest with minimal contamination from larger clusters.

H_2 clusters are easily formed. Figure 1 shows the distribution of various size cluster ions obtained by photoionizing a beam of H_2 expanded from 52 atm, through a 10 μ diameter liquid N_2 cooled nozzle at 744 Å. Only ions of odd numbered hydrogen atoms are observed, and intensity decreases with increasing mass except for H_5^+ and H_9^+, in accord with electron bombardment studies.[7] The H_2^+ signal in this experiment is approximately 1500 cps. For the purposes of obtaining a photoionization spectrum of $(H_2)_2$ uncontaminated by the fragmentation of higher polymers during the photoionization, the nozzle pressure was lowered to 18.4 atm. At this pressure the H_3^+ signal is 10 cps, and the H_5^+ yield is less than 10% of the H_3^+.

$(O_2)^+$ spectra and all other higher $(O_2)_n^+$ were obtained with 1 atm of O_2 backing a 120 μ diameter nozzle maintained at 160 K. The signal intensity decreased slowly with the increase of cluster size. No fragmentation yielding odd O atom numbered ion were observed. At 990 Å the $(O_2)_2^+$ count rate was about 4 cps.

The beam source is doubly differentially pumped, and after being chopped in the second differential chamber by a 150 Hz tuning fork, the molecular beam passes into the ionization chamber where it is crossed by the dispersed VUV photon beam. The ions formed are extracted at an angle perpendicular to both the molecular beam and photon beam, mass analyzed and counted with an ion counter. It should be noted that the pressures in the ionization chamber (2×10^{-7} torr) and differentially pumped detector chamber ($\sim 10^{-8}$ torr) are kept low enough to ensure collision free conditions.

The light source is a 9" capillary discharge lamp, producing either the hydrogen pseudo continuum (~900-1600 Å) or the helium Hopfield continuum (~650-950 Å) depending on the molecule and the range of wavelength under investigation. The light is dispersed by a 1 m near normal incidence monochromator (McPherson Model 225) set to ~3.3 Å resolution. The light intensity is monitored with either a sodium salycilate coated PMT or a nickel photoelectron detector. The relative photoionization efficiency (PIE) curve is then obtained by dividing the modulated ion signals at various wavelengths by the light intensity.

RESULTS

The photoionization spectrum of $(H_2)_2 \overset{h\nu}{\rightarrow} H_3^+ + H + e$ is shown in Fig. 2. Also shown for comparison is a spectrum of H_2^+ obtained at low pressure (no clusters) and identical resolution. Although the general trend of the increase of the ionization efficiency as a function of photon energy is quite similar for both $(H_2)_2 \rightarrow H_3^+ + H + e$ and $H_2 \rightarrow H_2^+ + e$, there are significant differences between them. Many prominent peaks which appeared in the spectrum of $H_2 \rightarrow H_2^+ + e$ are simiply missing, rather than smoothed over, in the $(H_2)_2 \rightarrow H_3^+ + H + e$ spectrum.

The spectra of larger $(H_2)_nH^+$ cluster ions are similar to that of H_3^+, except smoother. Thresholds for the production of $(H_2)_nH^+$ from $(H_2)_{n+1}$ are very hard to estimate due to low signal levels and the very slow increase of the ionization efficiency as the photon energy is increased. We conservatively estimate an H_3^+ threshold of 14.09 eV, which is ca. 0.39 eV higher than the thermodynamic threshold.[14]

We looked for stable H_4^+ at wavelengths from 750 to 950 Å. No m/e = 4 signal was observed with sensitivity of 0.1 c/sec.

The photoionization spectra of $(O_2)_n$ for n = 1 to 4 near the threshold of ionization are shown in Fig. 3.

DISCUSSION

A) Photoionization of $(H_2)_2$

Just like many other molecules, the photoionization of $(H_2)_2$ producing H_3^+ could go either through a direct ionization or through an autoionization process as shown below.

$$(H_2)_2 \xrightarrow{h\nu} (H_2)_2^+ + e \longrightarrow H_3^+ + H + e \qquad (1)$$

$$(H_2)_2 \xrightarrow{h\nu} (H_2)_2^* \longrightarrow (H_2)_2^+ + e \longrightarrow H_3^+ + H + e \qquad (2)$$

But, since the $(H_2)_2$ is only weakly bound by van der Waals forces, it is likely that the actual absorption of a photon by a $(H_2)_2$ mainly involves one of the H_2 molecules in $(H_2)_2$, and that the process would be better represented by

$$H_2{\cdot}H_2 \xrightarrow{h\nu} H_2{\cdot}H_2^+ + e \longrightarrow H_3^+ + H + e \qquad (3)$$

and

$$\begin{tikzcd}
H_2{\cdot}H_2 \arrow[r, "h\nu"] & H_2{\cdot}H_2^* \arrow[r] \arrow[dr] & H_2{\cdot}H_2^+ + e \arrow[r] & H_3^+ + H + e & (4) \\
 & & H_3^+ + H + e & & (5)
\end{tikzcd}$$

The photoionization spectrum of H_3^+ shown in Fig. 2 indeed shows the close similarity to that of H_2^+. Above the appearance potential H_2^+ (~804 Å), the peak positions in both spectra coincide.

Dehmer and Chupka[8] have measured[9] very high resolution photoionization spectrum of H_2. The spectrum consists of many sharp autoionization lines, superimposed on a weak direct ionization background. The line widths are typically 0.05 Å and typical line spacings are ca. 0.2 Å. With photon resolution of 3.3 Å, our H_2^+ spectrum can be understood as the resolution averaging of the line spectrum. The apparent peak structure and background in our spectrum is merely due to variation in the density and height of the fine line structure. Although the importance of direct ionization increases with increasing photon energy, in our spectrum direct ionization is not the main ionization pathway. Thus we expect that process (3) is not a major contributor to our H_3^+ spectrum, except at the highest photon energies.

Below the H_2^+ threshold, H_3^+ production is still possible through process (4), consisting of photon absorption by one of the H_2 molecules in the dimer, to a Rydberg state which then chemiionizes. This effect is actually observed in photoabsorption of H_2 at high pressure, although it is collision induced in this case.[9] Above the H_2^+ threshold, processes (4) and (5) both are possible although the distinction between the two is somewhat nebulous. The important thing is that the photon absorption step in both is to a discrete Rydberg state of H_2, giving rise to the similarity between the H_3^+ and H_2^+ spectra. Any shifts in the Rydberg levels due to the presence of the second H_2 in the dimer are too small to be resolved in this experiment.

There are some interesting differences between the spectra of H_2^+ and H_3^+. While the peak positions in both spectra coincide below 804 Å, the relative intensities of some of the peaks in H_3^+ are greatly reduced. For instance, in H_2^+ the peaks at 792 Å and 784 Å and to a lesser extent the peak at 780 Å are much more intense than the neighboring peaks. In H_3^+, the relative intensities of these peaks are greatly reduced. Interpretation of this difference requires some further examination of photoionization of H_2.

In H_2 photoionization, the dominant process is vibrational autoionization. The H_2 makes a transition to a state in a Rydberg series converging on some vibrational state of the H_2^+ core. If there is sufficient energy in the molecule, one or more quanta of vibrational energy can be transferred to the Rydberg electron, resulting in ionization. For instance, an H_2 state characterized by principle quantum number, $n = 20$, and $v = 3$, can ionize by transferring 1, 2, or 3 vibrational quanta, leaving an ion in the $v = 2$, 1, or 0 state. The rate of vibrational autoionization decreases rapidly with increasing number of vibrational quanta transferred. Typical lifetimes for $\Delta v = 1$ autoionization are about $10^{-10} - 10^{-11}$ sec.[8] For $\Delta v = 2$ lifetimes are on the order of 10^{-8} and increase further for $\Delta v = 3$ and 4. In addition lifetimes increase with increasing n, and decrease with increasing v.[8] The result is, that where possible, nearly all autoionization occurs via a fast $\Delta v = 1$ process. There are states (e.g., $n = 5$, $v = 4$) which can only autoionize via $\Delta v > 1$. In spite of the low rates for these processes, these states tend to be very intense; and in regions of the spectrum where there are group of these states, they may be the most important photoionization pathway. At the bottom of Fig. 1, we marked H_2^* states which must autoionizae via $\Delta v \geq 2$ processes.

In H_2, there are other decay pathways for the Rydberg levels; fluorescence or predissociation, which may deplete the autoionization intensity. These effects are presumably similar in the dimer and will not be considered in comparing the H_2^+ and H_3^+ spectra.

In the dimer however, vibrational predissociation of the vibronically excited dimer into $H_2^* + H_2$ would be expected to deplete H_3^+ intensity, particularly as the vibrational quantum number v increases.

The rates for the two competing processes, k_a and k_d, depend on n, v and Δv

$$\begin{tikzcd}
H_2\cdot H_2 \arrow[r, "h\nu"] & H_2\cdot H_2^*(n,v) \arrow[r, "k_a"] \arrow[dr, "k_d"] & H_2\cdot H_2^+(v') + e \arrow[r] & H_3^+ + H + e & (6) \\
 & & H_2 + H_2^*(n,v'') & & (7)
\end{tikzcd}$$

Now since the basic structure of the H_2^+ and H_3^+ spectra is the same, it seems that for autoionization with $\Delta v = 1$ is faster than preddissociation, that is $k_d < k_a$ $(\Delta v = 1)$. If we look at the H_3^+ peaks that are reduced, we see that in these regions, much of the autoionization must occur via $\Delta v \geq 2$ processes, which are much slower. We suggest that these peaks are missing in H_3^+ because the vibronically excited dimer is predissociating instead of autoionizing. We can estimate the predissociation lifetimes if the rate of vibrational autoionization of H_2 in $(H_2)_2$ is similar to that of isolated H_2 molecules.

Dehmer and Chupka[8] give the auotionization rates for some $v = 2$, states of H_2* which autoionize with $\Delta v = 2$ transitions as $\approx 10^8\ \mathrm{sec}^{-1}$ (R(1) 7pσ v = 2 (792 Å), Q(1) 7pπ v = 2 (791 Å)). Since $k_a(\Delta v = 1) = 10^{-10}\ \mathrm{sec}^{-1}$, we can bracket $k_d(v = 2)$ as $10^8\ \mathrm{sec}^{-1} < k_d(v = 2) < 10^{10}\ \mathrm{sec}^{-1}$. Assuming that the R(1) 5pσ v = 4 (784 Å) and R(1) 5pπ v = 4 (780 Å) completely predissociate we obtained $k_d(v = 4) \gtrsim 10^9\ \mathrm{sec}^{-1}$. As expected k_d increases with v. One might expect that the H_3^+ photoionization spectra would start to lose intensity relative to H_2^+ at higher energy, where k_d begins to compete with k_a even for $\Delta v = 1$. This can be seen in Fig. 2 and becomes much more pronounced at short wavelengths. It should be noted that these k_d are for vibronically excited molecules.

The predissociation rate for $H_2(v = 1) \cdot H_2$ has been calculated by Ewing[10] to be $\sim 4 \times 10^3\ \mathrm{sec}^{-1}$. In our case two effects are present that would be expected to raise this. In our dimer, the Rydberg electron has principle quantum number of at least 5, lending considerable ionic character to the excited hydrogen. This reduces the vibrational spacing in the excited molecule and presumably also increases the depth and steepness of the intermolecular potential. Both these effects are expected to lead to higher predissociation rates.[10,11] An increase in k_d with vibrational level is also expected.

The failure of observing $(H_2)_2^+$ in our photoionization experiment is not surprising. The reaction $H_2^+ + H_2 \rightarrow H_3^+ + H$ is exoergic by 1.7 eV.[12] Thus unless there is a barrier between $H_2^+ + H_2$ and $H_3^+ + H$ or a well for H_4^+ exceeding 1.7 eV in depth, the H_4^+ ion should be unstable. Experimental studies of $H_2^+ + H_2 \rightarrow H_3^+ + H$ have not shown evidence of a barrier.[13] Many theoretical calculations in the past[14,15] and a more recent calculation by Morokuma et al.[16] have shown that the ground state surface has no barrier going down from H_2^+ to H_2 to $H_3^+ + H$, but has a shallow well at a geometry corresponding to a complex between $H_3^+ + H$.

(B) Stability of $(O_2)_2^+$

The photoionization spectra of $(O_2)_n^+$ in Fig. 3 shows that the intense structures in the $(O_2)_2^+$ are rapidly washed out as cluster size increases. From examination of threshold behavior we obtained IP's of 11.80 ± 0.02 eV, 11.72 ± 0.02 eV, 11.66 ± 0.03 eV and 11.60 ± 0.04 eV for $(O_2)_2$, $(O_2)_3$, $(O_2)_4$ and $(O_2)_5$ (not shown).

The difference between IP's of O_2 (12.06 eV) and $(O_2)_2$ is due to the difference between the binding energies of $(O_2)_2^+$ and $(O_2)_2$. Since the binding energy of $(O_2)_2$ is only about 0.01 eV, the difference of 0.26 ± 0.02 eV should correspond to a lower bound of the binding energy of $(O_2)_2^+$. The difference between the ionization potentials of $(O_2)_{n-1}$ and $(O_2)_n$ should also give a lower bound of the dissociation energy of $(O_2)_n^+ \rightarrow (O_2)_{n-1}^+ + O_2$. For n = 3, 4 and 5 the values obtained from experimental threshold are 0.08, 0.08 and 0.06 eV. These values are relatively small, just about the same magnitude of binding energy one would expect from the charge induced dipole interaction. Similar behavior is also observed in the photoionization of clusters of rare gas atoms. For example, the difference in ionization potential between Kr^+ (13.99 eV) and Kr_2^+ is 1.14 eV, while the difference between the ionization potentials of Kr_2^+ (12.86 ± 0.02 eV[18]) and Kr_3^+ (12.79 ± 0.05 eV), which was measured in this experiment, is only 0.07 eV. The ionization potential of Kr_4 (12.76 ± 0.04 eV) is also found to be close to that of Kr_3.

(C) A Note About the Determination of Binding Energy via Photoionization

It should be noted that although there is some contamination of the photoionization spectra of particular clusters by fragmentation of larger clusters during the photoionization, this only broadens the spectra features and cannot affect the thresholds. This results from the fact that the threshold energy for $M_{n+1} \xrightarrow{h\nu} M_n^+ + M + e$ is always greater than the IP of M_n by at least the binding energy between the neutral cluster M_n and M.

There is another important caveat; that the photoionization threshold for any given process is always an upper limit to the thermodynamic threshold. Thus one must be careful in interpreting photoionization data. It is clear that in the case of direct ionization of many molecules and clusters, there will be a large geometry change on ionization and the Franck-Condon factors near the true ionization threshold will quite often be so small as to render observation of the true threshold impossible. Fortunately, in the majority of cases, this is not a serious problem because of many Rydberg levels spaced closely throughout the region of the threshold. In this case, the small direct ionization Franck-Condon factors are irrelevent, as photoionization is dominated by strong bound-bound transitions, followed by autoionization or the associative ionization of loosely bound molecules. As long as there are no large gaps in the Rydberg levels, then the photoionization threshold will fall very close to the true threshold. In a very small number of cases, mainly very simple systems with very few degrees of freedom such as He_2, Ne_2 and $(H_2)_2$ these gaps do occur. But, even if there is a gap between Rydberg levels, because of the existence of dense vibrational energy levels of excited dimers, it is possible to determine the true ionization threshold with an error bar much less than the gap of Rydberg levels. Nevertheless, the probability of reaching one of these vibrational levels is smaller and it requires an extremely sensitive apparatus to detect this. At the H_2^+ threshold the density of Rydberg levels is about 2 per angstrom, allowing determination of the true H_2^+ threshold to within an angstrom through autoionization. By the time we lower the energy to the expected appearance potential of H_3^+ from $(H_2)_2$, the density is much lower, with gaps of 10 to 20 Å. This low density, coupled with low light intensity from our two lamps in this spectral region makes it very difficult to pick any of the anticipated small autoionization "peaks" out of our baseline. These peaks can be seen in Fig. 2, slowly shrinking into the noise. The apparent peak at 895 Å lies at the position of a Rydberg band and is possibly real, in which case our threshold is 13.81 eV, or only 0.1 eV above the thermodynamic threshold of 13.72 eV.[12]

In many cases, it is possible to obtain fragmentation thresholds (e.g., $(HCl)_2^+ \rightarrow H_2Cl^+ + H$)[5] very accurately, because of the aforementioned cluster vibrational modes. As one slowly increases the photon energy, one sees first the threshold for $(HCl)_2^+$ production. This may at the thermodynamic threshold or may correspond to a weakly vibrationally excited dimer. As the photon energy is increased, more and more energy is left in the dimer ions, until at the threshold for fragment ion production (H_2Cl^+) the dimer ions begin to decompose. Thus by using the frequency of the ionizing photons to cntrol the upper limit of the dimer vibrational excitation, we have been able to obtain the appearance potential of the fragment ions very accurately.

In order for this to work it is necessary that the parent cluster ion be observed. In most cases studied (HCl, HBr, HI,[5] NH_3,[3] H_2O[2]) this is true. In a few cases (H_2, HF[2]), the dimer ion is not produced in photoionization and the fragment ion thresholds are only upper bounds.

ACKNOWLEDGMENT

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract No. W-7405-Eng-48.

REFERENCES

1. C. Y. Ng, B. H. Mahan and Y. T. Lee, J. Chem. Phys. 65, 1956 (1976); C. Y. Ng, P. W. Tiedemann, B. H. Mahan and Y. T. Lee, J. Chem. Phys. 66, 3985 (1977).
2. C. Y. Ng, D. J. Trevor, P. W. Tiedemann, S. T. Ceyer, P. L. Kronebusch, B. H. Mahan and Y. T. Lee, J. Chem. Phys. 67, 4235 (1977).
3. S. T. Ceyer, P. W. Tiedemann, B. H. Mahan and Y. T. Lee, J. Chem. Phys. 70, 14 (1979).
4. S. T. Ceyer, P. W. Tiedemann, B. H. Mahan and Y. T. Lee, J. Chem. Phys. 70, 2138 (1979).
5. P. W. Tiedemann, S. L. Anderson, S. T. Ceyer, T. Hirooka, C. Y. Ng, B. H. Mahan and Y. T. Lee, J. Chem. Phys. 71, 605 (1979).
6. C. Y. Ng, Ph.D. Thesis, University of California, Berkeley, 1976.
7. A. Van Lunig and J. Reuss, Int. J. Mass. Spec. Ion Phys. 27, 127 (1978).
8. P. M. Dehmer, W. A. Chupka, J. Chem. Phys. 65, 2243 (1976).
9. W. A. Chupka, M. E. Russel, and K. Refaey, J. Chem. Phys. 48, 1518 (1968).
10. G. Ewing, Chem. Phys. 29, 253 (1978).
11. J. A. Beswick and J. Jortner, Chem. Phys. Lett. 49, 13 (1977); J. A. Beswick and J. Jortner, J. Chem. Phys. 68, 2277 (1978); J. A. Beswick and J. Jortner, J. Chem. Phys. 69, 512 (1978).

12. Using $D_o(H_2^+)$ = 2.65 eV and the proton affinity of H_2, given as 4.35 3V in: L. Salmon and R. D. Poshusta, J. Chem. Phys. 59, 3497 (1973); G. D. Carney, and R. N. Porter, J. Chem. Phys. 60, 4251 (1974).

13. C. H. Douglass, D. J. McClure, W. R. Gentry, J. Chem. Phys. 67, 4931 (1977).

14. R. D. Poshusta and F. A. Matsen, J. Chem. Phys. 47, 4795 (1967); R. D. Poshusta et al., J. Chem. Phys. 58, 118 (1973).

15. M. E. Schwartz and L. J. Srhaad, J. Chem. Phys. 48, 4709 (1968).

16. Morokuma et al., Annual Review, Institute for Molecular Science, Okazaki, Japan, 1979.

17. P. M. Dehmer and W. A. Chupka, J. Chem. Phys. 62, 4525 (1975); K. P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure: IV Constants of Diatomic Molecules, New York, 1979, p.492.

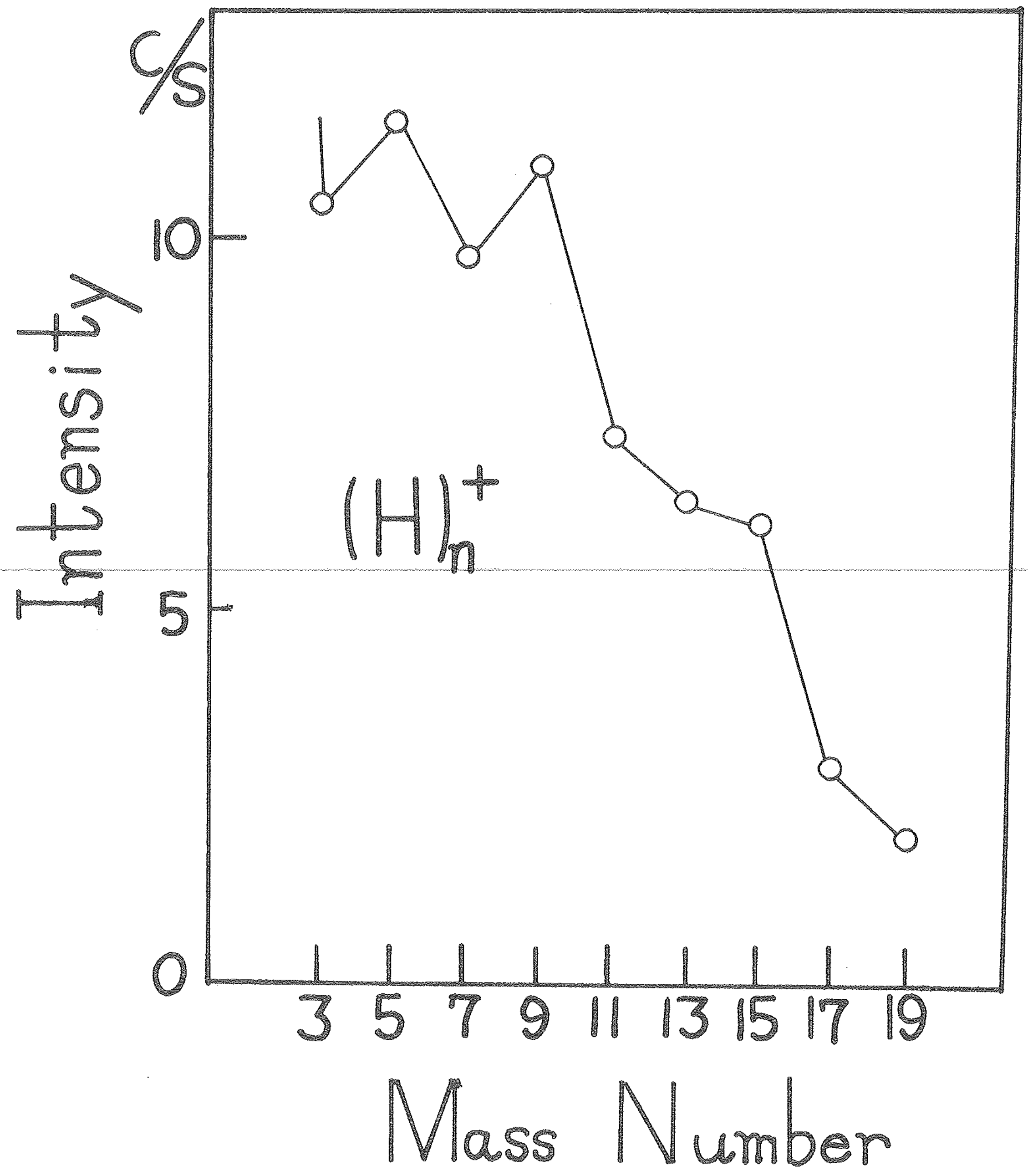
18. C. Y. Ng, D. J. Trevor, B. H. Mahan and Y. T. Lee, J. Chem. Phys. 66, 446 (1977).

FIGURE CAPTIONS

Fig. 1. Mass dependence of H_n^+ photoion yield.

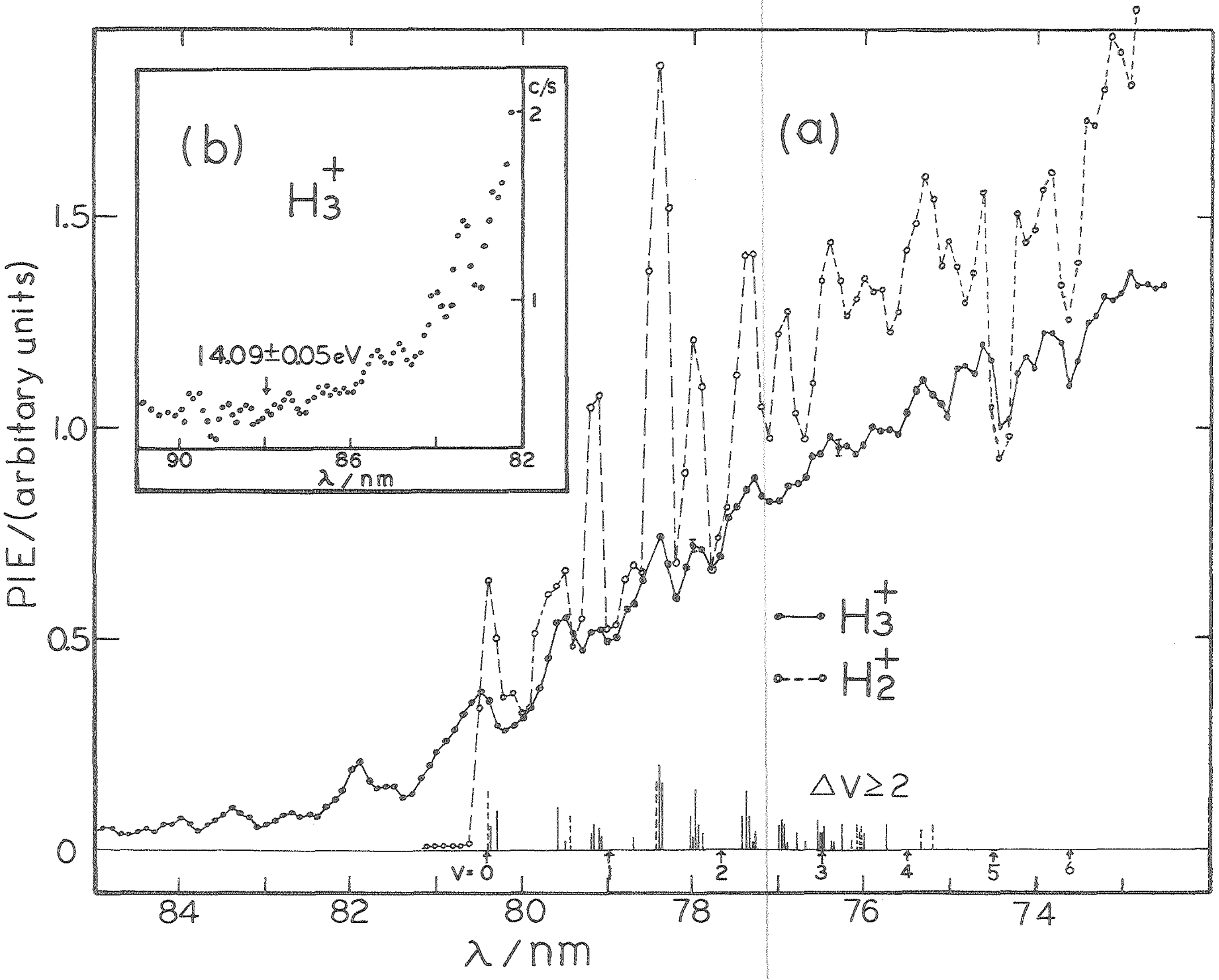
Fig. 2. Photoionization spectra of $H_3^+ + H_2^+$.

Fig. 3. Photoionization spectra for O_2^+, $(O_2)_2^+$, $(O_2)_3^+$ and $(O_2)_4^+$.



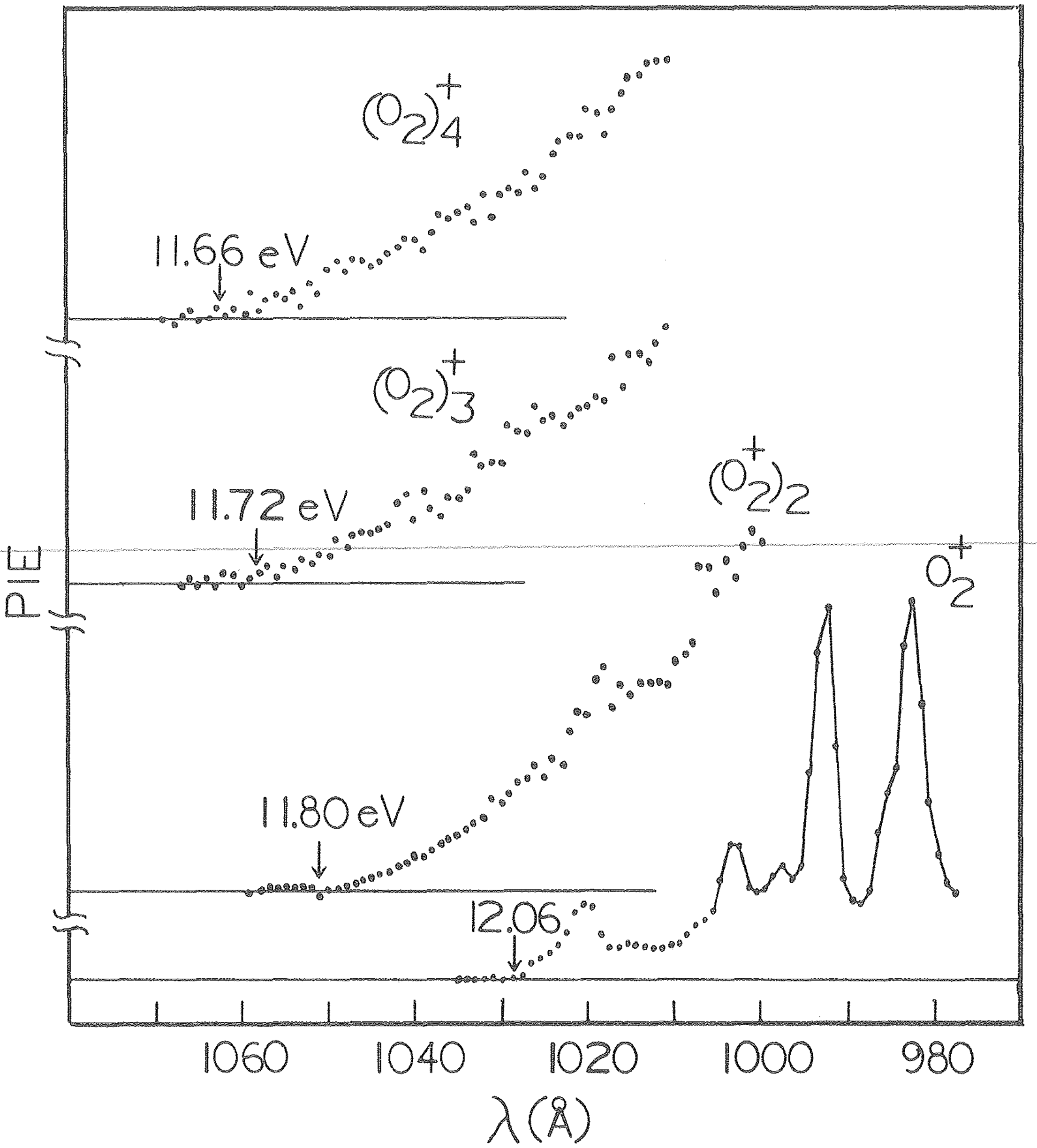
XBL 7812-13679

Fig. 1



XBL 791-7816

Fig. 2



XBL 806-9852

Fig. 3