

Infrared spectra of the cluster ions $\text{H}_7\text{O}_3^+ \cdot \text{H}_2$ and $\text{H}_9\text{O}_4^+ \cdot \text{H}_2$ ^{a)}

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In a pioneering experiment,¹ Schwarz measured the infrared absorption spectra of the ions $\text{H}_3\text{O}^+ \cdot n\text{H}_2\text{O}$ ($n = 3-5$) 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 ($\sim 4000 \text{ cm}^{-1}$). Upon absorption of a photon, the H_5^+ could dissociate to $\text{H}_3^+ + \text{H}_2$. 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 ($D_0 > 17 \text{ kcal/mol}$)^{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: $\text{H}_7\text{O}_3^+ \cdot \text{H}_2$ and $\text{H}_9\text{O}_4^+ \cdot \text{H}_2$. 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 discharge¹² 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%–10% of these ions had an H_2 molecule attached.

After the skimmer, the ions were accelerated to 350 eV, mass selected, 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 $\text{H}_7\text{O}_3^+ \cdot \text{H}_2$ (trimer) and $\text{H}_9\text{O}_4^+ \cdot \text{H}_2$ (tetramer) are shown in Fig. 1. These are the only major bands observed from 3000 to 4000 cm^{-1} . A section of Schwarz's tetramer spectrum¹ is shown in Fig. 1(b). 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. 1(a)],¹³ and are probably OH stretches of the three solvating H_2O ligands. 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^+ . On closer inspection, at least one band, the 3733 cm^{-1} band of $\text{H}_9\text{O}_4^+ \cdot \text{H}_2$, shows partially resolved structure, limited by the laser linewidth. Several other bands have irregular, asymmetric band shapes, implying that the observed linewidths are due in part to unresolved rotational structure.

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 ob-

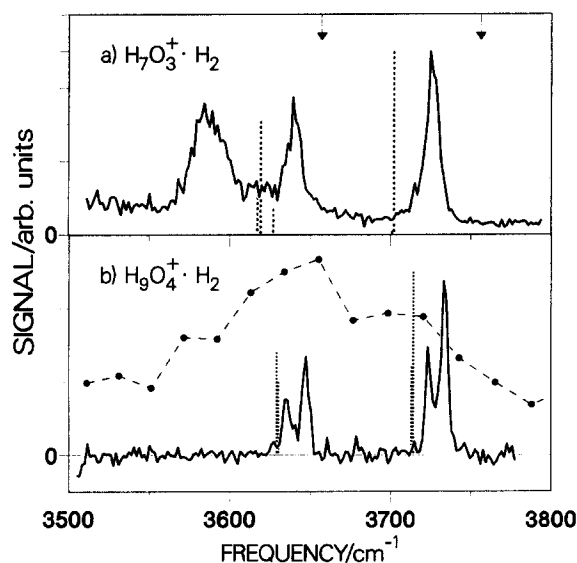


FIG. 1. (a) Infrared vibrational predissociation spectrum of $\text{H}_7\text{O}_3^+ \cdot \text{H}_2$ at a resolution of 1.2 cm^{-1} . Arrows at the top indicate vibrational band origins in H_2O , from Ref. 13. Stick spectra (...) are derived from *ab initio* SCF calculations of H_7O_3^+ (C_3 symmetry) by Remington and Schaefer, Ref. 9. The calculated harmonic frequencies were scaled (see the text). (b) Spectrum of $\text{H}_9\text{O}_4^+ \cdot \text{H}_2$. 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.

tained 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 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 *ab initio* frequencies of such strongly perturbed modes may be inaccurate and are carrying out a higher-level treatment. Despite low laser power, we have observed a featureless band at $\sim 2670 \text{ cm}^{-1}$ with a width of 100 cm^{-1} (FWHM) for $\text{H}_9\text{O}_4^+ \cdot \text{H}_2$ and absorption only below 2500 cm^{-1} for $\text{H}_7\text{O}_3^+ \cdot \text{H}_2$, 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 $\text{H}_7\text{O}_3^+ \cdot \text{H}_2$ and no detectable absorption for $\text{H}_9\text{O}_4^+ \cdot \text{H}_2$. H_2 is thus more weakly bound to the water clusters than to H_7^+ , i.e., $D_0 < 4 \text{ kcal/mol}$. Resolution of this

problem awaits spectra of the clusters either alone or bound to other messengers.

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Dynamical effects in the vibrational predissociation of ICl-rare gas complexes^{a)}

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In this communication, we report the highly peaked, nonstatistical rotational distribution of ICl photofragments formed upon vibrational predissociation of ICl-Ne and ICl-Ne van der Waals (vdW) complexes in the $B^3\Pi_{0+}$ state. The photodissociation of vdW complexes represents a unique opportunity to study the basic principles of simple fragmentation phenomenon.¹⁻³ The complexes are prepared at extremely cold temperatures, their dissociation is initiated in a state specific manner, and only a small amount of energy is disposed in products. The nascent rotational distribution provides an important key to the dynamics of the photodis-

sociation event, reflecting the details of the potential energy surface along the reaction coordinate.⁴⁻⁷ For a shallow and slowly varying potential surface, a statistical distribution over final rotational states is expected.⁸ The results presented here suggest a strongly repulsive final interaction between the departing rare gas atom and ICl molecule.

Optical-optical double resonance techniques are used to elucidate the unimolecular dissociation dynamics of ICl-rare gas vdW complexes. Optical excitation of the vdW satellite feature associated with the $I^35\text{Cl } B^3\Pi_{0+} (v_B = 2) - X^1\Sigma^+ (v_X = 0)$ transition prepares the complex in a subset