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THE VIBRATIONAL PREDISSOCIATION SPECTROSCOPY OF HYDROGEN CLUSTER IONS[a]

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Abstract

The first infrared spectra of protonated hydrogen clusters in the gas phase have been observed. Predissociation spectra were taken with a tandem mass spectrometer: mass selected hydrogen cluster ions were irradiated inside a RF ion trap by a tunable infrared laser, and the fragment ions created by photodissociation of the clusters were mass selected and detected. Spectra for each product channel were measured by counting fragment ions as a function of laser frequency. Low resolution spectra ($\Delta\nu$= 10 cm^{-1}) in the region from 3800 cm^{-1} to 4200 cm^{-1} were observed for the ions H_5^+, H_7^+ and H_9^+ at 3910 cm^{-1}, 3980 cm^{-1}, and 4020 cm^{-1} respectively. A band was also observed for H_5^+ at 3532 cm^{-1}. No rotational structure was resolved. The frequencies of the band maxima agree well with the frequencies predicted by previous *ab initio* calculations for the highest modes.

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Weakly bound ionic clusters have been studied extensively in thermochemical and kinetic experiments over the past decade(1). However, very little spectroscopy has been done(2,3), despite recent advances in molecular ion spectroscopy(4). Much of our understanding of the dynamics and structure of cluster ions to date has relied on the results of ab initio quantum calculations. Stimulated by the theoretical work, we have begun experiments on the infrared spectroscopy of cluster ions. In this communication we report the first spectroscopic observation of the protonated hydrogen clusters H_n^+ (n=5,7 and 9).

According to CI calculations(5), the hydrogen cluster ions are H_3^+ ions with hydrogen molecules complexed around it, with the first three molecules coordinated to the corners of the H_3^+. Several experiments have measured the enthalpies of $H_5^+ \rightarrow H_3^+ + H_2$ and $H_7^+ \rightarrow H_5^+ + H_2$. The most recent results(6,7) give dissociation energies of approximately 6 kcal/mol (2100 cm^{-1}) and 3 kcal/mol (1000 cm^{-1}) respectively, in agreement with the CI calculations of Yamaguchi, Gaw and Schaefer(5). Yamaguchi et al have also calculated the vibrational frequencies for H_5^+, H_7^+ and H_9^+. The highest frequency modes are red-shifted from the free H_2 frequency (4161 cm^{-1}) by 100 to 270 cm^{-1}, and correspond to stretching of the H_2 moieties. Next is a mode corresponding to the 3220 cm^{-1} symmetric stretch of H_3^+. Upon excitation of these modes, the clusters will vibrationally predissociate, and the absorption can be detected by monitoring the products.

The experiment is discussed briefly here(8). A molecular beam containing clusters of hydrogen molecules was formed by expanding hydrogen (stagnation conditions 130°K, 20 to 30 atm) through a 10 μ nozzle. Electron impact ionization of the neutral clusters produced odd mass cluster ions(9). The ion beam passed through a magnetic mass filter to select the parent cluster to be studied. The ions were then decelerated and stored in a radio frequency octupole ion trap for 0.5 ms, after which a tunable infrared laser was fired into the trap. After 1 ms, the ions were released from the other side of the trap into a quadrupole mass spectrometer to select and count only a specific product ion. The sequence was then repeated without the laser, and the signal was obtained by subtracting this background. Spectra were taken for each dissociation channel by counting product ions as a function of laser frequency.

A $LiNbO_3$ optical parametric oscillator(OPO), pumped by the far field of a Quanta Ray Nd:YAG laser, was tuned between 3800 and 4200 cm^{-1} to find the H_2 stretching modes. For these preliminary experiments, the linewidth was approximately 10 cm^{-1}. The Doppler width of the trapped ions was estimated to be <0.2 cm^{-1}. The peaks of the observed bands for H_5^+, H_7^+ and H_9^+ are listed in table I. The frequencies calculated for these transitions, after a semi-empirical correction(5), agree with our results to within 45 cm^{-1}. Initial searches were also performed below 3600 cm^{-1} using an F-center laser, with a resolution of 0.5 cm^{-1}. A band was observed for H_5^+ at 3532 cm^{-1}, ~70 cm^{-1} higher than predicted by theory.

The spectrum of H_5^+ is shown in figure 1. No rotational structure has been resolved, although the rotational spacing for the $\Delta J=\pm 1$ transitions is estimated from the CI geometry to be 6 to 7 cm^{-1}. The lack of structure may be due to i) the low resolution of the laser, ii) spectral congestion caused by the high internal temperature of the molecule, and/or iii) homogeneous broadening. Preliminary experiments using a narrow bandwidth laser ($\Delta\nu \sim 0.5$ cm^{-1}) yield essentially the same spectra, ruling out (i). The predissociation lifetimes are unknown, but we do expect the spectra to be congested. Upon ionization of the neutral cluster, the reaction $H_2^+ + H_2 \rightarrow H_3^+ + H$ occurs rapidly within the cluster, accompanied by release of 40 kcal/mol into the internal modes. The excess energy is dissipated as the cluster fragments, but dissociation leaves the cluster ion in a wide distribution of excited rovibrational states. In the near future, we hope to eliminate the spectral congestion by using high pressure discharge sources to create internally cold cluster ions

Another feature of the spectrum is the long tail to the blue. This may arise from combination bands involving the low frequency stretching of the H_3^+ and H_2 moieties. The CI calculations(5) indicate that this motion involves intramolecular proton exchange, $H_3^+ \cdot H_2 \rightarrow H_2 . H_3^+$ with little or no barrier. Because the center of charge oscillates across the center of mass, the transition moment will be very large(10). The spectrum of H_5^+ is qualitatively different from those of the larger clusters; this result may reflect the different structure and larger binding energy of H_5^+, as predicted by theory(5).

The spectra of H_7^+, also shown in figure 1, are considerably

narrower than that of H_5^+, and the shoulder to the blue, while still present, is much weaker. We have observed both product channels, H_3^+ and H_5^+, and have obtained spectra for each. The spectra are similar, although the dissociation to H_3^+ is broader, with more intensity in the wings.

Spectra for larger hydrogen clusters (up to H_{15}^+) have been observed as well. The predissociation spectra of H_9^+ and larger are similar in appearance to those of H_7^+, but shifted to higher frequencies. After H_9^+, the peaks shift no further than 20 cm^{-1}. Apparently, once the corners of the H_3^+ are occupied, the additional H_2 molecules neither interact strongly with the H_9^+ core, nor absorb IR photons efficiently.

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TABLE I. Infrared absorption frequencies in cm^{-1} for the cluster ions H_5^+, H_7^+ and H_9^+.

	Experimental[a]	Calculated origin[b]
H_5^+	3532	3464[c]
	3910	3906[c]
H_7^+	3980	4025[d]
H_9^+	4020	4020[e]

a. This work. Peak of the observed band, to within 10 cm^{-1}.
b. ab initio calculations, from Ref. 5. The frequencies reported in Ref. 5 are harmonic frequencies obtained by analytic gradient SCF and CI calculations. The frequencies in this column have been corrected for anharmonicity and systematic deviations by subtracting the difference between the harmonic frequency calculated for H_2 and the experimental H_2 ($1 \leftarrow 0$) origin.
c. (6s2p/4s2p) basis set, single and double excitation CI (SDCI). See Ref. 10.
d. DZ+P basis set, SDCI. See Ref. 5.
e. DZ+P basis set, SCF. See Ref. 5.

Figure Captions.

FIG. 1. The infrared absorption spectra of hydrogen cluster ions at a resolution of ~10 cm^{-1}, normalized to equal height. The spectra were recorded by detecting predissociation product ions as a function of laser frequency. Upper plot: the spectrum of H_5^+ detecting H_3^+ fragments. Lower plot: the spectrum of H_7^+ detecting H_5^+ fragments (solid curve), and detecting H_3^+ fragments (points).

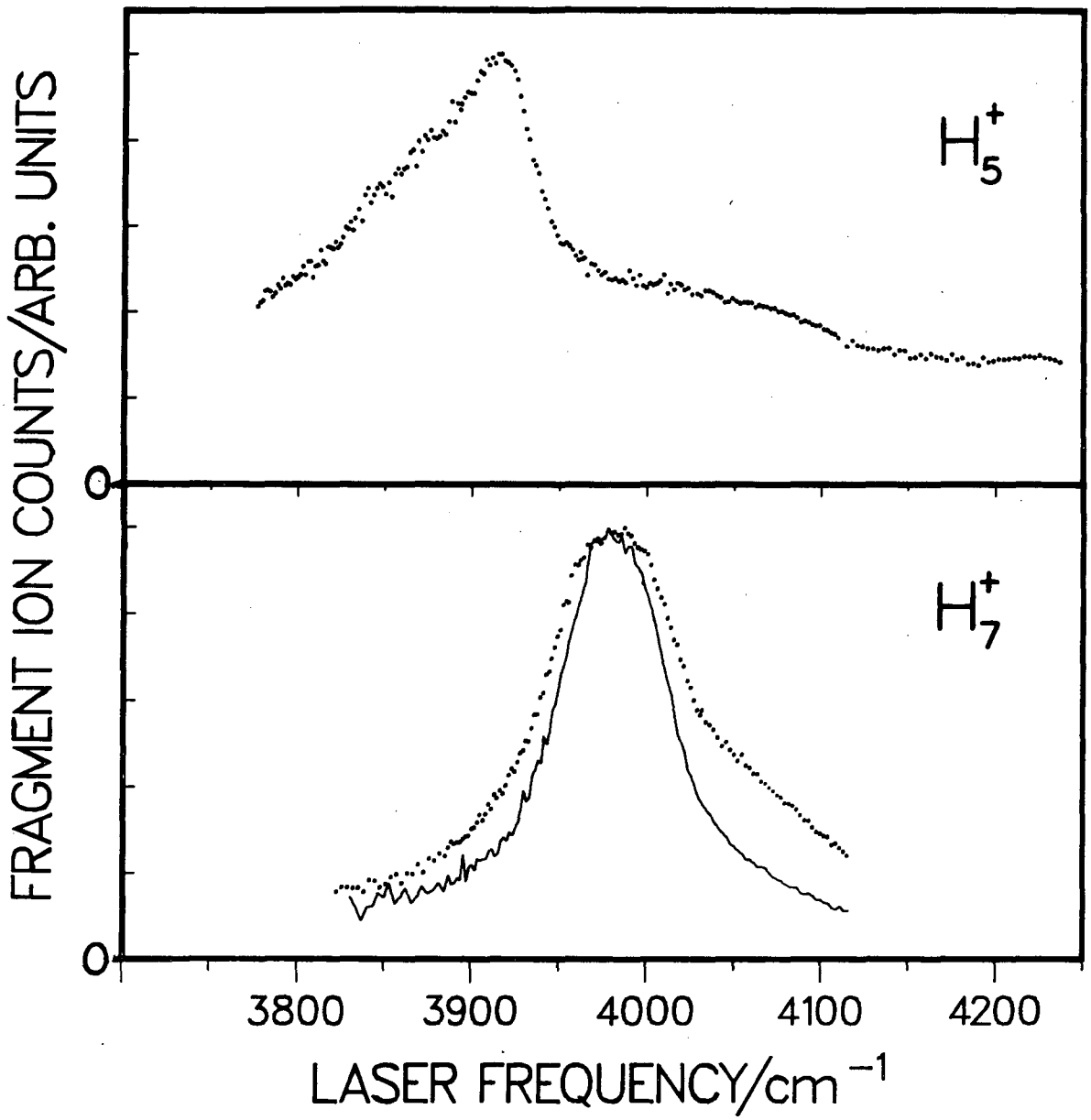

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Fig. 1

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