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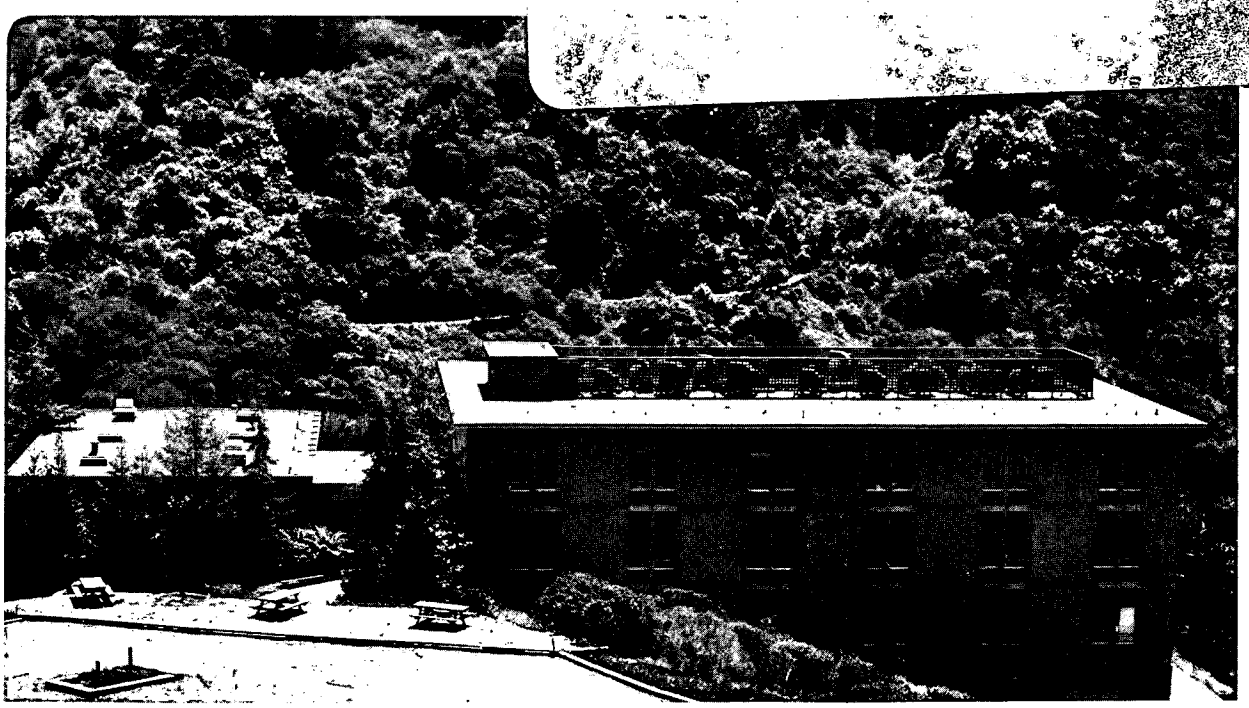

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INFRARED VIBRATIONAL PREDISSOCIATION SPECTRA OF LARGE WATER CLUSTERS

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ABSTRACT

The infrared absorption spectrum in the O-H stretching region of $(H_2O)_{19}$ clusters formed in a supersonic molecular beam is reported. It was obtained with mass-spectrometric detection and is compared with a similarly obtained spectrum of $(H_2O)_6$ and a large-cluster spectrum obtained with bolometric detection.

The mass-resolved spectra show a broad absorption band between ~ 3200 and 3600 cm^{-1}, reminiscent of the H-bonding feature in a condensed phase spectrum. The spectrum obtained with the bolometer is peaked in the blue of this region, suggesting that the level of H-bonding is much lower. It must be dominated by small and/or warm clusters such as dimers. Mass resolution is clearly advantageous in selectively obtaining spectra of large clusters, free of interference from smaller ones.

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I. Introduction

The chemical bonds that cause molecules to exist are largely understood, but the weaker forces between molecules are still challenging us. Hydrogen bonds between water molecules are among the most important and intriguing forces one needs to explore if one wishes to understand the behavior of water better.

Studies on various water clusters with molecular beams, currently the only medium which contains clusters completely free of perturbations from neighboring atoms and molecules, have recently been reported.[1-4] To date the experimental results have included values for electric dipole moments of clusters,[4] the microwave spectrum and structure of the dimer,[4] and infrared absorption spectra of clusters in the region of the O-H stretching vibration.[1-3] These works have provided important data for developing and testing models of the intermolecular potential energy function. The Watts group has found the "RWK2-M" potential, [Named after Reimers, Watts and Klein (Ref. 5), and modified to treat the O-H bonds as Morse oscillators] which reproduces the monomer's properties and simultaneously fits many of the thermodynamic data of the bulk phases. By using this potential and the "quantum simulation" calculation technique, they have reproduced the O-H stretching frequencies of the water dimer almost exactly,[6] and partially accounted for the trimer spectrum. But the infrared absorption spectra of larger clusters, and of the liquid and solid phases, are not accurately predicted thus far.[7-9] This is a symptom of hydrogen bonding, a rather strong intermolecular force: the molecules affected by it experience significant changes in shape, charge distribution, and vibrational frequencies. Hydrogen-bonded molecules

do not retain the monomeric properties which were used in the creation of a pair potential function. Thus the pair potential cannot exactly describe clusters larger than the dimer.

It is clearly useful to obtain IR spectra as a function of cluster size. This can lead to a step-by-step improvement in the intermolecular potential function. Dimer O-H stretching spectra have been reported.[2,3] Also, spectra have been obtained with samples whose polymer size distribution includes a range of n-mers.[1-3] In this communication, we report on the differences between our spectra of medium-sized (6 - 19 subunits) water clusters and the "large-cluster" spectra of the Watts group. The two sets of experimental techniques have different biases, with respect to cluster size distribution, that lead to somewhat different spectral appearances and interpretations. The key experimental difference is the use of a mass spectrometer instead of a bolometer to detect the clusters.

To obtain the spectra, both groups observe IR-pumping-induced vibrational predissociation (VPD), in which an IR photon has enough energy to fragment a cluster: $(H_2O)_n + h\nu_{IR} \rightarrow (H_2O)_m + (H_2O)_{n-m}$. A detector which responds to the decrease in parent $(H_2O)_n$ concentration or to the increase in fragment concentration is used to monitor the intensity of VPD. Consideration of the cluster dissociation energies suggests that the most likely dissociation channel has m = 1: a monomer is "evaporated". Depending on a cluster's geometry, splitting it into two polymers could require the fracture of more than one ~2000 cm^{-1} hydrogen bond. At energies below ~ 4000 cm^{-1}, the infrared photons used to excite O-H stretches are not sufficiently energetic to do so. If one assumes that the VPD probability (thought to be unit in the O-H

stretching range) is only weakly dependent on total photon energy, then the IR frequency (ν_{IR}) dependence of the VPD signal is the same as the $(H_2O)_n$ cluster IR absorption cross section.

II. Experimental

VPD spectra in this experiment are obtained as follows: A rare-gas/water mixture is expanded into vacuum through a nozzle and skimmed, forming a supersonic molecular beam. The cluster size distribution in the beam depends on the nozzle temperature, stagnation pressure, seed gas, and fraction of water in the gas mixture. To form stable clusters, the cooling of gaseous molecules must be sufficient to dissipate the heat of condensation. Formation of large clusters is supposedly favored when the nozzle temperature is lowered toward the dew point of the gas mixture, when the fraction of water is increased, or when the nozzle stagnation pressure is increased with the water fraction constant.

Detection of polymers is accomplished in two ways: the Watts group has used a bolometer operating at 1.8 °K to sense the total power in the molecular beam, which condenses on its surface. For a given beam velocity, the signal depends on the mass flux and internal energies of all the beam constituents. Clusters of a particular size cannot be selectively studied without interference from larger and smaller clusters. On the other hand, we used an RF quadrupole mass spectrometer with electron-bombardment ionization. It gives a signal dependent on the number density of the selected <u>cluster ion</u> $(H_2O)_mH^+$, which, due to ion fragmentation, is always smaller than, or the same size as, the parent cluster, $(H_2O)_n$ (i.e. $n > m$). Fragmentation from a

larger cluster can only be ignored when the largest polymer present in the sample is the one selected for detection. By controlling the nozzle stagnation conditions to limit the formation of clusters larger than the size of interest and using the mass spectrometer to reject the contributions from smaller clusters, it is possible to study the absorption spectra of clusters with a narrow size distribution.

Tunable infrared light overlaps the molecular beam along its axis. Absorption of a photon fragments a cluster; the fragments recoil with a non-negligible amount of kinetic energy which causes most of them to exit the beam.[1] The measurement of VPD is accomplished by noting the depletion of clusters in the molecular beam. Fragments scattered out of the beam do not contribute to the bolometer signal, nor do they give an ion signal at the original cluster mass. Monomers absorb light and remain vibrationally excited until they fluoresce, strike a surface, or are destroyed by ionization. Vibrating monomers contribute to the bolometer signal; since they deliver heat to it, they give a signal opposite in sign to the VPD signal. They do not cause a change in the cluster signal obtained with mass-spectrometric detection.

Whereas the Watts group used a Kr-ion-pumped color center laser to generate tunable IR light, we have used a pulsed, Nd:YAG laser-pumped optical parametric oscillator (OPO).[10] It covers the requisite 3000-3800 cm^{-1} range, but has a ~ 25 cm^{-1} gap at ~ 3500 cm^{-1} where its $LiNbO_3$ crystal has an absorption. With the pump laser running at 10 pulses per second, the average IR power available at the beam machine was 5-15 mW; the peak power, assuming ~ 5 nsec output pulses, was thus on the order of 100 KW. This would make the peak intensity about 1 MW/cm^2, since the IR beam, loosely focused into the molecular beam, was

~ 3 mm in diameter. We used a Scientech calorimeter for IR power measurements and placed its detector near the point where the IR beam entered the vacuum chamber. This told us the power actually reaching the molecular beam, and prevented errors due to atmospheric absorption, which can be important in the 2.7μ region. The new data we report here were obtained with the OPO in its low (~ 5 cm^{-1}) resolution mode.

III. Results

In this experiment we were specifically interested in looking at large clusters. Thus the mass spectrometer was tuned to detect the largest possible cluster and managed to reach m/e = 325, corresponding to $(H_2O)_{18}H^+$. This ion comes from $(H_2O)_{19}$ and larger clusters.

The supersonic beam came from an argon/water mixture with total pressure 1 atm and H_2O at 80°C, for an H_2O fraction of 44%. We kept the 70μ-dia. nozzle at 100°C. An estimate of the cluster size distribution comes from comparing cluster ion count rates. The monomer $(H_2O)^+$ signal overwhelmed the detector; dimer and trimer count rates exceeded 1 MHz, the tetramer $(H_2O)_3H^+$ rate was 600 kHz, hexamer $(H_2O)_5H^+$ gave 300 kHz, and the large cluster ions (17-19) had rates ~ 30 kHz. We emphasize the point that most of the water molecules in the mixture remained as monomers and small clusters.

The $(H_2O)_{19}$ absorption spectrum, obtained while detecting $(H_2O)_{18}H^+$, is shown in Fig. 1. It actually corresponds to the fractional depletion in the cluster signal normalized to the laser power at each wavelength. At the peak absorptions in the spectrum, we observed ~ 10% attenuation of the cluster signal. Inability to measure the fluctuating OPO power accurately was the major cause of error.

Data points were excluded from the spectrum when the laser power dropped below a certain value; this accounts for the missing points at 3425 and 3500 cm^{-1}. A couple of representative error bars are shown; their heights are proportional to the cross section at each wavelength. A smooth curve has been drawn through the data points, whose spacing is 25 cm^{-1} except around the sharp ~ 3715-cm^{-1} feature, where the interval is ~ 12 1/2 cm^{-1}. The IR absorption spectra of liquid water at ~ 40°C [11] and polycrystalline ice Ih at 150°K [12] are plotted on the same axes. The liquid spectrum's amplitude has been adjusted to approximate that of the $(H_2O)_{19}$ spectrum around 3500 cm^{-1}.

For comparison, the spectrum of the $(H_2O)_6$ cluster, also obtained by this group,[1] is shown in Fig. 2. The supersonic molecular beam conditions used to obtain this spectrum were adjusted to minimize contamination from $(H_2O)_7$ and larger clusters. A spectrum obtained by the Watts group,[3] in which a high-pressure water-rich gas mixture was used, supposedly to favor production of large clusters, is shown in Fig. 3. Since a bolometer was used for the detector, this spectrum contains contributions from clusters of many different sizes. Table I summarizes the beam conditions used to obtain each spectrum.

There are obvious similarities between the three cluster spectra (Figs. 1 - 3). First, there is a broad hump, centered around 3400-3500 cm^{-1}. Second, there is a narrow peak at ~ 3715 cm^{-1}, whose amplitude is about half that of the hump. There are some clear differences too. The sharp dips in Fig. 3 could come from the detection of vibrationally excited monomers, whose O-H stretching bands are near 3657 and 3756 cm^{-1}. Also, the hump in Fig. 3 has much less intensity in the low-frequency (~ 3200 cm^{-1}) region than in the $(H_2O)_6$ and $(H_2O)_{19}$

spectra (Figs. 1,2).

IV. Discussion

To explain the features of the cluster spectra, we use the "local mode" description of the O-H stretching vibrations of the water molecule. This model treats the O-H stretches as two weakly coupled, largely independent anharmonic oscillators, and reproduces the 3657 and 3756 cm^{-1} vibrational frequencies of the monomer.[13] The sharp 3715-cm^{-1} band in the cluster spectra is due to the "free" O-H bonds, in which the H atoms are not very near O atoms of other molecules and are not hydrogen bonded. This feature is absent in the liquid and ice spectra; it is believed that there are few free O-H bonds in macroscopic samples of the condensed phases.

Considering the O-H stretch of the H atoms which are not "free" (i.e. are hydrogen bonded) we find a band with a large (300 cm^{-1} or more) red shift from the monomer frequency. The ~ 400 cm^{-1} breadth of this band is supposed to be caused by varying degrees of perturbation from H-bonding, resulting in a range of O-H stretching frequencies. This would occur since a variety of H-bonding situations can exist in a single conformation of an n-mer. Also, n-mers could be formed in different stable configurations.[1,8,14] Since a detailed vibrational analysis of these broad humps is not possible, we proceed to ask simple questions about the clusters: Are they like liquids? Are they like solids? Figure 1 tells us that (a) the liquid spectrum peaks at ~ 3400 cm^{-1}, with half-intensity points around 3150 and 3600 cm^{-1}, and (b) the solid spectrum peaks near 3200 cm^{-1}, with a FWHM ~ 150 cm^{-1}. It is also known[1,3] that the water dimer's H-bonded O-H stretch band occurs

at ~ 3500 cm^{-1}, and is less than 100 cm^{-1} wide. Figures 1 and 2, on the other hand, show the qualitatively different behavior of the $(H_2O)_6$ and $(H_2O)_{19}$ absorptions: roughly uniform intensity between 3200 and 3500 cm^{-1}, with the half-maximum points at 3150 and 3600 cm^{-1}. Although this is different from the condensed-phase spectra, the enhanced absorption around 3200 cm^{-1} compared with the liquid shows that an "ice-like" aspect seems to be present. Evidently the clusters of size $n \geq 6$ are large enough to force some water molecules into local environments which resemble that of ice. On the other hand, they retain some of the structural randomness which is characteristic of liquids and causes many different environments to exist, broadening the absorption spectra. Unfortunately, the temperatures and structures of the clusters are not known.

The Watts spectrum (Fig. 3) has a hump suggestive of the liquid absorption; it peaks at ~ 3500 cm^{-1} and falls by 1/2 at ~ 3300 and 3600 cm^{-1}. It does not, however, match the liquid spectrum because the falloff at low frequency is too rapid. This behavior is opposite to that of Figs. 1 and 2. The spectrum must be dominated by clusters which are too small to reproduce the liquid absorption spectrum.

With that in mind, we make the following comparison. Figures 1 and 2 show spectra of size-selected cluster samples in which a fraction of the clusters was cold enough to "freeze". For example, the medium-sized polymers could form cyclic, rigid structures in their lowest-energy states, but would have looser, more open structures at higher temperatures. Figure 3 is a spectrum of a warmer sample with a broad distribution of smaller clusters, which are not rigid. Several facts support this view. First, it is difficult to create a molecular

beam sample in which large clusters predominate in a relatively modest expansion. Our mass-spectrometric assessment of the cluster size distribution shows a rapid "tailing off" with increasing size around n - 2-6. Second, absorption features which have been assigned to the dimer[1,3] and trimer[3] coincide closely in frequency with the envelope of Fig. 3. Third, it has been amply demonstrated[11,15] that as the temperature of a liquid sample is raised, its O-H stretching spectrum shows a shift in the intensity distribution: the 3500 cm^{-1} peak gains at the expense of the 3200 cm^{-1} feature. Figure 3 shows this tendency; this type of spectrum would be expected from a warm sample.

V. Conclusion

Differences in IR absorption spectra, the signatures of structure and bonding in a system, are crucial in formulating and testing theories of intermolecular interactions. An important consideration in the analysis of cluster IR spectra is an estimate of the cluster temperatures and size distribution of the sample. We have shown how the use of mass spectrometry in the study of hydrogen-bonded clusters can give of IR absorption spectra of a relatively well defined size distribution of water clusters. The elimination of contributions from small clusters showed that H_2O clusters of size $n \geq 6$ can act as though they are partly "frozen". The realistic simulation of a spectrum should involve a sum over cluster states with different sizes, internal energies, and geometries, and is therefore extremely challenging. Size selection with mass spectrometry can reduce the difficulty to a certain extent.

Improvements in the technology of cluster research are clearly to

be desired. A gentler form of ionization than electron-impact would reduce fragmentation and would allow selective detection of clusters of a particular size. Furthermore, some reliable means of determining the temperature of the clusters would improve the chance of interpreting the spectra in an unambiguous way. It is clear that methods need to be developed which will give high-resolution spectra of clusters with better-defined sizes, structures, and temperatures. This will aid greatly in the ultimate determination of the interactions between water molecules.

VI. Acknowledgement

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Table I. Beam conditions in various experiments.

Figure	Temperature(°C)		seed	total pressure	%	nozzle
	H_2O reservoir	nozzle	gas	(Torr)	H_2O	diam.(μ)
1	80	100	Ar	810	44	70
2	84	125	--	417	100	180
3	160	163	He	8770	52	35

Figure Captions

Fig. 1 O-H stretching region IR VPD spectrum with mass spectrometer tuned to monitor $(H_2O)_{18}H^+$ ions. See Table I for beam conditions. On the same axes are plotted the absorption spectra of H_2O liquid at 40°C [11] and ice Ih at 150°K.[12]

Fig. 2 IR VPD spectrum of $(H_2O)_6$, obtained by Vernon et al.[1] Molecular beam conditions were adjusted for minimum contamination from larger clusters, and mass-spectrometric detection was used. See Table I for beam conditions.

Fig. 3 O-H stretching region IR VPD spectrum obtained by the Watts group with bolometric detection of all beam constituents. Reproduced from Ref. 3 with permission. See Table I for beam conditions.

IR absorption spectra of H_2O in solid, liquid, and cluster form

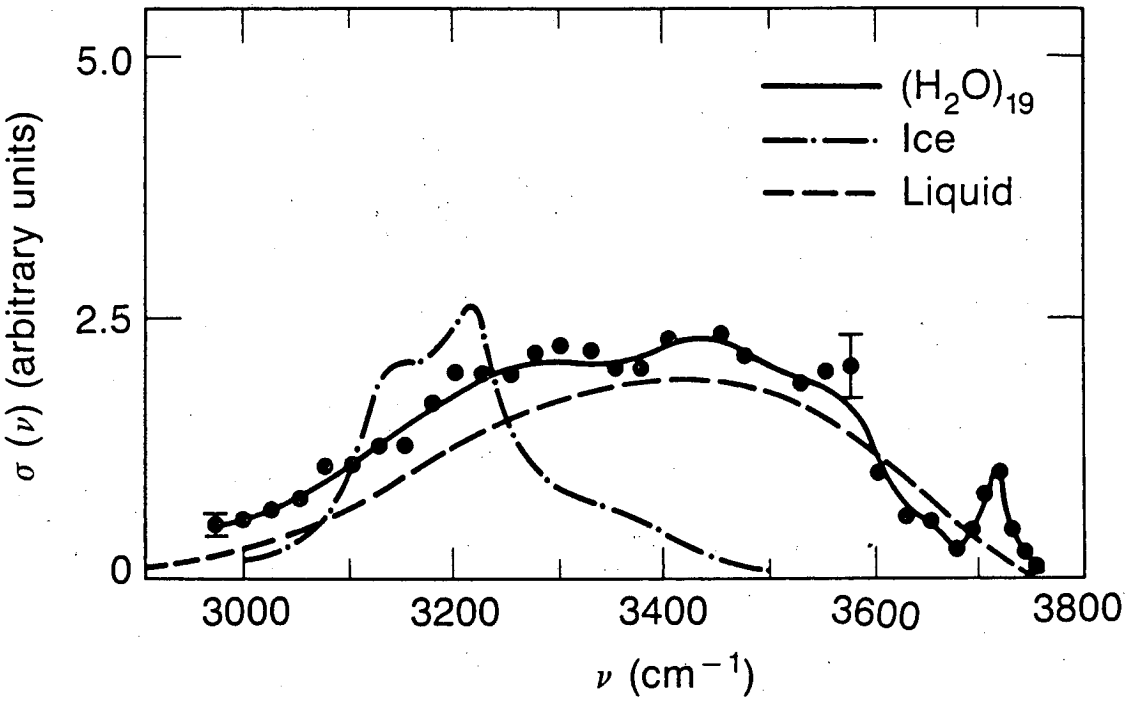

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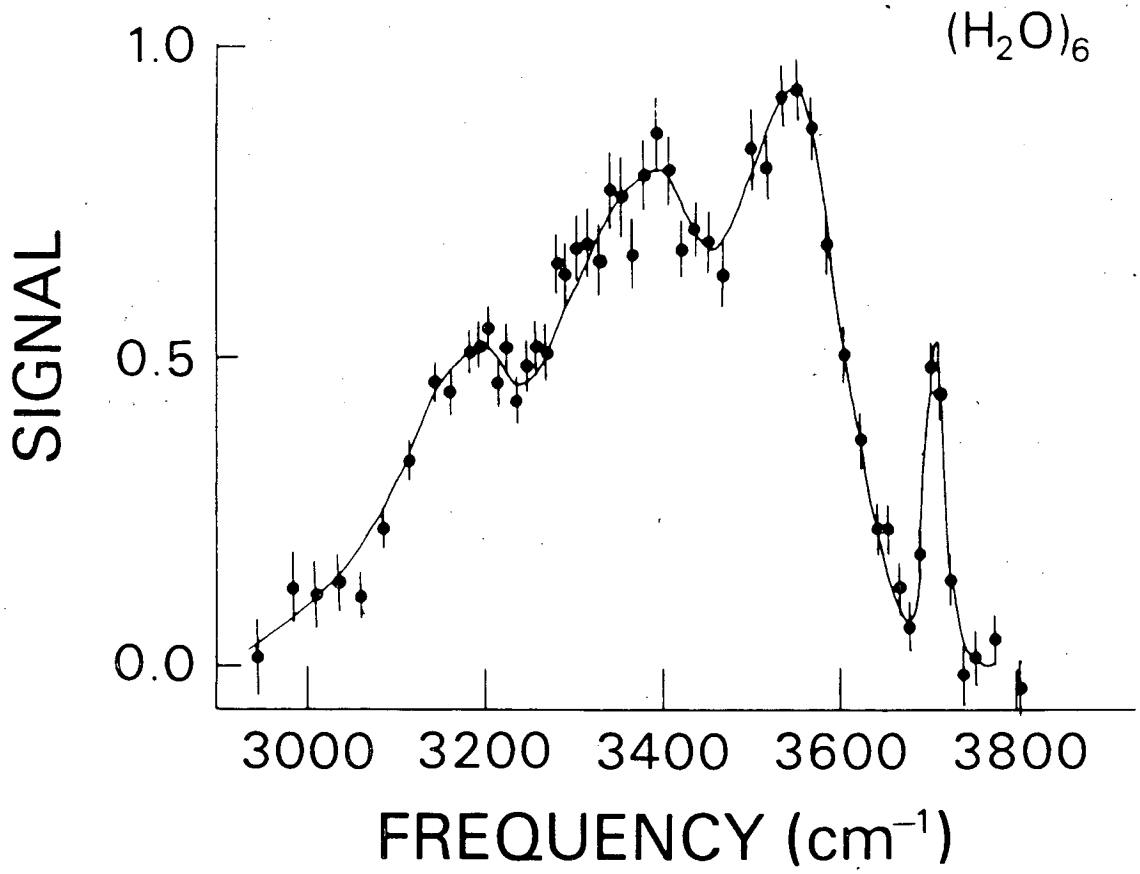
Fig. 1


1.0
0.5
0.0
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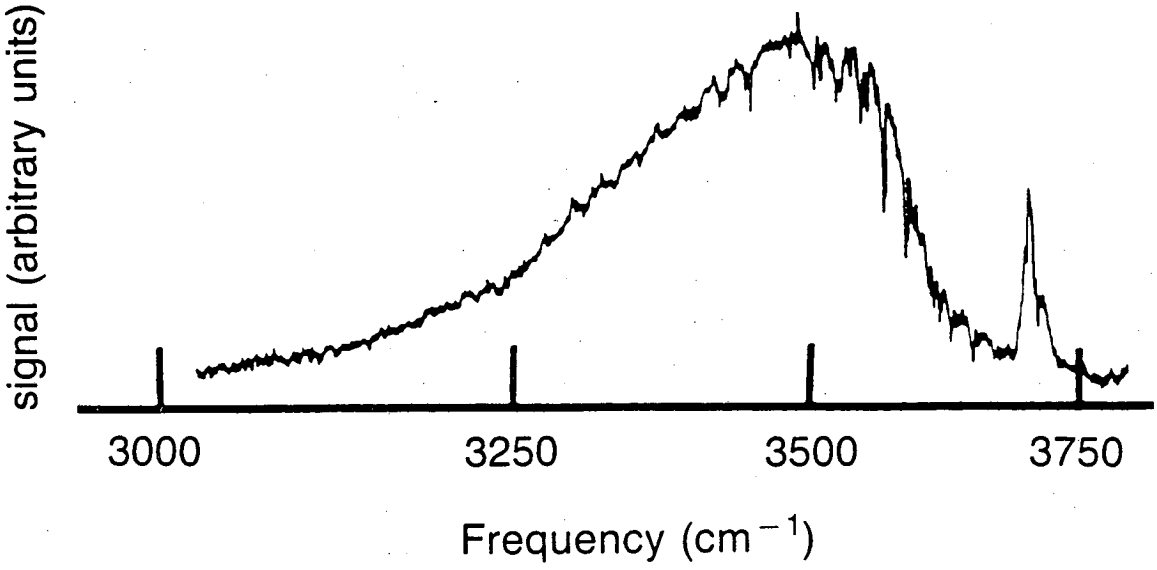
3000
3200
3400
3600
3800
FREQUENCY (cm^{-1})
XBL 819-1335

Fig. 2



XBL 872-6158A

Fig. 3

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