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Observation of the infrared spectrum of the triatomic molecular ion H_2D^+

J.-T. Shy, John W. Farley, and William H. Wing
Department of Physics and Optical Sciences Center, University of Arizona, Tucson, Arizona 85721

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The infrared vibrational-rotational spectrum of the H_2D^+ molecular ion has been observed. Nine resonances between 1800 and 2000 cm^{-1} have been measured to a precision of 0.0005 cm^{-1} or 0.3 ppm (at 68% confidence level). This triatomic molecular ion is the simplest asymmetric top in nature. The quantum numbers of the observed transitions have not yet been unambiguously identified. This species is of great astrophysical interest in view of its important role in the chemistry of molecular clouds in the interstellar medium.

The triatomic hydrogen molecular ion consists of three nuclei, arranged in an equilateral triangular configuration, and two electrons. There are four radioactively stable isotopic variants: H_3^+, H_2D^+, HD_2^+, and D_3^+. Until very recently, the spectrum of these simple molecular ions had eluded detection. The infrared rotational-vibrational spectra of the two homonuclear variants have been observed recently: The spectra of H_3^+ and D_3^+ were found by Oka[1] and by our group,[2] respectively. The homonuclear variants possess a higher degree of symmetry and exhibit a correspondingly simpler spectrum than the heteronuclear variants.

Molecular ions play an important role in the chemistry of dense molecular clouds in the interstellar medium,[3,4] which are believed to be the site of protostar formation. It appears from detailed computer models of cloud chemistry that the observed abundances of simple interstellar molecules can be reproduced by sequences of ion-molecule reactions.[5] Molecular ions also play an important role in the heating and cooling mechanisms of clouds. H_3^+ is one of the more important molecular ions; it initiates a major chain of reactions and is a source of hydrogen to a number of molecules.

At first glance, it might seem that H_2D^+ would be much less abundant than H_3^+, because the cosmic [D]/[H] abundance ratio is approximately 2×10^{-5}. However, it is widely accepted that pronounced isotopic fractionation can occur in the interstellar medium, based on the different zero-point energies for H- and D-containing molecules. Hence [D]/[H] abundance ratios in specific molecules differ dramatically (by some four or five orders of magnitude in the case of the $[DCO^+]/[HCO^+]$ ratio[6,7]) from the cosmic abundance ratio. H_2D^+ is believed to be the major intermediate species in the chain of fractionation reactions, and is probably present in substantial quantities. It has not yet been identified in the interstellar medium,[8] perhaps because its spectrum was insufficiently well known. Isotopic fractionation is presumably more pronounced in cooler clouds.[4]

Apart from its intrinsic interest, isotopic fractionation is important as a systematic correction which must be applied to the [D]/[H] abundances observed in molecules in order to obtain the true cosmic [D]/[H] isotopic abundance ratio. Models of interstellar clouds are strongly dependent on the assumed cosmic abundance ratio.[3,9] The cosmic [D]/[H] abundance presumably partially reflects the isotopic abundance produced in big-bang nucleosynthesis, and hence has cosmological significance.

In this Communication, we report the first observation of the infrared vibrational-rotational spectrum of H_2D^+. We employed the same experimental techniques previously used[10,11] to make the first observations of the spectra of HD^+ and $^4HeH^+$. The Doppler-tuned fast-ion-beam laser-spectroscopic method[12] and the construction and operation of the ion source[13,14] have been described elsewhere and will only be mentioned in passing here. Briefly described, a beam of molecular ions is intersected at a small (~ 10 mrad) angle by an infrared beam from a stable CO laser. The ions are Doppler tuned into resonance by sweeping the beam accelerating voltage. After interaction with the laser radiation, the ion beam is partially charge-exchange neutralized by collision with a gas target (we have used argon or oxygen for H_2D^+), momentum analyzed by small crossed magnetic and electric fields, and then collected in a Faraday cup. A resonance is observed in the Faraday cup signal.

Observation of the resonances with our high-precision technique entailed important search problems in view of the large uncertainty attached to the theoretical estimates. Our apparatus can search approximately 1 cm^{-1} per day, whereas the uncertainty in the best theoretical estimates[15–17] was approximately an order of magnitude greater. In our previous work on diatomic molecular ions,[10,11] we were able to use the position of the early resonances discovered to guide our search for the later ones. This process, made possible by unambiguous identification of the transitions, converged rapidly. In the present case, however, this convergence procedure cannot be employed until a large number of resonances have been observed, because of the higher density of energy levels and less complete state of the existing theoretical calculations.

Lacking theoretical guidance, we have reduced searching time somewhat by operating the spectrometer in a new fast-scan mode in addition to the traditional slow-scan mode. In the fast-scan mode, the line-selective grating in the CO laser was replaced by an infrared mirror, causing laser oscillation on approximately 15 molecular CO lines. The spectrometer thereby achieved a "multiplex advantage," scanning 15 segments of the spectrum simultaneously and reducing the mean search time between resonances by the same factor. Our resonance search procedure consisted of two stages. First, the spectrometer was operated in the fast-scan (multiline) mode in order to find the resonances. This step determines the resonance beam voltage but does not identify the particular CO laser line driving the transition. Second, the spectrometer was operated in the slow-scan (single-line) mode in order to identify the individual CO laser line. The interval in the molecular ion is thereby measured unambiguously.

In principle, a resonance could be induced in any one of a number of molecular ionic species produced by the ion source. We employed two techniques to ensure that the resonant species was indeed H_2D^+. First, the momentum analysis employed before the Faraday cup ensures that only ions with mass-to-charge ratio of 4 are collected. A second independent check on the mass was provided when a given ionic transition was driven by two different CO laser lines. Because the calculation of the Doppler shift entails knowledge of the ionic mass, the consistency of the resulting values of the transition intervals is a second test of the mass-to-charge ratio. In the four transitions for which data are available, the excellent agreement shown in Table I is proof that the ionic species has mass-to-charge ratio of 4. There remains the possibility that the observed resonance might be attributable to some other ion with the same mass-to-charge ratio. There are two possibilities. H_4^+ may be stable,[18] but it is not produced by our ion source.[14] D_2^+ is present in the ion beam with a density an order of magnitude lower than that of H_2D^+. The intervals in D_2^+ are calculated[19] to fall in the frequency band of our spectrometer. However, in this species the center of mass coincides with the center of charge. Consequently, one cannot drive electric dipole rotational-vibrational transitions in this species. The lowest nonvanishing interactions are electric quadrupole or magnetic dipole transitions, which are

TABLE I. Summary of measurements of H_2D^+ vibrational-rotational transitions. Unless otherwise stated, uncertainty in the molecular interval is 0.0005 cm^{-1} at 68% confidence level. The quantum numbers and frequencies of the $^{12}C^{16}O$-laser lines driving the transitions are listed. The laser beam was antiparallel to the ion beam in all cases. Some of the observed resonances seem to occur in pairs with relative intensities of 2 or 2.5 to 1, perhaps corresponding to the 3:1 statistical weights of ortho (spin triplet) and para (spin singlet) states. The quantum numbers of the H_2D^+ levels involved have not yet been unambiguously identified. In four cases, a molecular-ion transition was driven by a second $^{12}C^{16}O$ laser line. This provides an important consistency check. The uncertainty in the pair splittings is approximately 5 MHz at 68% confidence level.

$^{12}C^{16}O$-laser transition		H_2D^+ transition				
(v',N')[a]-(v'',N'')[b]	Assumed frequency[c] (cm^{-1})	Resonance voltage (V)	FWHM (MHz)	Resonance intensity (ppm of ion beam)	Observed interval (cm^{-1})	Splitting (GHz)
(6,15)-(5,16)	1948.7270	5361.15	13	3.7	1952.0234	
(6,19)-(5,20)	1931.6929	4134.65	13	2.7	1934.5621	11.001
(7,13)-(6,14)	1931.4053	5005.80	13	2.0	1934.5621	
(6,19)-(5,20)	1931.6929	3145.10	12	2.5	1934.1951	
(7,13)-(6,14)	1931.4053	3910.55	13	2.4	1934.1952	
(8,16)-(7,17)	1893.5147	4184.30	13	1.1	1896.3441	10.492
(7,22)-(6,23)	1893.2523	5000.00	12	1.3	1896.345[d]	
(8,16)-(7,17)	1893.5147	3213.80	14	2.2	1895.9941	
(7,22)-(6,23)	1893.2523	3931.50	15	3.0	1895.994[d]	
(8,17)-(7,18)	1889.3424	5424.38	14	3.8	1892.5571	0.490
(8,17)-(7,18)	1889.3424	5369.45	16	1.5	1892.5408	
(10,18)-(9,19)	1834.5792	5376.90	12	0.8	1837.6870	3.417
(10,18)-(9,19)	1834.5792	4990.00	12	1.9	1837.5730	

[a] Upper state

[b] Lower state

[c] Reference 21

[d] Uncertainty 0.002 cm^{-1}

too weak to detect. Finally, in order to exclude absolutely the possibility of a D_2^+ resonance, we rescanned the resonances reported in Table I, using a pure D_2^+ ion beam. No resonances were found.

In a typical resonance run, the beam voltage was incremented in steps of 0.375 V (2.0 to 4.5 MHz, depending on beam voltage), with an integration time of 16 sec per step. A total frequency range of 75 cm^{-1} (2250 GHz) has been searched as of this writing. A typical resonance yielded a signal-to-noise ratio of 15 in an observation time of 15 min, sweeping through about 10 linewidths. Full widths at half maximum of the resonance signals ranged from 10 to 16 MHz. Major contributions to the observed linewidths are the kinetic energy spread in the ion beam, laser power broadening, and the angular divergences of the two intersecting beams. Hyperfine structure, estimated to be less than 1 MHz, is unresolved.

Our results are summarized in Table I. The observed transition frequencies are accurate to an error of 0.0005 cm^{-1} (15 MHz), or 0.3 ppm (at 68% confidence level). For all precision measurements, the laser was locked so as to oscillate on two longitudinal modes simultaneously, yielding enhanced frequency reproducibility.[20] Nonetheless, the largest source of uncertainty (approximately 10 MHz) is the uncertainty in the laser frequency, arising principally from errors in the CO spectroscopic constants[21] and frequency shifts with laser tube current and pressure. Smaller contributions to the uncertainty come from contact potentials, voltage calibration, space-charge potentials in the ion source and ion beam, and possibly from endothermic or exothermic gas-phase reactions in the ion source. All the resonances reported in Table I were obtained with the laser beam directed antiparallel to the ion beam.

It is not possible at present to assign quantum numbers unambiguously to the observed transitions. Nonetheless, in view of the importance of the spectrum, we feel that it is important to publish now as an aid to theoretical analysis. Definite assignment will have to await the observation of a larger portion of the spectrum. We expect additional resonances to be found soon; we have covered only 15% of the spectral region accessible to us.

Although definite assignments cannot be made, preliminary estimates, based on *ab initio* calculations by Porter[15] and Carney,[16,17] indicate that the observed transitions lie in the $(0,0,1) \rightarrow (0,0,0)$ and $(0,1,0) \rightarrow (0,0,0)$ vibrational bands. We use the notation (v_1, v_2, v_3), where the quantum numbers v_1, v_2, and v_3 represent, respectively, the symmetric breathing mode, the symmetric bending mode, and the antisymmetric bending mode, all of which are optically active. The assignment of rotational quantum numbers is more difficult. Lines calculated by Carney and Porter in the range of our observations have values of the rotational angular momentum J in the range 2 to 8. As a possible aid to identification, we note that some of the resonances reported in Table I occur in pairs, perhaps corresponding to the two different mutual orientations of the two protons. If this hypothesis is correct, the stronger line of each doublet would be a transition between ortho (spin triplet) states, and the weaker line would be a transition between para (spin singlet) states. The experimentally observed intensities are often reasonably close to the 3:1 ratio of saturated intensities expected from the ratio of statistical weights.

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