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INFRARED SPECTRA OF THE CLUSTER IONS $H_7O_3^+ \cdot H_2$ and $H_9O_4^+ \cdot H_2$ [a]

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ABSTRACT

Infrared spectra of hydrated hydronium ions weakly bound to an H_2 molecule, specifically $H_7O_3^+ \cdot H_2$ and $H_9O_4^+ \cdot H_2$, have been observed. Mass-selected parent ions, trapped in a radio frequency ion trap, are excited by a tunable infrared laser; following absorption, the complex predissociates with loss of the H_2, and the resulting fragment ions are detected. Spectra have been taken from 3000 to 4000 cm^{-1}, with a resolution of 1.2 cm^{-1}. They are compared to recent theoretical and experimental spectra of the hydronium ion hydrates alone. Binding an H_2 molecule to these clusters should only weakly perturb their vibrations; if so, our spectra should be similar to spectra of the hydrated hydronium ions $H_7O_3^+$ and $H_9O_4^+$.

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In a pioneering experiment(1), Schwarz measured the infrared absorption spectra of the ions $H_3O^+ \cdot nH_2O$ (n=3-5) in the gas phase. Physical chemists have studied hydronium ion hydrates for several decades(2-9), but previous IR spectra, all taken in the condensed phase, have often been difficult to interpret. Uncertainty arising from low resolution (40 cm^{-1}) and lack of mass selectivity has led to recent questioning of some assignments of the broad features Schwarz observed(8,9). We report new infrared spectra of the $H_7O_3^+$ and $H_9O_4^+$ clusters, obtained from the vibrational predissociation of the complexes of these ions with an H_2 molecule.

In a previous paper(10), we have reported IR spectra of the protonated hydrogen clusters H_n^+ (n=5,7,9) in the H_2 stretching region (~4000 cm^{-1}). Upon absorption of a photon, the H_5^+ could dissociate to $H_3^+ + H_2$. Spectra are recorded by counting the fragment H_3^+ produced as a function of photon frequency. Initial mass selection allows unambiguous identification of the absorbing species. Unfortunately, the hydrogen bonds in hydrated hydronium ions are too strong (D_0>17 kcal/mol)(3,5,9) to be broken by exciting a single OH stretch quantum . To apply our technique to these ions, we have investigated water clusters with an H_2 molecule attached: $H_7O_3^+ \cdot H_2$ and $H_9O_4^+ \cdot H_2$. Our assumption is that the H_2 would bind weakly, resulting in small perturbations of the vibrations of the cluster(11). The H_2 acts as a "messenger"; detection of the water cluster/H_2 complex predissociation allows us to indirectly observe absorption by the hydrated hydronium ion itself.

The ions were created in a high pressure corona discharge(12) of hydrogen (200 torr, -10°C). The plasma was expanded through a 75μ nozzle and skimmed. To eliminate collisional heating, the electric field between nozzle and skimmer was less than 0.5 V/cm. This source could create rotationally cold ions with vibrations equilibrated with the source temperature. Trace water impurity in the gas line resulted in a mass spectrum dominated by water clusters; 1% to 10% of these ions had an H_2 molecule attached.

After the skimmer, the ions were accelerated to 350 eV, mass analyzed, decelerated to 0.5 eV, and trapped in a radio frequency octupole ion trap. After 1 ms, an infrared laser was fired into the trap. The laser was a difference frequency laser (Quanta Ray IR-WEX) tunable from 2200 to 6500 cm^{-1}, with a pulse energy of 0.2 to 1 mJ and a linewidth of 1.2 cm^{-1}. After photolysis, the ions were released from the trap, and detected with a quadrupole mass spectrometer.

Spectra of $H_7O_3^+ \cdot H_2$ (trimer) and $H_9O_4^+ \cdot H_2$ (tetramer) are shown in Fig. 1. These are the only major bands observed from 3000 cm^{-1} to 4000 cm^{-1}. A section of Schwarz's tetramer spectrum(1) is shown in Fig. 1b. He was unable to observe the trimer spectrum, but did conclude that the tetramer spectrum included trimer contributions. The broad envelope observed by Schwarz has been reduced in the current spectrum to four sharp peaks whose positions match the partially resolved structure. The improvement results from higher resolution, low rotational temperature, and lack of absorption from other clusters.

The tetramer spectrum consists of two doublets centered at 3640 and 3730 cm^{-1}. They lie close to the vibrational origins of the free H_2O symmetric and antisymmetric stretches at 3657 and 3756 cm^{-1} respectively(arrows in Fig. 1a)(13), and are probably OH stretches of the three solvating H_2O ligands. The doublets may arise from splitting of the triply degenerate vibrations into A and E normal modes. In the trimer spectrum, two corresponding bands appear along with a third peak to the red at 3590 cm^{-1}. We assign this last band to the free O-H stretch of the H_3O^+.

Stick spectra in Fig. 1 are from Hartree Fock SCF calculations (DZ+P basis set) of the hydrated hydronium ions (without messenger) by Remington and Schaefer(9). They have empirically scaled the harmonic frequencies obtained at optimized geometries to account for systematic error and anharmonicity(14). The agreement is satisfactory, given the level of theory and the floppiness of the clusters.

Schwarz has assigned stretches of the hydrogen-bonded OH bonds to bands at 2660 cm^{-1} and 3000 cm^{-1} in $H_9O_4^+$ and to an absorption at 2200 cm^{-1} in $H_7O_3^+$. (DZ+P)/SCF theory does not support this assignment(9), suggesting instead that the 2660 cm^{-1} band belongs to $H_7O_3^+$; however, Remington and Schaefer concede that scaling <u>ab initio</u> frequencies of such strongly perturbed modes may be inaccurate. Despite low laser power, we have observed a band at ~2650 cm^{-1} for $H_9O_4^+ \cdot H_2$ and absorption only below 2500 cm^{-1} for $H_7O_3^+ \cdot H_2$, confirming Schwarz's conclusion.

The primary uncertainty in our spectra lies in the extent of perturbation caused by the H_2 messenger. Hydration of H_3O^+

delocalizes the charge, resulting in a weak bond between H_2 and the water cluster. H_2 tends to bond to the proton of protonated species(11), and may bind to the trimer at the free OH of the H_3O^+, decreasing the frequency of that stretch. 3590 cm^{-1} would be a lower limit for the unperturbed value. The tetramer is likely to be less perturbed than the trimer; like the cluster H_9^+, it forms a completed inner shell. We previously observed that binding an H_2 to H_9^+ shifted the ion's 4020 cm^{-1} band by only 8 cm^{-1}.

Another measure of the perturbation comes from the intensity and frequency of the H_2 stretch absorption. The fundamental of H_2 is a dipole-forbidden transition at 4161 cm^{-1}(15), which red-shifts and becomes allowed when the H_2 is bound to an ion(11). This absorption is red-shifted by 140 cm^{-1} in H_9^+(10). We have observed a weak band with a 50 cm^{-1} shift for $H_7O_3^+ \cdot H_2$ and no detectable absorption for $H_9O_4^+ \cdot H_2$. H_2 is thus more weakly bound to the water clusters than to H_7^+, i.e. D_0<4 kcal/mol. Resolution of this problem awaits spectra of the clusters either alone or bound to other messengers.

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FIGURE CAPTION

FIG. 1. a) Infrared vibrational predissociation spectrum of $H_7O_3^+ \cdot H_2$ at a resolution of 1.2 cm^{-1}. Arrows at the top indicate vibrational band origins in H_2O, from Ref. 13. Stick spectra (·····) are derived from ab initio SCF calculations of $H_7O_3^+$ (C_s symmetry) by Remington and Schaefer, Ref. 9. The calculated harmonic frequencies were scaled (see text). b) Spectrum of $H_9O_4^+ \cdot H_2$. Stick spectra (·····) are from ab initio calculations of $H_9O_4^+$ (C_{3v} symmetry) by Remington and Schaefer, Ref. 9. (-●-) Absorption spectrum of $H_9O_4^+$ at a resolution of 40 cm^{-1} obtained by Schwarz, Ref. 1.

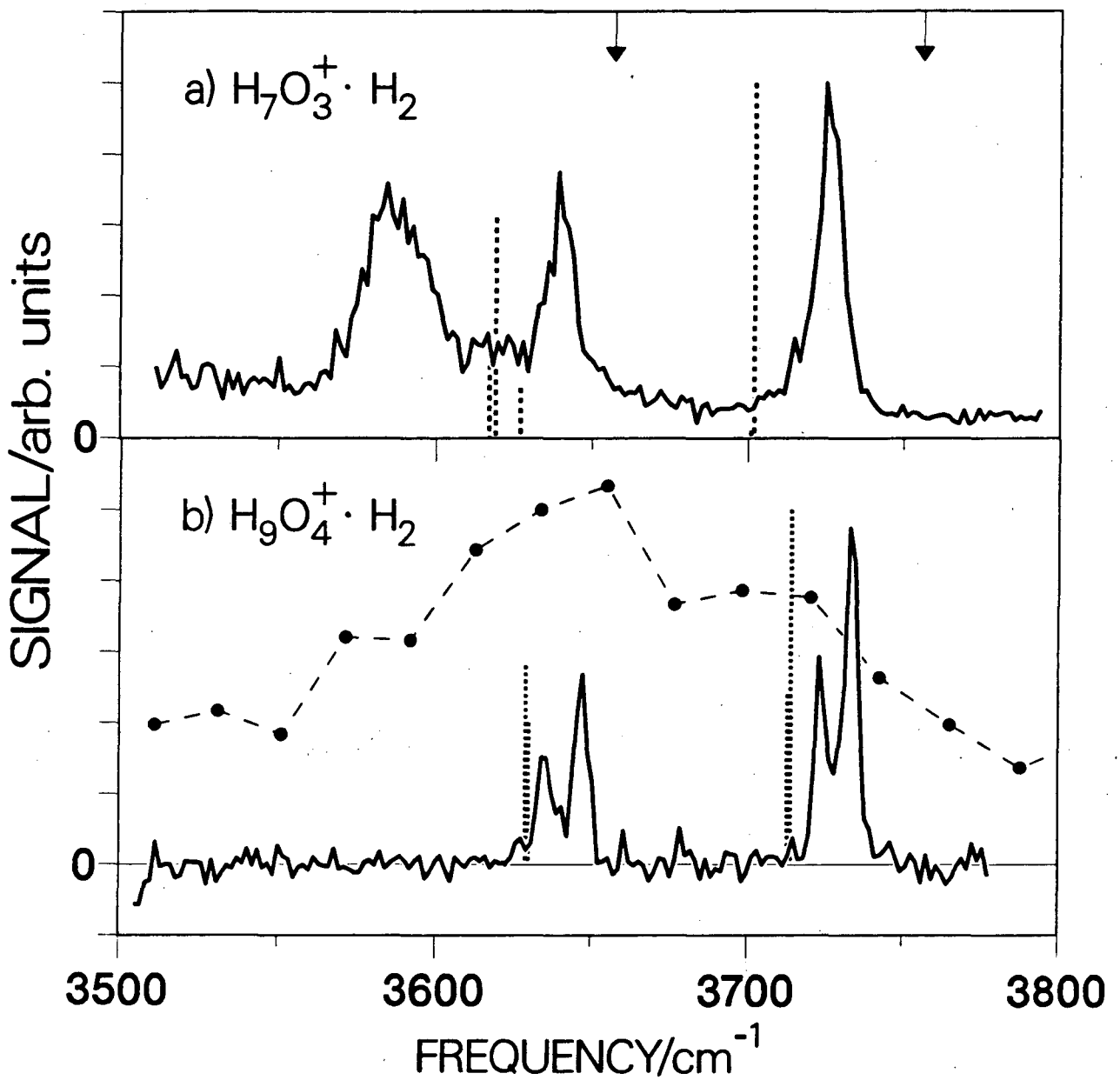

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Fig. 1

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