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February 1989

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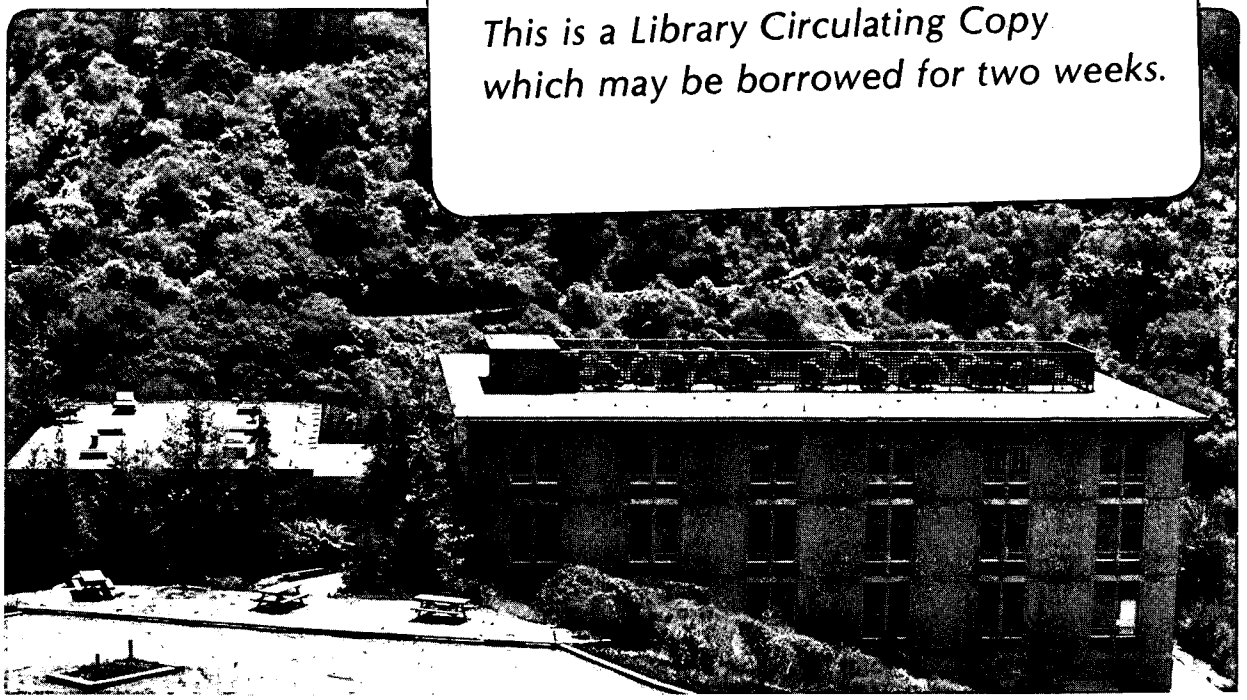

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

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Infrared Spectra of the Solvated Hydronium Ion: Vibrational Predissociation Spectroscopy of Mass-Selected $H_3O^+ \cdot (H_2O)_n \cdot (H_2)_m$

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ABSTRACT

Infrared spectra of the mass-selected clusters $H_3O^+ \cdot (H_2O)_n \cdot (H_2)$ and $H_3O^+ \cdot (H_2)_n$ (n = 1,2 and 3) were observed by vibrational predissociation spectroscopy. The clusters were mass-selected, and then trapped in a radio frequency ion trap. Cluster dissociation by loss of H_2 followed excitation of OH or H_2 stretches. Spectra were recorded by detecting fragment ions as a function of laser frequency. From spectra of $H_3O^+ \cdot (H_2O)_n \cdot (H_2)$, we were able to determine the spectrum of the hydrated hydronium ion $H_3O^+ \cdot (H_2O)_n$, because the H_2 formed weak complexes with the hydrates. Spectra in the OH stretching region (3000 to 4000 cm^{-1}) were observed at a resolution of 1.3 cm^{-1} for clusters n = 1, 2, and 3. The structure of the clusters, and the perturbing effect of the H_2 were inferred from a comparison with recent unpublished *ab initio* vibrational frequencies calculated by Remington and Schaefer. Observation of the hydrogen-bonded OH stretch in $H_3O^+ \cdot (H_2O)_3$ at 2670 cm^{-1} confirmed the assignment of the low resolution spectrum obtained by Schwarz. Infrared spectra of the hydronium ion solvated by H_2 were also reported. In the clusters $H_3O^+ \cdot (H_2)_n$ (n = 1, 2, and 3), all OH and H_2 stretching vibrations were observed. In several bands of $H_3O^+ \cdot (H_2)$, rotational structure was partially resolved, with the resolution limited by the laser-linewidth of 0.8 cm^{-1}.

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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, relied 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 Wolynes[1] 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 $H_3O^+ \cdot (H_2O)_n$. The generally accepted model[2] 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,[3] and a detailed understanding of solvent effects on processes such as proton transfer is actively being pursued.[4,5]

One approach for investigating ion-solvent interactions has been to study solvated ions in the gas phase.[6] 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.[7,8] Experiments have primarily explored their thermochemistry, association kinetics, and dissociation dynamics.[9,10] There has been recent success in the IR vibrational predissociation spectroscopy of cluster ions.[11,12,13] Here we describe our study of the infrared spectra of the solvated hydronium ion $H_3O^+ \cdot (X)_n$, where X = H_2O, H_2.

Vibrational spectroscopy has been an important technique for elucidating the nature of hydrogen bonded species in both the gas and condensed phases.[14] There have been many studies of the infrared and Raman spectroscopy of the hydronium ion hydrates both in solution and in solids.[15,16] The spectra however tend to be broadened and the analysis is often ambiguous. The positions and intensities of the

bands assigned to $H_3O^+ \cdot (H_2O)_n$ are often sensitive to the nature of the medium, e.g. a salt crystal or ionic solution.

In 1977, Schwarz[17] obtained the first infrared absorption spectra of these clusters in the gas phase, recording low resolution (40 cm^{-1}) IR absorption spectra of $H_3O^+ \cdot (H_2O)_n$, $n = 3$, 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,[18] based on *ab initio* calculations of the harmonic frequencies. This work, an extension of earlier *ab initio* calculations on the smaller hydrates,[19] largely agreed with Schwarz's results. There have been many other *ab initio* studies of these clusters with varying degrees of sophistication as well.[20] The development of analytic derivative methods has facilitated *ab initio* calculations of vibrational frequencies. In unpublished work, Remington and Schaefer[21] 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 spec-

trum of the hydronium ion H_3O^+ using velocity modulation spectroscopy.[22,23] Although three out of four vibrational bands of H_3O^+ have now been observed at high resolution,[24,25,26] no further spectra of the larger clusters have been reported.

The IR spectroscopy of weakly bound ions in the gas phase is experimentally challenging. The approach developed in our laboratory has been to obtain IR spectra of such ions by detecting their photodissociation after exciting a vibrational transition, to take advantage of the inherently high sensitivity of ion counting techniques. Mass selection of both the parent ion prior to excitation, and the product ions after dissociation allows unambiguous identification of the dissociation process.

We have previously observed vibrational spectra of the hydrogen cluster ions H_n^+, where n = 5, 7, 9, 11, 13, and 15.[11] 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^+.

In this paper, we present new results on the infrared spectra of the H_3O^+ ion solvated by H_2 and H_2O molecules. Using the vibrational predissociation method, we have observed spectra of the clusters $H_3O^+ \cdot (H_2)_m$, with m = 1 to 3. Excitation of an H_2 or OH stretch leads to loss of one or more H_2. We expect these clusters to be similar in many respects to the hydrogen cluster ions. They also provide a prototype for solvation effects in the more complex hydrated clusters. Furthermore, the infrared spectroscopy of the hydronium ion itself has been studied extensively at high resolution, providing a useful basis for understanding its solvation by H_2 ligands.

This technique cannot be applied directly to the hydrated hydronium ions, which

are bound far more strongly than the H_n^+ clusters. A single infra-red photon exciting an OH stretching vibration cannot dissociate these 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.[27,28,29] 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 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

$$H_3O^+ \cdot (H_2O)_n \cdot (H_2) \rightarrow H_3O^+ \cdot (H_2O)_n + H_2. \qquad (1)$$

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 $H_7O_3^+$. The $H_3O^+ \cdot (H_2)_m$ spectroscopy provides additional insights into how the H_2 perturbs the larger hydrates.

The "messenger" technique relies on the small influence of the H_2. How does the H_2 bind to a large cluster ion? Recent *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.[30,31] 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.[30] 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.

The messenger approach is not necessary, if an ion can absorb several photons to reach the dissociation limit. Since completion of this work, spectra of the hydrated hydronium clusters alone (without messengers) have been obtained in our laboratory using one and two laser infra-red multiphoton dissociation schemes.[32] 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 excited by a F-center laser. The results from the new experiment on $H_5O_2^+$, $H_7O_3^+$, and $H_9O_4^+$ verify the assignments and allow us to quantify the perturbations to the hydrate ion modes induced by the H_2 messenger. These results are discussed elsewhere,[32] and will be summarized below.

II. EXPERIMENTAL

The clusters $H_3O^+ \cdot (H_2O)_n \cdot (H_2)_m$ were produced in a weak corona discharge of 200 to 300 torr of H_2 (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 75 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 minimizing the ion energy spread. The expanded gas passed through a skimmer 7 mm from the nozzle. The ions were then

accelerated to 350 eV, and hydrated ions $H_3O^+ \cdot (H_2O)_n \cdot (H_2)$ of a given size n with an H_2 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 $H_3O^+ \cdot (H_2O)_n$. 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 (> 0.01 cm^{-1}) — did not apply to this experiment, which used a pulsed, low resolution laser.

Using 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.[33] The proton affinity of water is 166.5 kcal/mol,[34] 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 $H_3O^+ \cdot (H_2O)_n$ 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 Spectra Physics. The IR photons were produced by mixing the 1.06 μ 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 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 observed spectra of the clusters $H_3O^+\cdot(H_2)_m$, with m = 1, 2, and 3, over the frequency range from 3100 cm^{-1} to 4200 cm^{-1} from their vibrational predissociation

$$H_3O^+\cdot(H_2)_m \rightarrow H_3O^+\cdot(H_2)_{(m-m')} + m'H_2. \quad (2)$$

Composites of low resolution scans are shown in Fig. 4. For all three clusters, we observed fundamental bands of the OH and H_2 stretches, as well as several weak combination or overtone bands. Several bands exhibited partially resolved rotational structure. In the spectrum of $H_3O^+\cdot(H_2)$ for example, detailed scans have shown that the structure in the 3500 cm^{-1} and 4045 cm^{-1} bands is real, while the spikes seen in the bands below 3300 cm^{-1} are due primarily to noise (scaled up by power normalization).

For the $H_3O^+\cdot(H_2)$ ion, we detected the H_3O^+ ion. For both the $H_3O^+\cdot(H_2)_2$ and the $H_3O^+\cdot(H_2)_3$ 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 $H_3O^+\cdot(H_2)$ respectively. $H_3O^+\cdot(H_2)_2$ 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 $H_3O^+\cdot(H_2)_3$ 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 contribution from the loss of all three H_2 was larger, 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 $H_3O^+\cdot(H_2)_3$ is between 3.1 and 3.9 kcal/mol.

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. 5. 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. 6. The ion count at mass 41 was about a factor of five lower than at mass 39 ($H_5O_2^+ \cdot (H_2)$), so the signal-to-noise ratio was substantially poorer. All of the observed peaks shown in Fig. 5 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 $H_5O_2^+ \cdot (H_2)_n$ and $H_7O_3^+ \cdot (H_2)$ at 4105 cm^{-1} and 4115 cm^{-1} respectively, but were unable to find any absorptions in this region by $H_9O_4^+ \cdot (H_2)$.

The vibrational frequencies of the hydrogen-bonded OH stretches should be red-shifted significantly from 3400-3500 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. 7. 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.

IV. SPECTRA OF THE CLUSTERS $H_3O^+ \cdot (H_2)_m$

An investigation of the clusters $H_3O^+ \cdot (H_2)_m$ 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.[35] Theorists[31] 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 X-$H^+ \cdots H_2$ bond, forming a T-shaped complex. These proton bound dimers are the transition complexes for the proton transfer reactions $X + H_3^+ \rightleftharpoons XH^+ + H_2$. 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.*[30] 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,[36] and in conjunction with thermochemical measurements, provide indirect evidence in favor of the theoretical structures.

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

nium ion solvated by H_2 molecules, but the theoretical studies on other $XH^+ \cdot H_2$ clusters provide an adequate guide. The proton affinity of H_2O is ~66 kcal/mol greater than that of H_2.[34] 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 $OH\cdots H_2$ bond, as illustrated in Fig. 8. Additional H_2 would bind to the remaining OH bonds to form the larger clusters $H_3O^+ \cdot (H_2)_2$ and $H_3O^+ \cdot (H_2)_3$.

A. Low Resolution Spectra

The three vibrational spectra shown in Fig. 4 can be interpreted in terms of the hypothesized structure of H_2 forming hydrogen bonds with the hydronium ion.

The high frequency stretching vibrations near 4000 cm^{-1} are readily assigned to the H_2 stretch in the clusters, which will be red-shifted from the H_2 monomer value[37] at 4161 cm^{-1} due to the presence of the charge. The rovibrational absorption of the H_2 monomer, at 4161 cm^{-1}, is dipole-forbidden.[37] In $H_3O^+ \cdot (H_2)$, this vibration is probably coupled to and borrows intensity from the motion of the hydrogen-bonded OH stretch. These bands are however substantially weaker than the others at lower frequency, which are presumably fully allowed transitions.

The frequencies of the H_2 absorptions in $H_3O^+ \cdot (H_2)_n$ are 4046 cm^{-1}, 4055 cm^{-1}, and 4065 cm^{-1} for $n = 1$, 2, and 3 respectively. In the clusters $H_3^+ \cdot (H_2)_n$ the H_2 stretches are 3910 cm^{-1}, 3980 cm^{-1}, and 4020 cm^{-1} for the same n. The smaller red-shifts in the $H_3O^+ \cdot (H_2)_n$ clusters indicate that the H_2 are bound more weakly to H_3O^+ than to H_3^+. The H_2 frequencies also change very little (20 cm^{-1}), suggesting that each H_2 bonds almost equally strongly to the H_3O^+ ion. In contrast, the vibrational frequencies in the hydrogen cluster ions vary over 100 cm^{-1}, and the $H_3^+ \cdot (H_2)_n$ dissociation energies are 6.6 kcal/mol, 3.1 kcal/mol, and <3.1 kcal/mole for $n = 1$,

2, and 3.[36] The proton affinity of H_2O is 66 kcal/mol higher than H_2, so each H_2 will not greatly perturb the H_3O^+.

Note that the frequency and dissociation energy for H_9^+ are both close to that observed for $H_3O^+\cdot(H_2)_n$. These results suggest that the H_2 vibrational frequency provides a measure of the strength of the intermolecular bond.

In $H_3O^+\cdot(H_2)$, the next lower vibrational band is broad and structured, and ranges from 3450 cm^{-1} to 3700 cm^{-1}, while in $H_3O^+\cdot(H_2)_2$, there is a band at 3550 cm^{-1}. This set of bands occur near the stretching frequencies of H_3O^+, which are 3522 cm^{-1} and (predicted at) 3400 cm^{-1}.[23] Therefore, we have assigned them to the free OH stretches of the H_3O^+ moiety in the cluster. This band is notably absent in $H_3O^+\cdot(H_2)_3$, in which there are no free OH, since H_2 ligands bind to all three OH. This result provides strong evidence for our hypothesized structure of these complexes.

As in other hydrogen bonded species, the donor OH vibration of the H_3O^+ will be red-shifted, and will have an enhanced intensity. The lowest frequency bands lie 200 to 400 cm^{-1} below the free OH stretch frequencies. In $H_3O^+\cdot(H_2)$, there is a single band at 3120 cm^{-1}. In $H_3O^+\cdot(H_2)_2$, there are two bands at 3180 cm^{-1} and 3275 cm^{-1}, which are the symmetric and antisymmetric hydrogen-bonded OH stretches.

In $H_3O^+\cdot(H_2)_3$, two bands lie at 3200 cm^{-1} and 3290 cm^{-1}. The latter band is significantly broader, as might be expected for a perpendicular transition. If we assume that the cluster has C_{3v} symmetry, 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, although other broadening mechanisms may be involved. Resolved rotational spectra are needed for a definite assignment. Assuming the assignment based on widths, we find that the relative order of the symmetric and antisymmetric stretches of H_3O^+ in this cluster are the same as in H_3O^+ monomer, but are reversed

in $H_9O_4^+$.[18,44] Our tentative assignment here, with the E mode higher in frequency than the A_1 mode, implies that the hydronium ion in the $H_3O^+ \cdot (H_2)_3$ cluster is not perturbed enough to change the ordering of the frequencies of these two modes.

B. Comparison with *ab initio* Results

Following our observation of the $H_3O^+ \cdot (H_2)$ spectrum, Remington and Schaefer performed a DZ+P SCF calculation[21] on the $H_3O^+ \cdot (H_2)$ ion, and obtained a structure as we had anticipated, with the H_2 forming a hydrogen bond with one OH group. Their structural parameters are given 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 $H_3O^+ \cdot (H_2)_3$. 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. Furthermore, SCF calculations do not yield accurate dissociation to energies for weakly bound complexes.[30]

Remington and Schaefer have made preliminary calculations for the vibrational frequencies, and intensities, of $H_3O^+ \cdot (H_2)$ at the DZ+P SCF level. With one exception, their scaled frequencies are in excellent agreement with the results of our experiment, given the relatively low level of theory (DZ+P SCF). The agreement for the donor OH stretching mode at 3120 cm^{-1} is poor. 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. They also predict a harmonic frequency of 322 cm^{-1} for the intermolecular stretch.

C. Rotationally Resolved Structure in $H_3O^+ \cdot (H_2)$

The three strongest bands of the H_3O^+ cluster are shown expanded in Fig. 9. The most striking aspect of the H_2 and free OH stretch bands (bottom and middle spectra) is the partial resolution of rotational structure.

In the H_2 stretch band at 4046 cm^{-1} the P, Q, and R branches are resolved,and rotational lines in the P and R branches are partially resolved at a laser linewidth of 1.2 cm^{-1}. Prior to this spectrum, no rotational structure had been observed in the spectra of weakly bound cluster ions. Bogey *et al.* have now reported beautiful microwave spectra of the cluster $Ar \cdot H_3^+$.[39] We have demonstrated that, as for neutral van der Waal's clusters,[40] 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 $H_3O^+ \cdot (H_2)$ 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 $OH \cdots H_2$ bond. Remington and Schaefer's calculation[21] predict rotational constants of A=9.5 cm^{-1}, B=1.08 cm^{-1}, and C=1.03 cm^{-1}. As in H_5^+, the H_2 stretch borrows intensity by coupling to motion of the central proton; the transition moment thus lies along the *a* axis.

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}, yielding $(B + C)/2 \approx 1.0$, in good agreement with the *ab initio* results.

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,[41] the vibrational origins of the v=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 Levy[42] have observed an ortho/para splitting of about 1.5 cm^{-1} in the laser induced fluorescence dispersed emission spectra of the $I_2 \cdot H_2$ van der Waal's complex.

Another possible source of the splitting is a small inversion doubling[25] arising from the umbrella motion of the H_3O^+. The size of the splitting in such floppy molecules is generally mode-specific.[43] One would expect a small splitting for this vibration, because it is 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, requires a spectrum taken at much higher resolution.

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. We expect an *a* type band and a *b* type band, *i.e.,* excitation of the symmetric and antisymmetric OH stretching modes. The *b* type band gives rise to the strong Q branches 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 $2(A'-C) \approx$ 17 cm^{-1} from the *ab initio* predictions. Given the assumed geometry, it is unlikely that $2(A-C)$ 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 cm^{-1} is split into $s-s$ and $a-a$ bands with origins at 3519 and 3533 cm^{-1}.[23] This gives an upper bound on the expected doubling in $H_3O^+ \cdot (H_2)$. The inversion doubling will depend strongly on mode; the OH stretch should have a much larger

doubling than the H_2 mode due to stronger coupling.

The band origin of the symmetric stretch could lie anywhere within the congested set of lines between 3450 and 3600 cm^{-1}. We estimate that a maximum occurs near 3490 cm^{-1}. From its position relative to the series of Q branches, one could assign a band occuring 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 assign the partially resolved structure, we cannot make a definitive assignment here. We note that the *ab initio* theory supports our assignment of the possible 3490 cm^{-1} band as the symmetric stretch of the free OH groups.

No rotational structure was resolved in the 3100 cm^{-1} band. Although the laser power was low, comparison with the other bands indicates that rotational lines should have been observed. This result suggests that some broadening is occurring. The donor OH bond may be more strongly coupled to other modes, resulting in additional congestion, or it may be more strongly coupled to the dissociation continuum, resulting in homogeneous broadening.

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. 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}. This is fairly close to the *ab initio* harmonic frequency of 322 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.

In the $H_3O^+ \cdot (H_2)_2$ and $H_3O^+ \cdot (H_2)_3$ bands no individual rotational lines are resolvable. The H_2 stretch of $H_3O^+ \cdot (H_2)_2$ does exhibit fine features at 4050 cm^{-1},

4055 cm^{-1}, and 4062 cm^{-1}, which may be 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. From estimated rotational constants derived from the structural parameters for $H_3O^+\cdot(H_2)$, assuming that the second H_2 binds similarly to the hydronium ion, we find that the rotational spacing is roughly comparable to the laser linewidth and we do not expect to resolve rotational structure for the larger clusters.

D. Summary

The spectra of the $H_3O^+\cdot(H_2)_n$ clusters can be interpreted in terms of H_2 ligands bonding to the OH to form "hydrogen bonds," as seen in Fig. 8. All of the H_2 and OH stretches are then observed. The free OH absorptions lie near the hydronium ion monomer absorptions, while the vibrational frequencies of the donor OH bonds are shifted by 200 to 400 cm^{-1}. The H_2 absorptions are near 4050 cm^{-1}, redshifted by 110 cm^{-1}. From the observed fragmentation patterns, we deduced that the H_2 bind to H_3O^+ with average energies of between 3.1 and 3.8 kcal/mol.

V. SPECTRA OF THE LARGER HYDRATES $H_3O^+\cdot(H_2O)_n\cdot(H_2)$

In this section, we discuss the vibrational spectra of the hydrates $H_3O^+\cdot(H_2O)_n$ by interpreting the spectra of the messenger-bound species $H_3O^+\cdot(H_2O)_n\cdot(H_2)$. 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. The H_2 should bind to these larger clusters more weakly than in the clusters $H_3O^+\cdot(H_2)_n$. There is predicted to be a large partial charge on the protons in H_3O^+,[21,38] which is substantially reduced by hydration. 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 $H_3O^+ \cdot (H_2O)_n$ at the same location as the next additional H_2O would bind. The expected structures are shown in Fig. 11. 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. As in $H_{11}O_5^+$, 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. $H_9O_4^+$

The main features of the spectrum of $H_3O^+ \cdot (H_2O)_3 \cdot (H_2)$, or $H_9O_4^+ \cdot (H_2)$, are readily interpreted assuming H_2 weakly perturbs the hydrate. In the cluster $H_9O_4^+$, the H_3O^+ ion has a complete inner coordination shell, i.e. one water molecule on each OH bond. With all OH bonds participating in hydrogen bonds, the hydronium ion OH stretches will all be significantly red-shifted, while the H_2O stretching frequencies should be only weakly red-shifted. We have observed two doublets in the free OH stretch region (3600 to 3750 cm^{-1}), and a broad band at 2670 cm^{-1}. Two weak bands at 3803 and 3824 cm^{-1} lie about 90 cm^{-1} above the free OH stretch absorptions. The doublets are assigned to OH stretches of the water ligands, while the 2670 cm^{-1} band is assigned to the stretching modes of the hydrogen bonded H_3O^+ stretches. No H_2 stretching band was observed, although it was seen in all other clusters, indicating that the H_2 is very weakly perturbed.

The H_2O stretch bands. The spectrum of $H_9O_4^+ \cdot (H_2)$ shown in Fig. 5 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 antisymmetric stretches of the solvent H_2O groups. A higher resolution scan

at 0.75 cm^{-1} 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 spectrum[17] 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. 5. 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. By contrast, the bands observed here are sharp and clearly resolved, and can be unambiguously assigned to $H_9O_4^+ \cdot (H_2)$.

The reported bands are in good agreement with the *ab initio* predictions of Remington *et al.*[21] The frequencies scaled to the H_2O frequencies are below the lower frequency components by 5 and 10 cm^{-1}. Curiously, the frequencies scaled to the H_3O^+ frequencies agree to within five cm^{-1} of the high frequency peaks in each doublet. However, the (H_2O) scaling should be used, because these vibrations are essentially vibrations of the solvating H_2O groups.

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. Only one of the H_2O would be perturbed, while two would remain unperturbed, accounting for the observed 2:1 intensity ratio. The *ab initio* theory predicts that the A_1 and E combinations of H_2O stretches would have approximately a 2:1 intensity ratio. However, the predicted splitting is effectively zero, indicating that there is no

harmonic coupling of the H_2O stretches. The two modes involve different relative phases of vibration of the three H_2O molecules, and it is unlikely that the modes will be split significantly.

The magnitudes of the shifts are also reasonable. Perturbations induced by H_2 should be similar to those seen in a neutral $H_2O{\cdot}H_2$ complex. This complex has not been observed; however, the hydrogen bonded complex $HF{\cdot}H_2$ has recently been studied theoretically and experimentally.[49]

As in complexes with protonated species, all evidence indicates that the H_2 forms a hydrogen bond with the HF in a loosely bound T-shaped complex. The HF vibration shifts by $\approx$8 cm^{-1} (compared to an *ab initio* value of 15 cm^{-1}), 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. The cluster dissociation energy D_e is calculated to be 0.86 kcal/mol, somewhat lower than the binding energies of H_2 to H_3O^+. In summary, the results 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.

While these arguments strongly support our assignment of the doublet, they are circumstantial. Definitive evidence requires the $H_9O_4^+$ spectra without the messenger,[32] as observed in the two color IRMPD spectrum discussed later. These results confirm the subtle effects that a messenger or spy can have on the spectrum of a cluster.

The 2670 cm^{-1} band. The strong, broad band at 2670 cm^{-1} seen in Fig. 7 appears at the same frequency as the band seen by Schwarz (Fig. 1), confirming his assignment of this band to $H_3O^+{\cdot}(H_2O)_3$. These results indicate that his deconvolution of the

spectra is probably correct for the strongest, most distinguishable peaks. As expected, hydrogen bonding of solvent water molecules significantly broadens and red-shifts the OH stretching bands of the H_3O^+.

The experimental results do not agree with the scaled *ab initio* frequencies of Remington and Schaefer of 3020 and 2997 cm^{-1}. As in $H_3O^+ \cdot (H_2)$, *ab initio* calculations give poor predictions of strongly anharmonic, hydrogen bonded OH frequencies.

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 3733 cm^{-1} and 3648 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 to the dissociative coordinate. 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 HF·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.

Schwarz also observed a shoulder at approximately 3000 cm^{-1}. He assigned this band to the symmetric A_1 stretching mode, and the 2660 cm^{-1} band to the antisymmetric stretching mode of the hydrogen bonded OH's. The *ab initio* calculations predict a very small splitting of 33 cm^{-1} between the symmetric and antisymmetric stretches, indicating little harmonic coupling of the vibrations. We did not observe this shoulder; however, the laser power was particularly low, and we cannot definitively exclude the existence of a band at 3000 cm^{-1}.

The 3803 and 3824 cm^{-1} bands. There are several possible assignments for the identity of these weak bands, seen in the lower plot of Fig. 5. 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. If these bands are combination bands arising from the antisymmetric 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 3648 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 $OH\cdots H_2O$ stretching frequency would be either 70-90 cm^{-1}, or 158-178 cm^{-1}. Remington and Schaefer[21] predict harmonic, unscaled frequencies of 247 and 319 cm^{-1}; this stretch is strongly anharmonic, so the agreement is reasonable. A final possibility is the antisymmetric H_2O stretch in combination with the internal rotation of the H_2O ligand about the intermolecular band. However, the expected rotational spacing is $\approx$55 cm^{-1}, much too small to account for the observed frequency.

B. $H_7O_3^+$

In $H_3O^+\cdot(H_2O)_2$, 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. 11.

We have observed three bands in the spectral region of OH absorption, from 3000 cm^{-1} to 4000 cm^{-1}, shown in Fig. 5. Again, two bands, at 3642 and 3726 cm^{-1}, are red-shifted slightly(15 cm^{-1} and 30 cm^{-1}) from the two absorption bands of the H_2O monomer. These are the symmetric and antisymmetric stretch modes of the solvating H_2O. The red shift is larger than in $H_9O_4^+$, and the perturbation of the H_2O groups can be clearly seen to increase as the hydration number decreases.

We assign a third, lower frequency band at 3587 cm^{-1} to the OH stretch of the H_3O^+ ion. The H_2 messenger will bind to this OH group, decreasing the OH vi-

brational frequency and enhancing its intensity. Thus, the observed frequency of 3587 cm^{-1} is a lower limit to the true frequency of this mode. We have scanned all of the observed bands at 0.8 cm^{-1} resolution without observing any new features.

The *ab initio* transitions, shown as stick spectra in Fig. 5, 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 at 3640 cm^{-1}, we observe a more intense 3587 cm^{-1} band. If the H_2 binds to the OH of the H_3O^+ moiety, it will red shift and intensify that band. Assuming that the relative *ab initio* frequencies are correct, the free OH stretch of H_3O^+ will lie 20 cm^{-1} above the solvent H_2O symmetric stretch, and is red-shifted approximately 65 cm^{-1} by the H_2.

The red-shift of the OH stretch is much less than the shift of $\sim$200 cm^{-1} seen in $H_3O^+ \cdot (H_2)_3$. This result is consistent with the differences in the red-shifts of the messenger H_2 stretches. In $H_7O_3^+ \cdot (H_2)$, the H_2 band is shifted by 46 cm^{-1}, whereas in $H_3O^+ \cdot (H_2)_3$, the shift is 96 cm^{-1}. We conclude that the $H_3O^+ \cdots H_2$ interaction is significantly weaker in the hydrated species.

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. Schwarz[17] has observed absorption near 2300 cm^{-1}, which he attributed to $H_7O_3^+$ from the time dependence. We have found a broad absorption in the region below 2500 cm^{-1}, but the low laser energy, generally less than 0.1 mJ, prevented us from getting good signal. From the scaled *ab initio* frequencies, one expects a strong vibrational band near 2650 cm^{-1}. We have found no absorption in the region 2500—2800 cm^{-1}.

C. $H_5O_2^+$

The structure of the $H_5O_2^+$ ion is still controversial. Although it is nominally the singly hydrated species $H_3O^+ \cdot (H_2O)$, many studies[20,21,45,46,47] indicate that the

central proton lies symmetrically between the two H_2O groups, to form the symmetric ion $H_2O\cdots H^+\cdots OH_2$. Although several condensed phase experiments, such as X-ray diffraction studies,[48] 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.[21,47] 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 $O\cdots O$ distance is stretched a small amount.

We have observed four bands in the OH stretching region, shown in Fig. 5. 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 antisymmetric stretches. The red shifts are 40 cm^{-1} and 63 cm^{-1} respectively, farther than in $H_7O_3^+ \cdot (H_2)$ or $H_9O_4^+ \cdot (H_2)$. The other two bands at 3528 and 3662 cm^{-1} can be assigned as free OH stretches of the H_3O^+. In fact, all of the frequencies of the OH stretches are 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.

The spectrum of the $H_5O_2^+ \cdot (H_2)_2$ cluster is shown in Fig. 6 plotted along with the $H_5O_2^+ \cdot (H_2)$ spectrum. The major change upon adding a second H_2 is to increase the frequency of the 3528 cm^{-1} band by 37 cm^{-1}, and to double its intensity. The peak at 3662 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.

There are no previous gas phase spectra of $H_5O_2^+$ alone. Schwarz[17] observed a transient absorption at 3170 cm^{-1}, which he assigned to $H_5O_2^+$. We found no strong absorptions from 3100 cm^{-1} to 3500 cm^{-1}.

Remington *et al.* have calculated harmonic normal mode spectra for the two lowest energy configurations, the symmetric C_{2v} structure $H_2O\cdots H^+\cdots H_2O$, and the asymmetric C_s $H_3O^+\cdot(H_2O)$. The relative positions and intensities of the bands in observed spectrum agree well with the calculated spectrum for the asymmetric C_s structure. For the symmetric C_2 structure of $H_5O_2^+$, the calculations give only two absorption bands, as one would expect if the two H_2O groups were identical by symmetry. 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 results indicate that this band is perturbed by the H_2.

A comparison with the theoretical predictions leads us to conclude that the $H_5O_2^+$ ion possesses the asymmetric $H_3O^+\cdot(H_2O)$ structure when bound to an H_2. Even assuming that the *ab initio* theory is correct, we cannot deduce the structure of the hydrate $H_5O_2^+$ from the messenger bound spectrum.

Although we are trying to distinguish between the geometries **1** and **2** shown in Fig. 12, it appears that the H_2 will bind to an OH and stabilize the H_3O^+ ion, forming the asymmetric ion **3**. 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 $H_3O^+\cdot(H_2)_3$ 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. Because the potential energy surface is so flat, attaching the H_2 should skew the potential to create the cluster **3**. As a result, spectra obtained using H_2 as a messenger cannot unambiguously yield the correct structure of the $H_5O_2^+$ cluster.

VI. DISCUSSION

A. Messengers

This experiment has provided preliminary $\approx$1 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, because the two techniques suffer from a common limitation, namely uncertainty concerning effects induced by the "environment."

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 OH bonds of the H_3O^+ ion, shifts the vibrational frequencies of those bonds by 10 to 90 cm^{-1}, and intensifies the transitions. Other bands are generally not perturbed (except in the case of $H_5O_2^+$). 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^+ in those clusters is undoubtedly an upper limit to the binding energy of H_2 to the larger hydrates.

The interpretation of the $H_5O_2^+$ spectrum however is uncertain, due to the presence of the H_2. In the other clusters, only vibrational bands directly involved in bonding to H_2 are perturbed. For ions like $H_5O_2^+$ with flat potentials near their equilibrium

geometry or several low energy conformers, 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 exernal 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 $XH^+ \cdot H_2$ complexes. Their peak locations are plotted in Fig. 13. The hydrogen cluster ions, which are bound by 2 to 6 kcal/mol have the largest red shifts relative to the H_2 monomer. H_9^+, with a dissociation energy of 3.1 kcal/mol, absorbs at 4020 cm^{-1}, 140 cm^{-1} below H_2. The $H_3O^+ \cdot (H_2)_m$ 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 $H_3O^+ \cdot (H_2)$.

When the H_2 binds to the hydrates $H_3O^+ \cdot (H_2O)_n$, the H_2 vibrations are red shifted by only 45 and 55 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 with hydrated ions, and the weaker H_2 vibrational transitions, support the idea that as hydration delocalizes the charge, it reduces the strength of the interaction between the ion and the H_2 molecule.

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 an H_2 messenger on the vibrational frequencies of the hydrates. These results, summarized in Table II, are discussed in detail elsewhere.[32] For $H_3O^+ \cdot (H_2O)_n$, n

= 2 and 3, the results confirm our interpretation and quantify the effects of the messenger. Those modes associated with H_2O stretches are esentially unchanged; bands perturbed by the messenger are shifted to the red. For n=2, the free OH vibration of the H_3O^+ ion is shifted 80 cm^{-1}. For n=1, the spectrum suggests that $H_5O_2^+$ is symmetric, indicating that the H_2 strongly disturbs the structure and the infrared spectrum of this ion, despite the relatively weak intermolecular bond.

B. Linewidths

We have observed a wide range of linewidths, from the 100 cm^{-1} FWHM of the hydrogen bonded OH absorption in $H_9O_4^+ \cdot (H_2)$, to the laser limited widths of the rotational transitions seen in $H_3O^+ \cdot (H_2)$. Many other bands had contours suggesting unresolved rotational sub-bands.

The well resolved structure in the free OH and H_2 stretching modes of $H_3O^+ \cdot (H_2)$ contrast sharply with the broad absorption by the hydrogen-bonded $OH \cdots H_2$ 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.[58]

In $H_9O_4^+$, the absorption band of the $O\text{-}H \cdots O$ vibration, i.e. the hydrogen bonded OH of the H_3O^+ core, is approximately 100 cm^{-1} wide, and is the widest band observed in this experiment. The band is over an order of magnitude wider than the free OH stretches of $H_9O_4^+$ near 3700 cm^{-1}. The H_2O bands are all less than 10 cm^{-1} FWHM. This sets an upper limit on the lifetime broadening due to predissociation,

because the vibrations of the H_2O bound to the H_2 are likely to be coupled more strongly to the dissociative channel than the hydrogen bonded OH mode of the H_3O^+.

The broad peak is therefore intrinsic to the $H_9O_4^+$ cluster. The 2660 cm^{-1} band observed by Schwarz is about a factor of two broader, and the difference cannot be attributed merely to instrumental resolution. This temperature dependent width suggests that hot bands contribute to the linewidth observed by Schwarz.

C. Comparison with the Pulsed Radiolysis Results

Schwarz[17] reported spectra from 2000 cm^{-1} to 4000 cm^{-1} for the large hydronium ion clusters $H_9O_4^+$, $H_{11}O_5^+$, and $H_{13}O_6^+$, at a resolution of 40 cm^{-1}. A distribution of cluster sizes were simultaneously present in his cell, and questions were raised[50] 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. We saw no evidence for an absorption at 3170 cm^{-1}, which Schwarz had assigned to $H_7O_3^+$ or smaller ions.

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 *ab initio* predictions.

D. *Ab Initio* Calculations

The scaled *ab initio* results of the highest frequency modes[21] 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 $H_3O^+ \cdot (H_2)$ 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. Newton[18] 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 of the solvent H_2O 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 $H_3O^+ \cdot (H_2)$, the scaled theoretical frequency is 3304 cm^{-1}, 200 cm^{-1} above the experimental result.

We obtain better agreement 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 $H_3O^+ \cdot (H_2)$ 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 $H_9O_4^+$, much closer to the observed value of 2670 cm^{-1}.

There are several possible reasons for the failure of theory. The *ab initio* calculation overestimate force constants, and ignore anharmonicities, errors which are corrected by scaling. It is not clear that scaling will correctly estimate the error for a vibration perturbed by hydrogen bonding. 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_5^+, DZ+P SCF may be inadequate to obtain the correct geometry. 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. The anharmonic coupling of the modes involved in the hydrogen bond is strong,[14] suggesting that a more sophisticated treatment of the vibrational problem is necessary.

VII. SUMMARY

We have observed infrared spectra of mass-selected clusters of partially solvated hydronium ion clusters $H_3O^+\cdot(H_2)_n$, and $H_3O^+\cdot(H_2O)_n(H_2)$.

We observed all OH and H_2 stretching modes of $H_3O^+\cdot(H_2)_n$, for $n = 1, 2, 3$. The H_2 form hydrogen bonds with the OH, and in $H_3O^+\cdot(H_2)_3$, the free OH bands are absent. The H_2 vibrations are red-shifted by $\approx$100 cm^{-1}, close to that seen for H_9^+. The OH stretches shift by 200 to 400 cm^{-1} upon forming bonds with H_2 ligands. These complexes appear to be somewhat more weakly bound than analogous $H_3^+\cdot(H_2)_n$ complexes. From the fragmentation pattern, we found the bond energy to be between

3 to 4 kcal/mol, similar to that of H_9^+. Rotationally resolved bands were observed for the complex $H_3O^+ \cdot (H_2)$.

A single IR photon cannot dissociate the hydrated H_3O^+ clusters. By attaching an H_2 molecule to hydronium ion hydrate clusters $H_3O^+ \cdot (H_2O)_n$, $n = 1 - 3$, we have been able to use vibrational predissociation spectroscopy to observe the infrared spectra of the mass-selected hydrate clusters. In this scheme, we detect loss of the H_2. The H_2 thus acts as a mass label or "messenger." The spectra were primarily of the free OH vibrations of the H_2O and H_3O^+, although the messenger H_2 vibrations were also observed for $n = 1, 2$.

H_2 has a proton affinity of 101 kcal/mol. As a result, it tends to form complexes with protonated species such as H_3O^+ having bond energies of up to 6 kcal/mol. The H_2 forms weak bonds with the $H_3O^+ \cdot (H_2O)_n$, and appears to slightly perturb the spectra, although much less than it perturbs the spectrum of the H_3O^+ ion alone.

Detection of the hydrogen-bonded OH stretch at 2670 cm^{-1} in $H_3O^+ \cdot (H_2O)_3 \cdot (H_2)$ confirms the spectrum Schwarz observed of hydronium ions formed by pulsed radiolysis. The experimental results disagree with recent *ab initio* calculations, and point to errors stemming from the empirical scaling of *ab initio* harmonic frequencies. The bandwidth is 100 cm^{-1}, an order of magnitude larger than that of the ligand H_2O stretches, and appears to be intrinsic to the cluster, and not due to dissociation lifetime broadening.

ACKNOWLEDGMENTS

We are very grateful to R. B. Remington and H. F. Schaefer III for providing us with the results of unpublished calculations. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy, Contract no. DE-AC-0376SF00098.

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TABLE I. Dissociation energies of several $XH^+ \cdot nH_2$ clusters in kcal/mol. Theoretical values from Hirao and Yamabe, Ref. 31. Experimental values from Kebarle, Ref. 6, except as noted.

XH^+		P.A. of X[a]	$XH^+ \cdots H_2$	$XH^+ \cdot H_2 \cdots H_2$
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

[a]Lias *et al.*, Ref. 34 and Moylan and Brauman, Ref. 52.

[b]Beuhler *et al.*, Ref. 36.

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

Cluster ion	Experiment $M^+ \cdot H_2$[b]	Experiment 2 color[c] MPD	Experiment Schwarz[d]	Theory[a] (Scaled) H_3O^+	Theory[a] (Scaled) H_2O	Assignment
$H_5O_2^+$	3528			3549		$H_3O^+ \cdot H_2$ stretch
						3565 in $H_5O_2^+ \cdot 2H_2$
	3617	3609.8		3607	3594	H_2O sym stretch
	3662			3633		H_3O^+ stretch
	3693	3684.4		3692	3678	H_2O asym stretch
	4105					H_2 stretch
$H_7O_3^+$	~2300		2200	2655		H-bonded H_3O^+ stretch
				2722		
	3587	3667.0		3631	3627	$H_3O^+ \cdot H_2$ OH stretch
	3642	3637.4	3620	3622	3619	H_2O sym stretch
	3726	3721.6	3710	3717	3702	H_2O asym stretch
	4115					H_2 stretch
$H_9O_4^+$	2670		2660	2997		H-bonded H_3O^+ stretch
				3020		
	3636					$H_2O \cdot H_2$ sym stretch
	3648	3644.9	3620	3643	3629	H_2O sym stretch
				3645	3630	
	3723					$H_2O \cdot H_2$ asym stretch
	3733	3730.4	3710	3728	3713	H_2O asym stretch
				3629	3614	
	3803	3798				weak combination bands
	3824	3825				or overtones

[a]DZ+P SCF calculations from Ref. 21.
[b]This work.
[c]Ref. 32.
[d]Direct absorption, Ref. 17.

FIGURE CAPTIONS

FIG. 1 Infrared absorption spectra of the clusters $H_3O^+ \cdot (H_2O)_n$ with n = 3, 4, and 5 at a resolution of 40 cm^{-1} from ref. 17. 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. 21

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 μA. The water clusters were produced from trace impurities in the gas.

FIG. 4 Infrared spectra of the clusters $H_3O^+ \cdot (H_2)_m$, with m = 1, 2, and 3. The fragment ions detected were H_3O^+, H_3O^+, and $H_3O^+ \cdot (H_2)$, 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. 38).

FIG. 5 Infrared spectra of $H_5O_2^+ \cdot (H_2)$, $H_7O_3^+ \cdot (H_2)$, and $H_9O_4^+ \cdot (H_2)$. 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 respecitve $H_3O^+ \cdot (H_2O)_n$ clusters,

made by Remington and Schaefer at the DZ+P SCF level. See Ref. 21. 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. 6 Comparison of the infrared spectra of $H_5O_2^+ \cdot (H_2)$ and $H_5O_2^+ \cdot (H_2)_2$. The relative intenisties of the two molecules are correct only to within 20%. In both cases, the $H_5O_2^+$ daughter ion was detected.

FIG. 7 Infrared spectrum of the $H_9O_4^+ \cdot (H_2)$ antisymmetric stretch of the hydrogen-bonded O-H$\cdots$O.

FIG. 8 Geometry of $H_3O^+ \cdot (H_2)$ predicted by *ab initio* calculations of Remington and Schaefer with the DZ+P SCF theory. See Ref. 21.

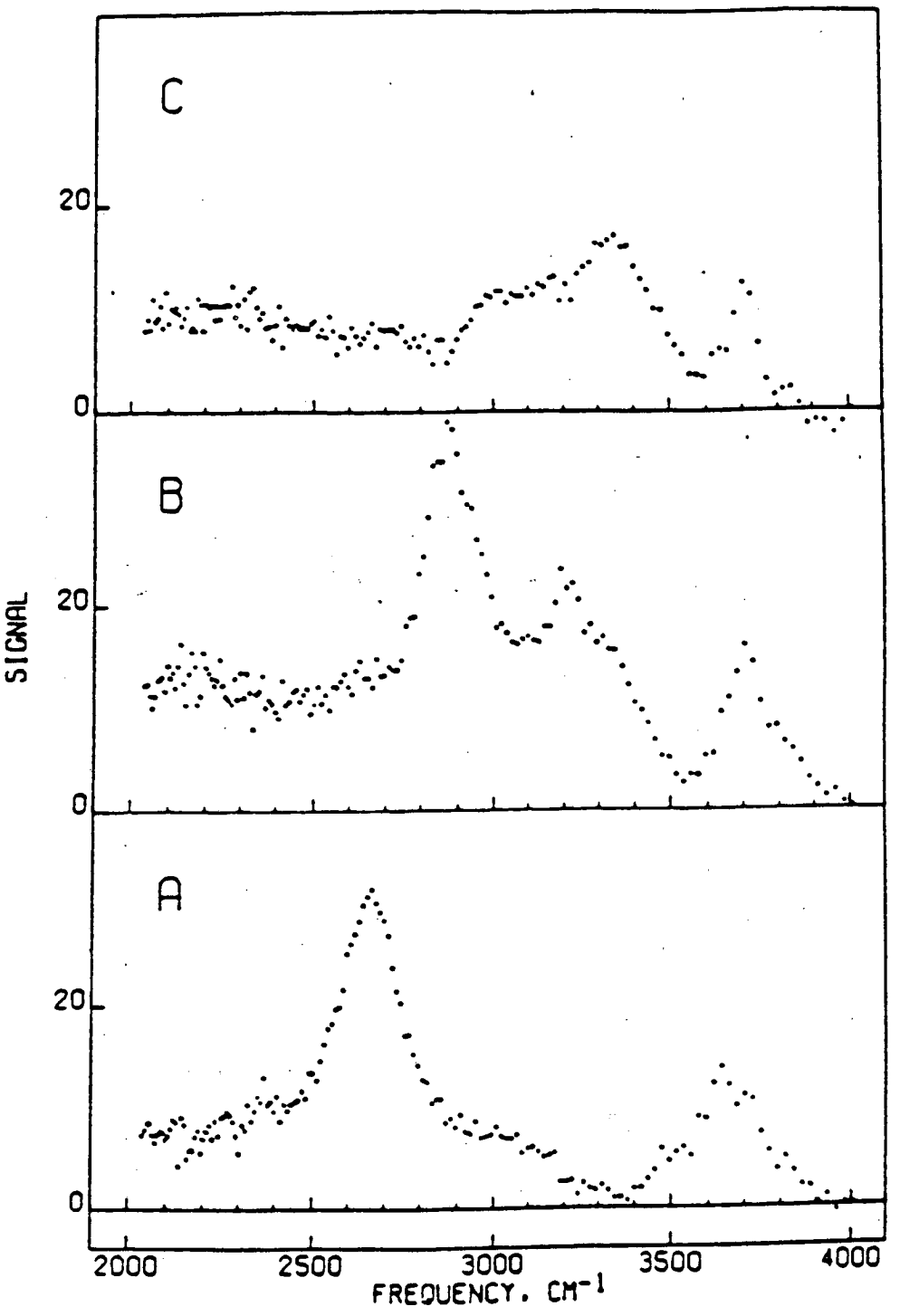
FIG. 9 Details of the vibrational predissociation spectrum of the $H_3O^+ \cdot (H_2)$ cluster, detecting the H_3O^+ product ion. Partially resolved rotational strucuture can be seen in the 3560 cm^{-1} and the 4046 cm^{-1} bands.

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 Postulated location of H_2 binding to larger hydronium ion hydrates.

FIG. 12 Energetics and geometries of $H_5O_2^+ + H_2$, and $H_5O_2^+ \cdot (H_2)$. The symmetric C_2 structure **2** is predicted to be 0.2 kcal/mol more stable than the asymmetric C_s structure **1**, from *ab initio* CISD calculations (Ref. 47). Complex **3** bond energy is unkown, but less than 3 kcal/mol.

FIG. 13 Observed peak frequencies of vibrational bands assigned to H_2 stretches in various $XH^+ \cdot H_2$ clusters.



XBL 8612-5044

Fig. 1

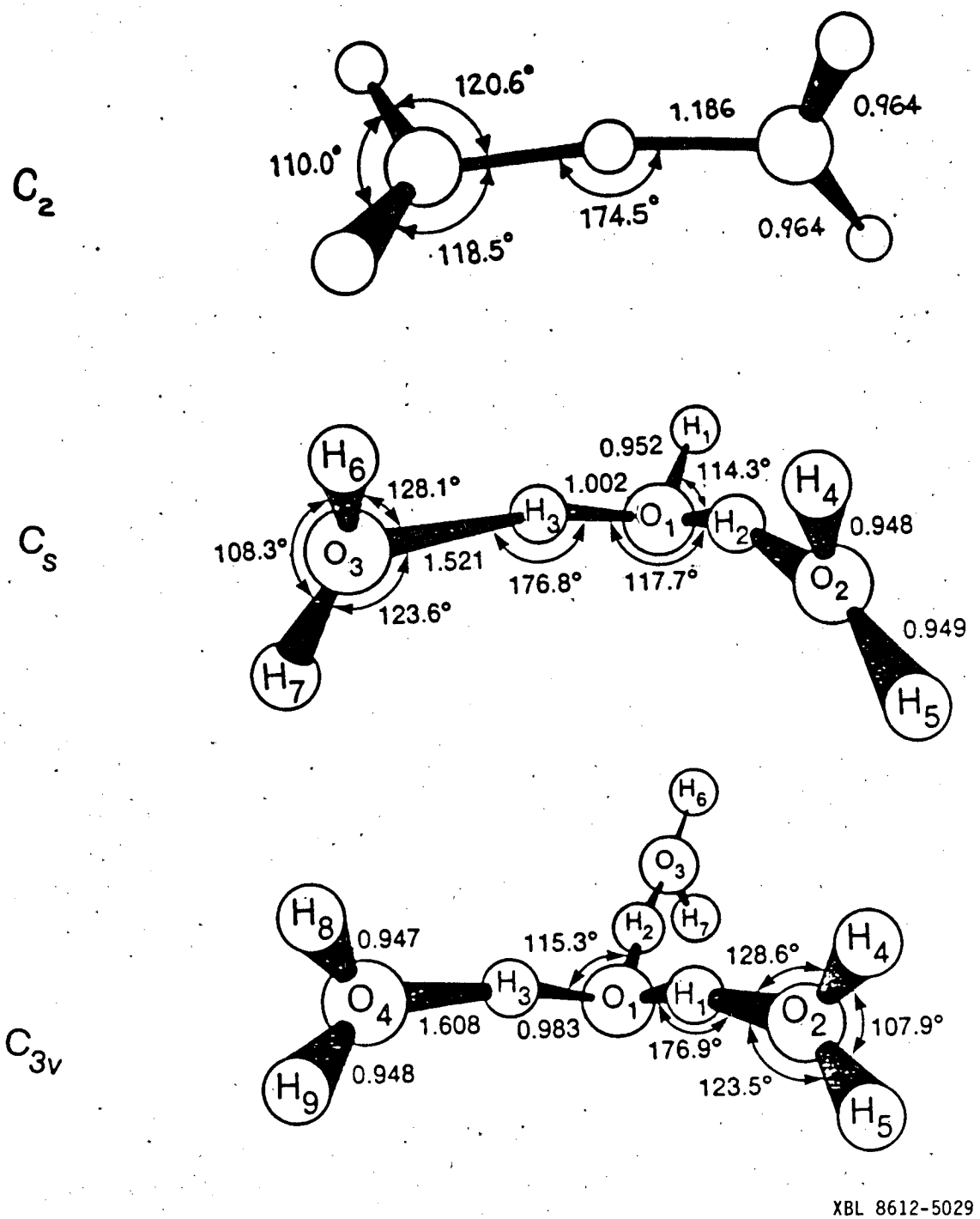
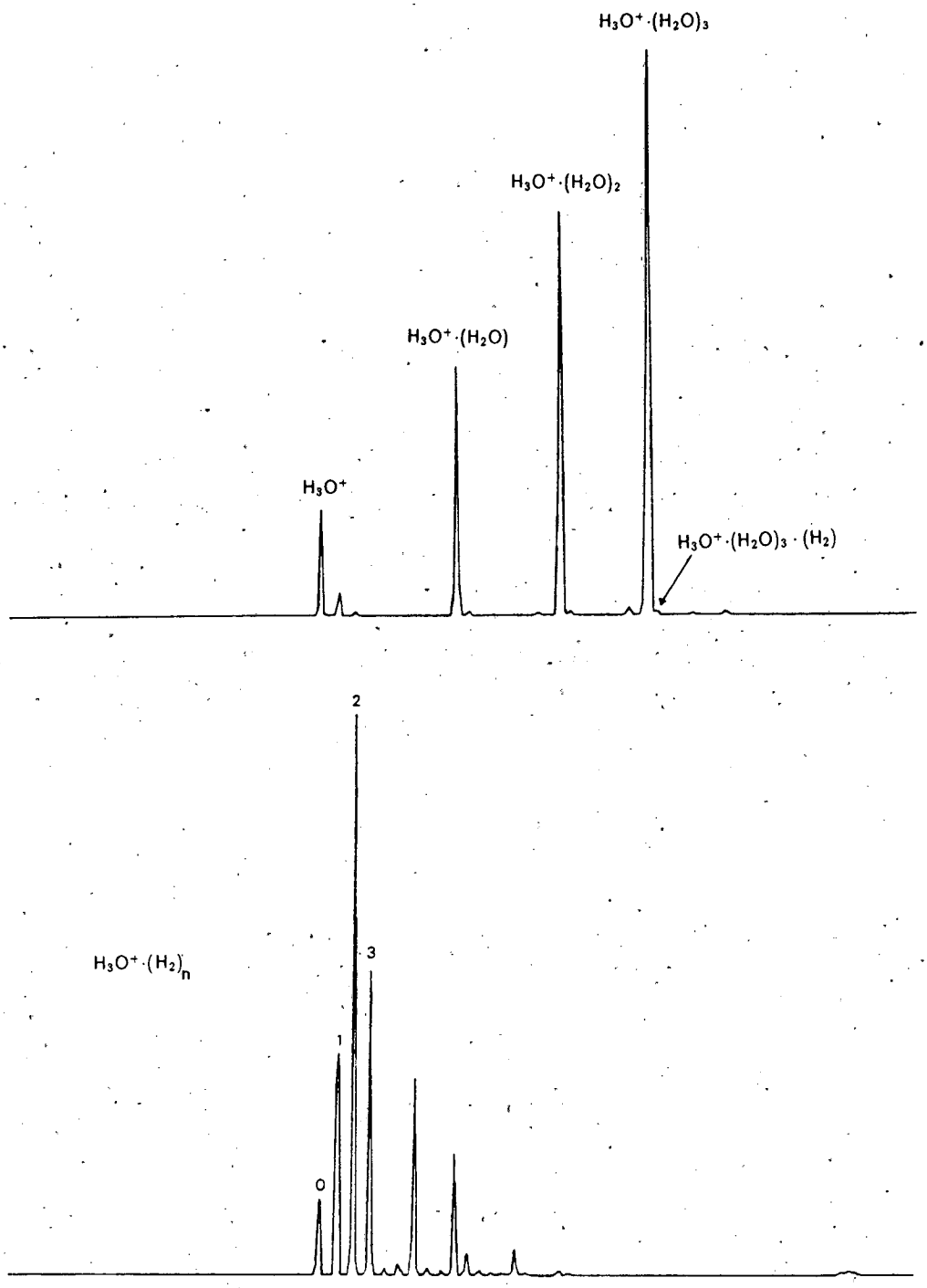

C2
120.6°
110.0°
118.5°
1.186
174.5°
0.964
0.964
Cs
H6
128.1°
108.3°
O3
1.521
123.6°
H7
H3
1.002
176.8°
H1
0.952
O1
114.3°
117.7°
H2
H4
0.948
O2
0.949
H5
C3v
H6
O3
H8
0.947
O4
1.608
H9
0.948
H3
115.3°
0.983
H2
H7
O1
H1
176.9°
128.6°
H4
O2
107.9°
123.5°
H5
XBL 8612-5029

Fig 2.



XBL 8612 5050

Fig. 3

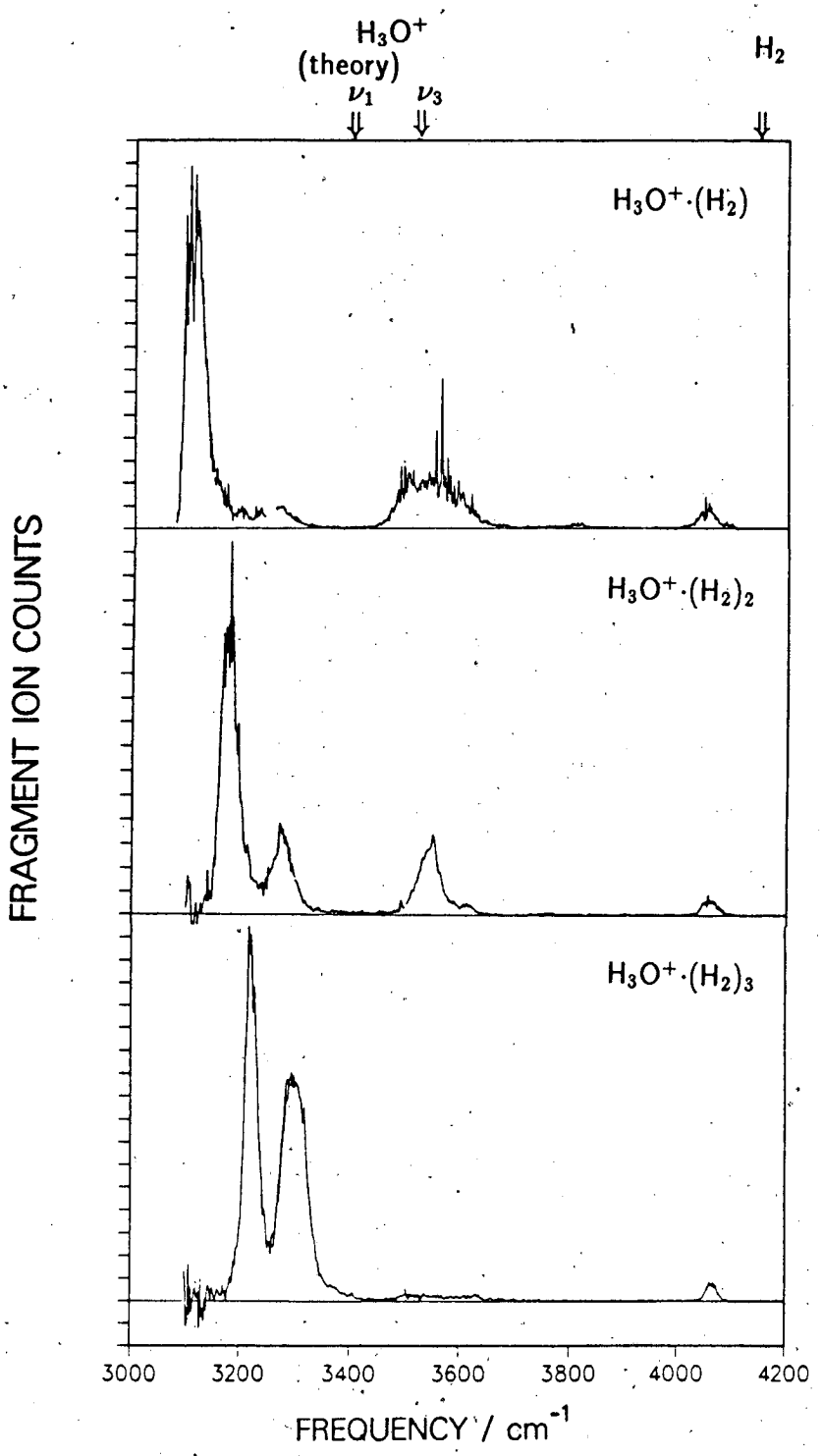
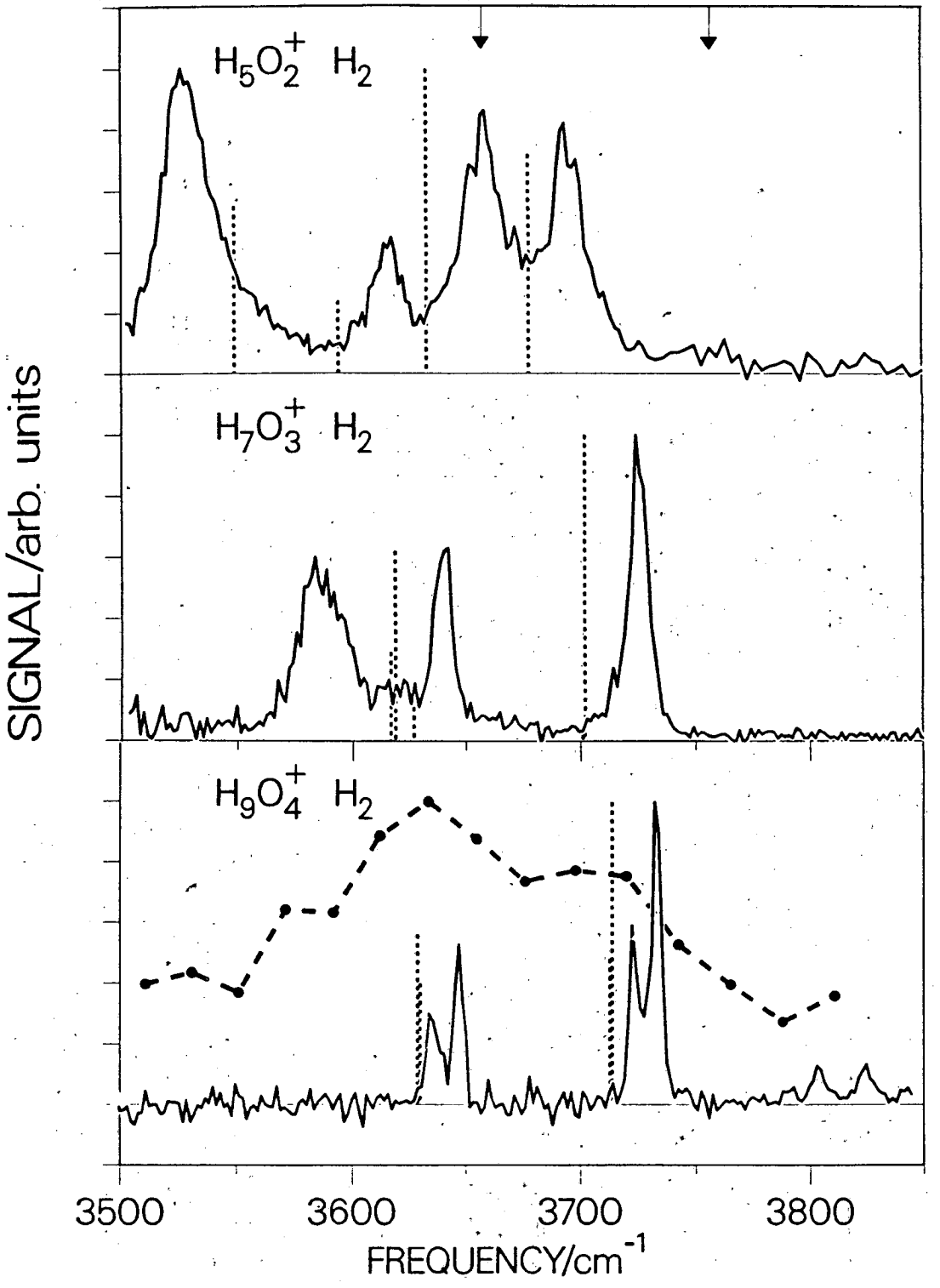
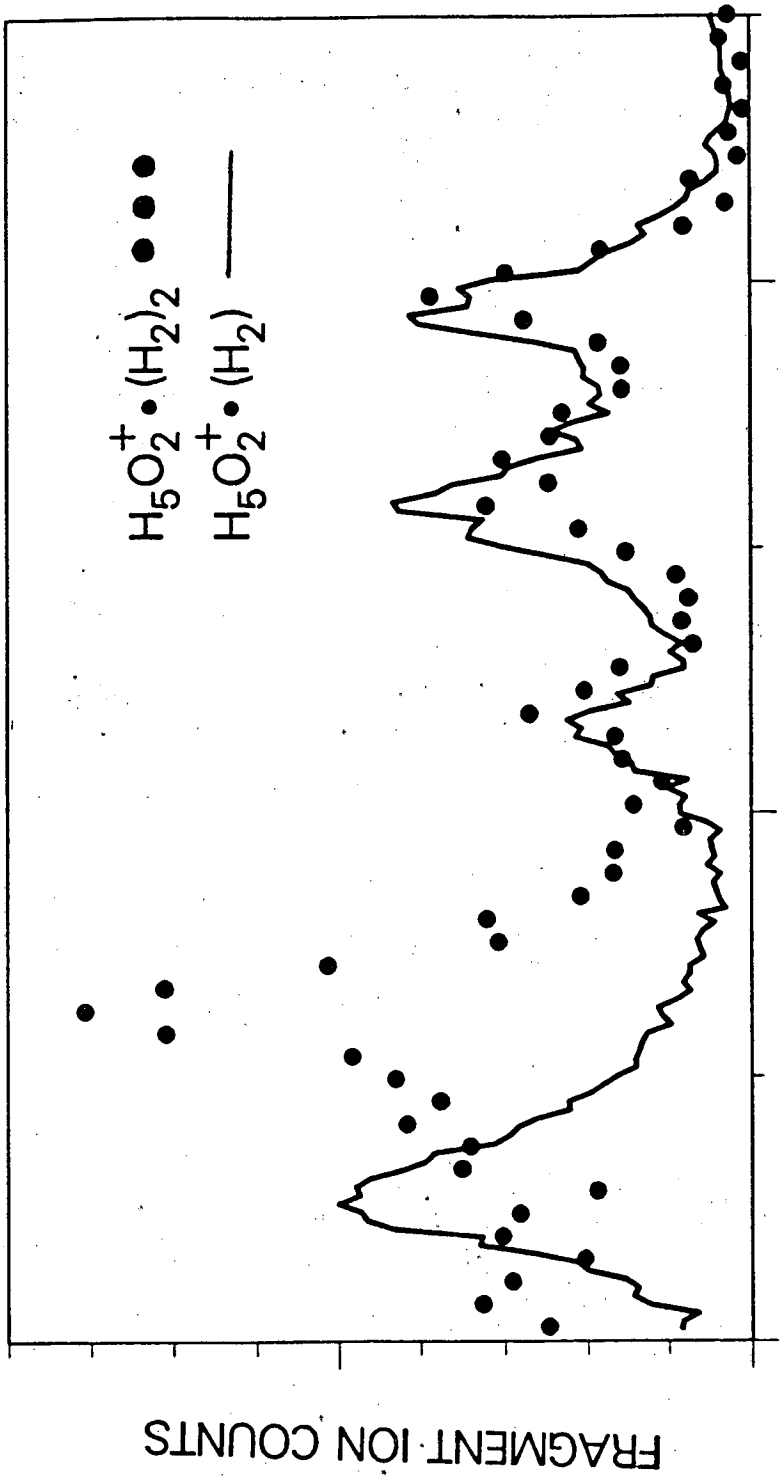

H_3O^+
(theory)
ν_1
ν_3
H_2
$H_3O^+\cdot(H_2)$
$H_3O^+\cdot(H_2)_2$
$H_3O^+\cdot(H_2)_3$
FRAGMENT ION COUNTS
3000
3200
3400
3600
3800
4000
4200
FREQUENCY / cm^{-1}
XBL 8612-5030

Fig. 4



XBL 8612 5049

Fig. 5



XBL 8612-5032

Fig.6

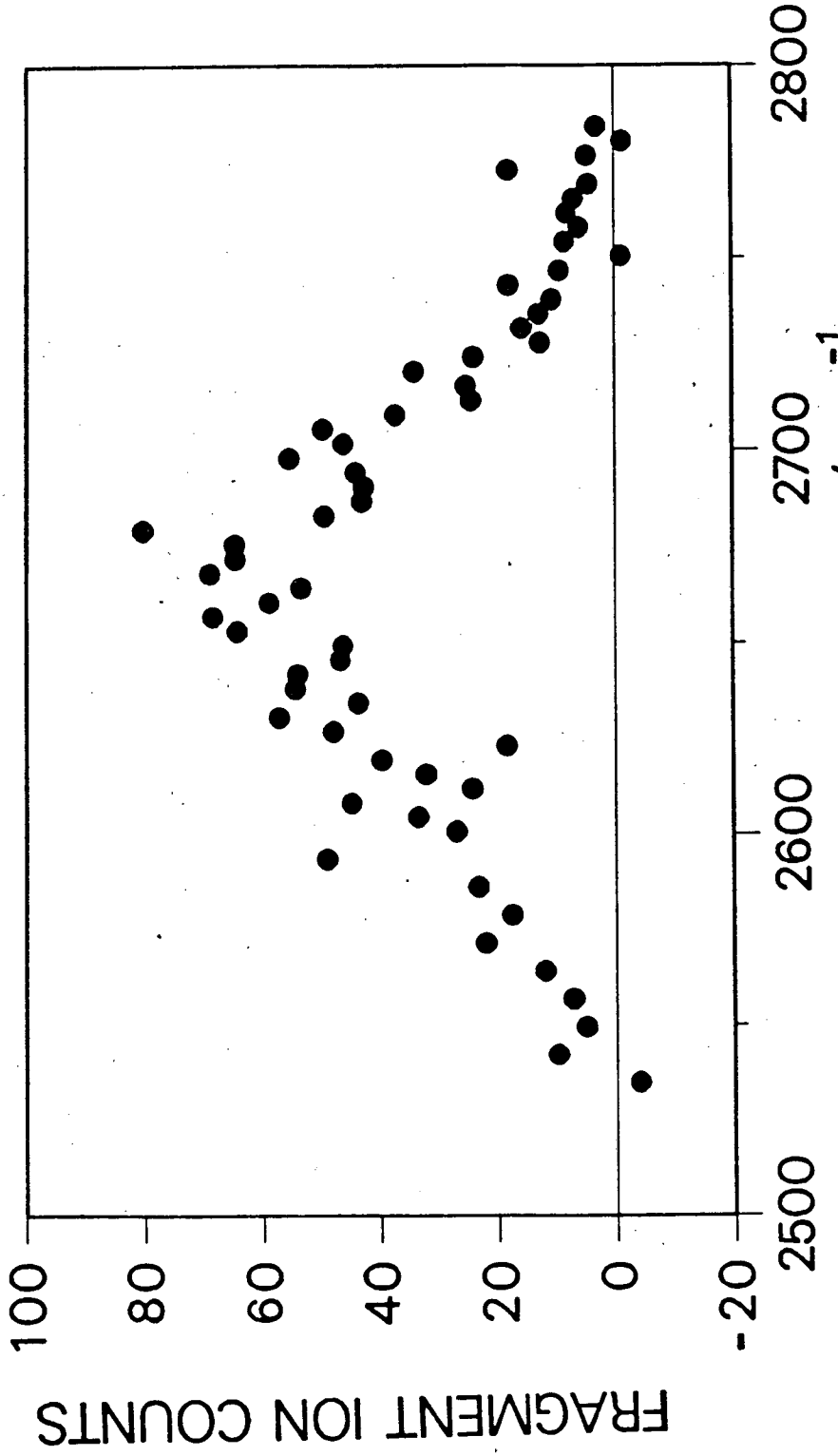


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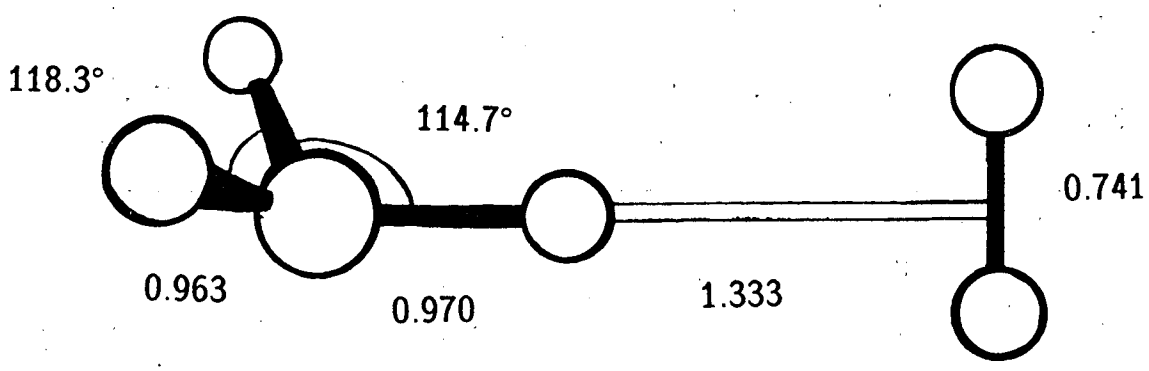
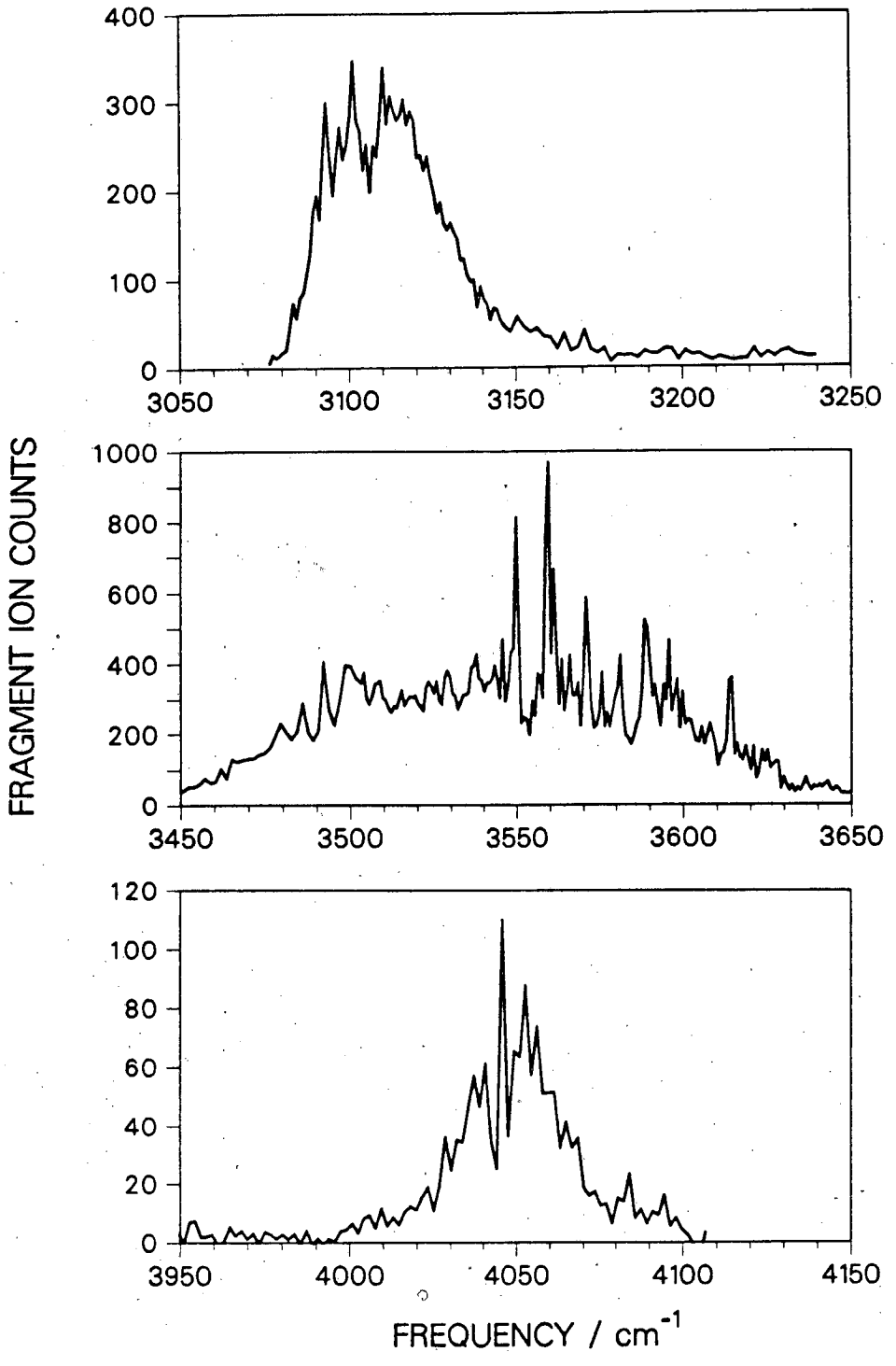
Fig. 7



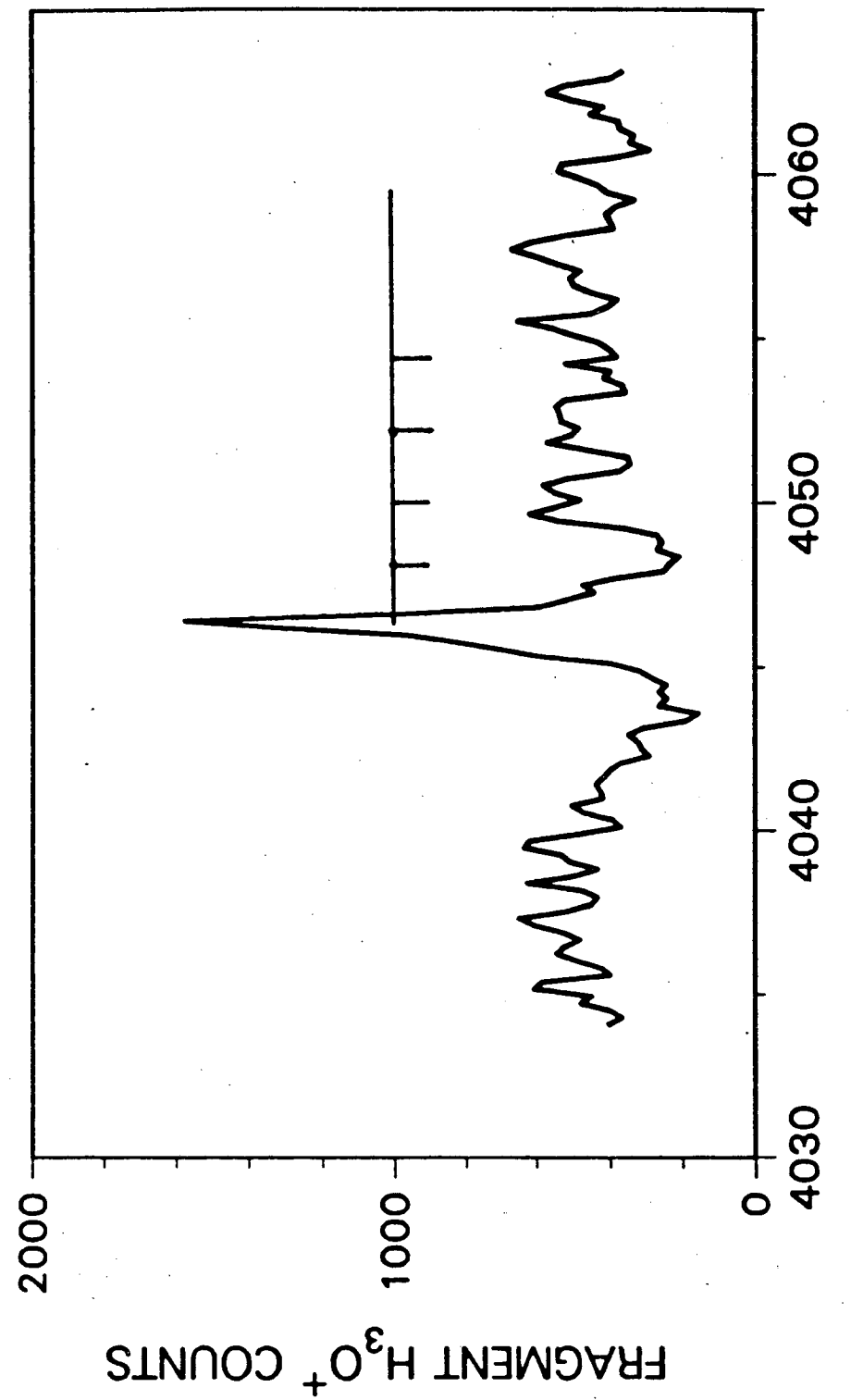
XBL 8612-5028

Fig. 8



XBL 8612 5051

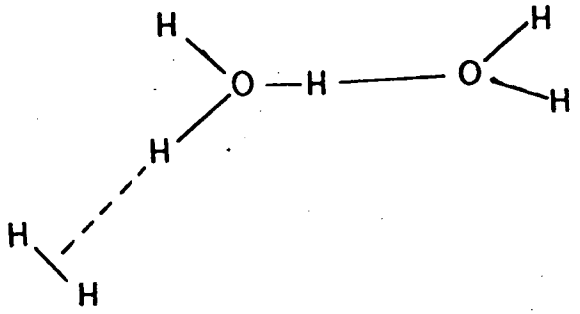
Fig. 9



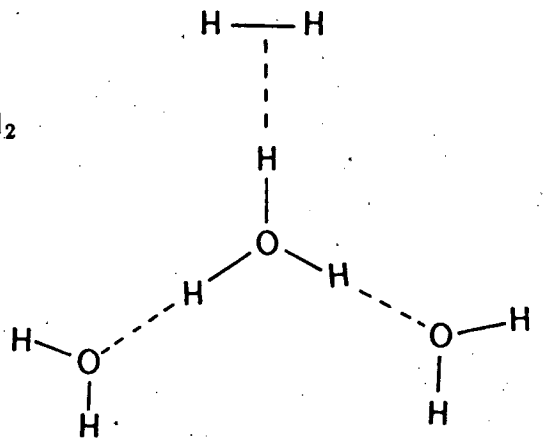
XBL 8612-5037

Fig. 10

$H_3O^+ \cdot (H_2O) \cdot H_2$



$H_3O^+ \cdot (H_2O)_2 \cdot H_2$



$H_3O^+ \cdot (H_2O)_3 \cdot H_2$

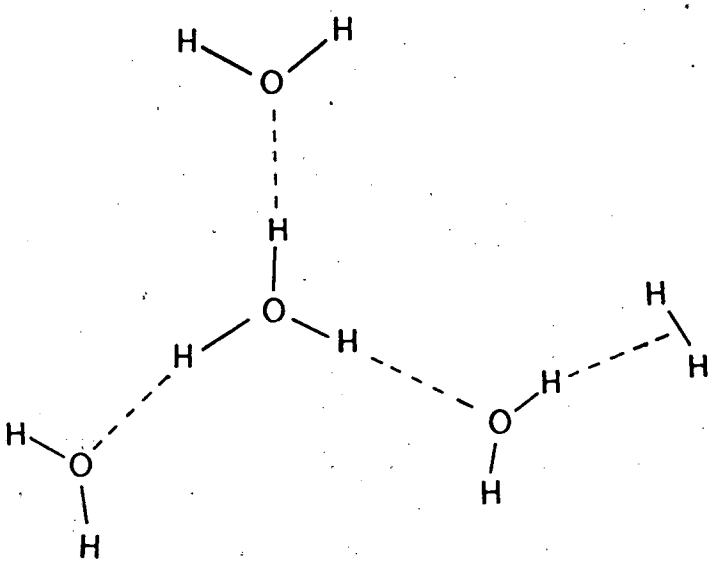


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Fig. 11

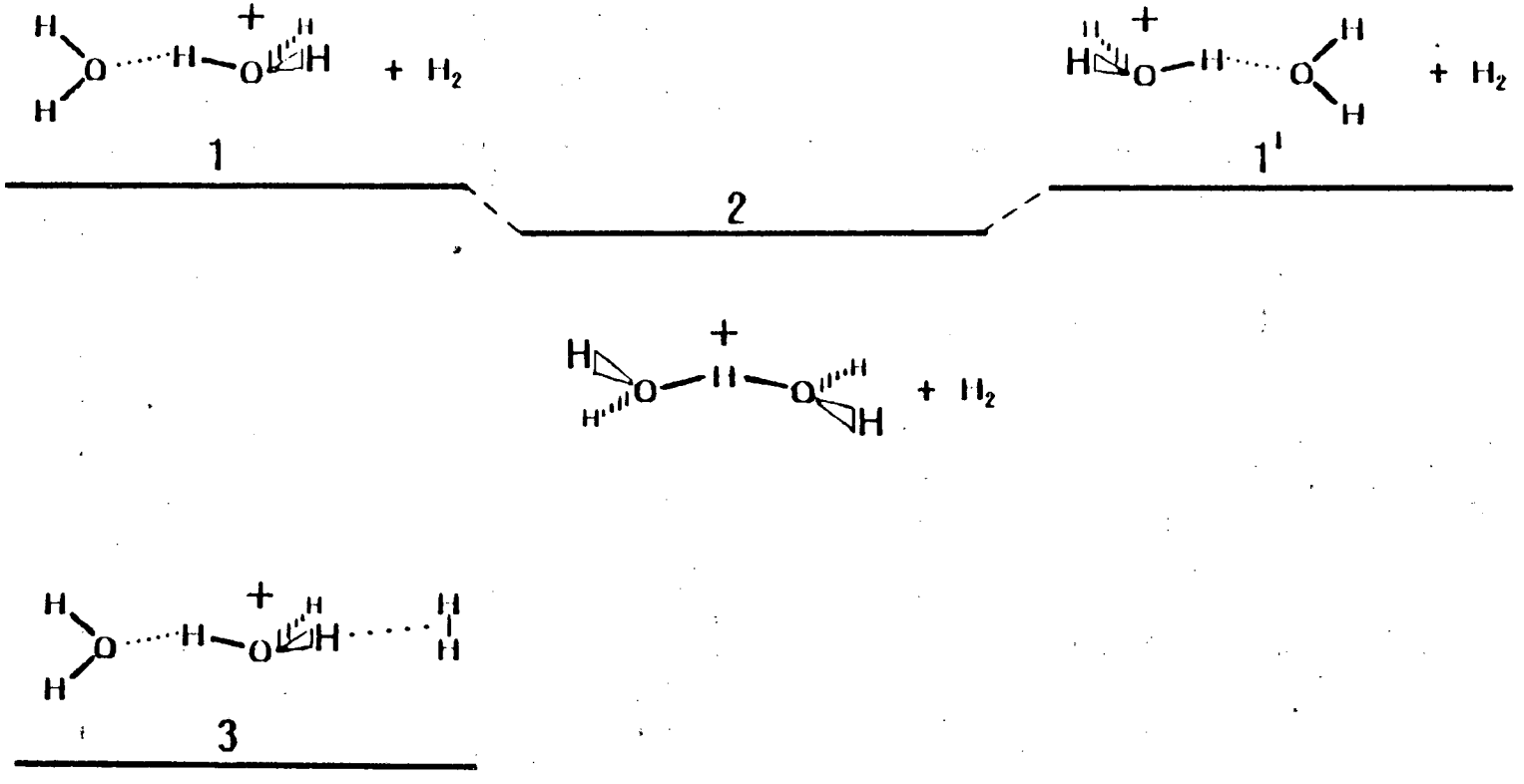

Fig. 12

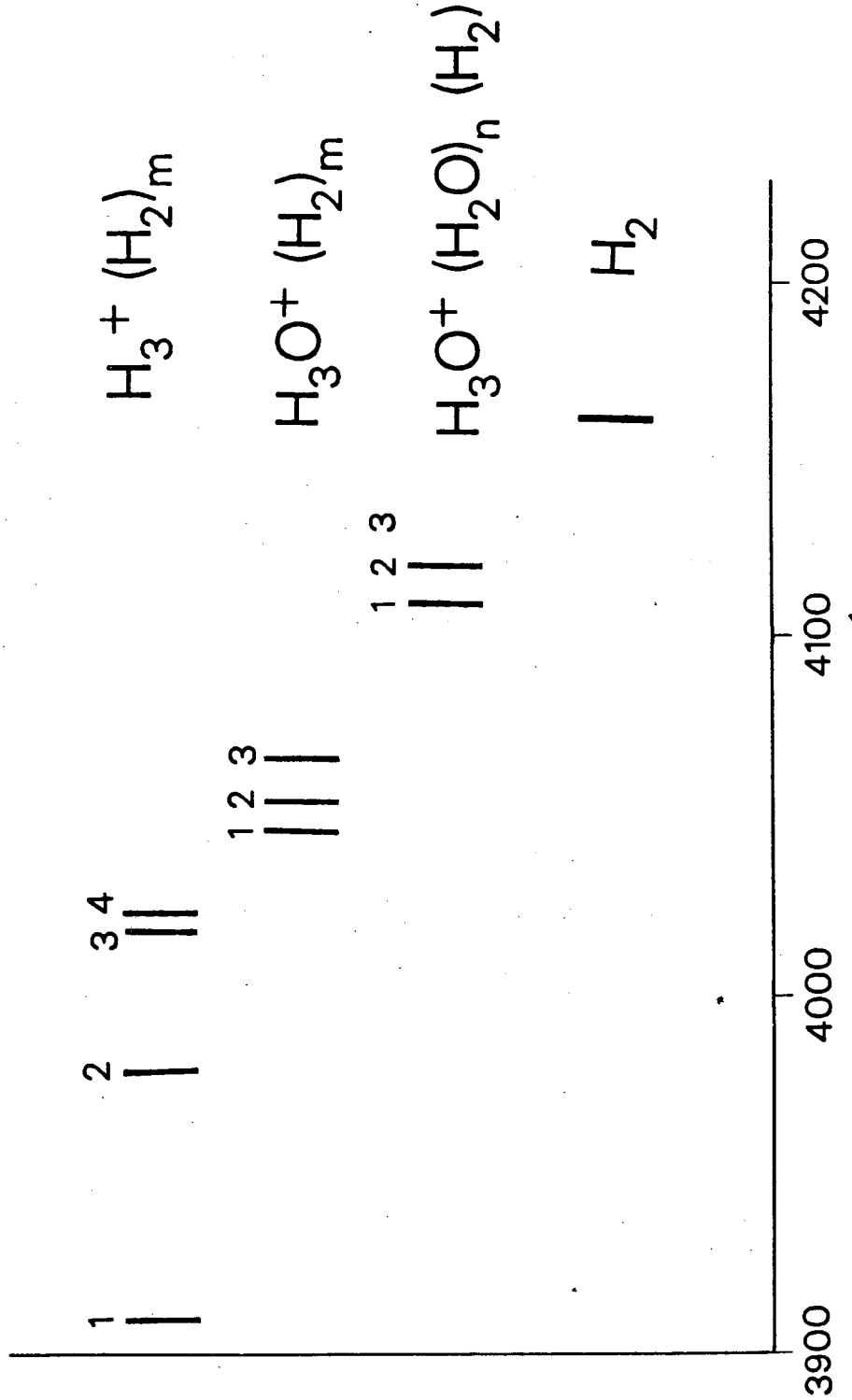

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Fig. 13

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