

Amano,⁶ but it has not been possible to observe the lower J value transitions.

In spite of the weakness of the signals, the different tests we have presented seem sufficiently conclusive to prompt radioastronomers to carry out new interstellar searches.

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- ¹C. M. Leung, E. Herbst, and W. F. Huebner, *Astrophys. J. Suppl. Ser.* **56**, 231 (1984).
²T. L. Allen, J. D. Goddard, and H. F. Schaefer, *J. Chem. Phys.* **73**, 3255 (1980), and references therein.
³N. N. Haese and R. C. Woods, *Chem. Phys. Lett.* **61**, 396 (1979).
⁴P. S. Dardi and C. E. Dykstra, *Astrophys. J.* **240**, L171 (1980).
⁵R. S. Altman, M. W. Crofton, and T. Oka, *J. Chem. Phys.* **80**, 3911 (1984).
⁶T. Amano, *J. Chem. Phys.* **81**, 3350 (1984).
⁷R. S. Altman, M. W. Crofton, and T. Oka, *J. Chem. Phys.* **81**, 4255 (1984).
⁸T. J. Lee and H. F. Schaefer, *J. Chem. Phys.* **80**, 2977 (1984).
⁹M. Bogey, C. Demuynck, and J. L. Destombes, *Astron. Astrophys. Lett.* (in press).
¹⁰F. C. De Lucia, E. Herbst, G. M. Plummer, and G. A. Blake, *J. Chem. Phys.* **78**, 2312 (1983).
¹¹C. V. Speller, M. Fitaire, and A. M. Pointu, *J. Phys. (Paris) Lett.* **43**, L499 (1982).

The vibrational predissociation spectroscopy of hydrogen cluster ions^{a)}

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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 result 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^+ ($n = 5, 7, \text{ and } 9$).

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 (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

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

	Experimental ^a	Calculated gin ^b	ori-
H_5^+	3532	... ^c	
	3910	3844 ^d	
H_7^+	3980	3992, 3995 ^e	
H_9^+	4020	4015 ^e	

^aThis 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 (1-0) origin.

^cThere is no empirical correction available for this mode. The symmetric stretch mode of the isolated H_3^+ ion has not been observed.

^dDZ + P basis set, full CI. See Ref. 10.

^eDZ + P basis set, SCF. See Ref. 5.

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 LiNbO₃ 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 H₂ 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 H₅⁺, H₇⁺, and H₉⁺ are listed in Table I. The frequencies calculated for these transitions, after a semiempirical correction,⁵ agree with our results to within 70 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 H₅⁺ at 3532 cm⁻¹, which we assigned as the H₃⁺ symmetric stretch analog.

The spectrum of H₅⁺ is shown in Fig. 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 H₂⁺ + H₂ → H₃⁺ + 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 H₃⁺ and H₂ moieties. The CI calculations⁵ indicate that this motion involves intramolecular proton exchange, H₃⁺ · H₂ → H₂ · H₃⁺ 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 H₅⁺ is qualitatively different from those of the larger clusters; this result may reflect the different structure and larger binding energy of H₅⁺, as predicted by theory.⁵

The spectra of H₇⁺, also shown in Fig. 1, are considerably narrower than that of H₅⁺, and the shoulder to the blue, while still present, is much weaker. We have observed both product channels, H₃⁺ and H₅⁺, and have obtained spectra for each. The spectra are similar, although the dissociation to H₃⁺ is broader, with more intensity in the wings.

Spectra for larger hydrogen clusters (up to H₁₅⁺) have been observed as well. The predissociation spectra of H₉⁺ and larger are similar in appearance to those of H₇⁺, but shifted to higher frequencies. After H₉⁺, the peaks shift no

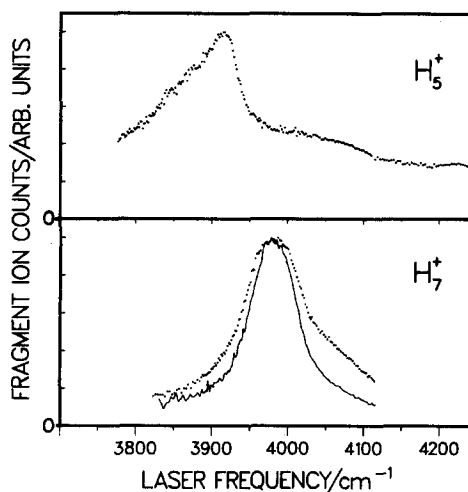


FIG. 1. The infrared absorption spectra of hydrogen cluster ions at a resolution of ~ 10 cm⁻¹, normalized to equal height. The spectra were recorded by detecting predissociation product ions as a function of laser frequency. Upper plot: the spectrum of H₅⁺ detecting H₃⁺ fragments. Lower plot: the spectrum of H₇⁺ detecting H₅⁺ fragments (solid curve), and detecting H₃⁺ fragments (points).

further than 20 cm⁻¹. Apparently, once the corners of the H₃⁺ are occupied, the additional H₂ molecules neither interact strongly with the H₃⁺ core, nor absorb IR photons efficiently.

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³P. Kebarle, *Annu. Rev. Phys. Chem.* **28**, 445 (1977); E. E. Ferguson, F. C. Fehsenfeld, and D. L. Albritton, in *Gas Phase Ion Chemistry*, edited by M. T. Bowers (Academic, New York, 1979), Vol. 1, p. 45; T. D. Mark and A. W. Castleman, Jr., *Adv. At. Mol. Phys.* **20**, 65 (1985); M. F. Jarrold, A. J. Illies, and M. T. Bowers, *J. Chem. Phys.* **82**, 1832 (1985).

⁴H. A. Schwarz, *J. Chem. Phys.* **67**, 5525 (1977); **72**, 284 (1980).

⁵M. Heaven, T. A. Miller, and V. E. Bondybey, *J. Chem. Phys.* **76**, 3831 (1982); L. F. DiMauro, M. Heaven, and T. A. Miller, *Chem. Phys. Lett.* **104**, 526 (1984).

⁶*Molecular Ions: Spectroscopy, Structure, and Chemistry*, edited by T. A. Miller and V. E. Bondybey (North-Holland, Amsterdam, 1983); R. J. Saykally and C. S. Gudeman, *Annu. Rev. Phys. Chem.* **35**, 387 (1984); R. J. Saykally and R. C. Woods, *ibid.* **32**, 403 (1981).

⁷Y. Yamaguchi, J. F. Gaw, and H. F. Schaefer III, *J. Chem. Phys.* **78**, 4074 (1983), and references therein.

⁸R. J. Beuhler, S. Ehrenson, and L. Friedman, *J. Chem. Phys.* **79**, 5982 (1983).

⁹M. T. Elford, *J. Chem. Phys.* **79**, 5951 (1983).

¹⁰M. Okumura, L. I. Yeh, and Y. T. Lee (in preparation). For further details see S. W. Bustamente, Ph.D. thesis, University of California, Berkeley, 1983; S. W. Bustamente, M. Okumura, D. Gehrlich, L. R. Carlson, H. S. Kwok, and Y. T. Lee (in preparation).

¹¹A. van Deursen and J. Reuss, *Int. J. Mass Spectrom. Ion Phys.* **11**, 483 (1973); A. van Lumig and J. Reuss *ibid.* **27**, 197 (1978).

¹²Y. Yamaguchi, J. F. Gaw, and H. F. Schaefer III (unpublished results).