Observation of the Infrared Spectrum of the Triatomic Deuterium Molecular Ion D$_3^+$

J.-T. Shy

Optical Sciences Center, University of Arizona, Tucson, Arizona 85721

and

J. W. Farley, Willis E. Lamb, Jr., 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 D$_3^+$ isotope of the simplest polyatomic molecule is observed. Eight intervals between 1750 and 1850 cm$^{-1}$ have been measured to an error of 0.0005 cm$^{-1}$ or 0.3 ppm (at 70% confidence level). Four have been identified as members of the fundamental degenerate vibrational band. The rest apparently involve unidentified higher vibrational-rotational levels.

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Historically, stable atoms and molecules containing one or two electrons were crucial to the development of modern quantum theory, since only they are simple enough in structure to permit highly precise comparisons of the predictions of theory with the results of experiment. Up to the present, precise spectroscopic data have been lacking for one molecule among these, that composed of two electrons and three nuclei. With use of nonradioactive hydrogen isotopes, four isotopic variants can be formed: H$_3^+$, HD$^+$, HD$_2^+$, and D$_3^+$. The two homonuclear isotopes have the higher symmetry and thus the simpler spectra. Spectroscopically, the advantage of D$_3^+$ is that its fundamental, optically active vibrational band (degenerate mode) falls conveniently in the same spectral region as the emission lines of the CO laser (1550–1920 cm$^{-1}$). Its disadvantage is that the sample population will be distributed among more states, and hence line intensities will be less in the D$_3^+$ case than in the H$_3^+$ case, because of the former's smaller rotational constants.

In this Letter, we report observation of the vibrational-rotational spectrum of D$_3^+$. The measurements reported here and the measurements by Okad$^3$ on the spectrum of H$_3^+$ constitute the first high-precision spectroscopic data for this important system. We have observed eight transitions between vibrational-rotational levels of the ground $^1A_1$ electronic state. The measurements described here employed the Doppler-tuned fast-ion-beam laser-spectroscopic method previously used$^{2-4}$ to make high-precision measurements of the spectra of HD$^+$ and HeH$^+$. Details of the ion-source construction and performance have been published separately.$^{5,6}$ Briefly described, a beam of molecular ions is crossed by

FIG. 1. Resonance trace of the (1, 1, 1)-(2, 2, 0) D$_3^+$ resonance. Voltage step size was 0.2 V; integration time was 16 sec per step. Because the laser oscillates on two longitudinal cavity modes as part of the frequency-stabilization scheme, the resonance trace shows two peaks separated by the laser free-spectral range of 100 MHz. The D$_3^+$ beam current was $3 \times 10^{-13}$ A or 2 ppm of the beam current. Full width at half maximum was 15 MHz.
a nearly collinear infrared CO-laser beam. The ions are Doppler tuned into resonance by sweeping the beam accelerating voltage. The resonances are exceptionally narrow because of kinematic compression of the ion's velocity spread during acceleration. After interaction with the laser light, the ions are partially charge-exchange neutralized by collision with a target gas. A resonance is observed as a modulation in the surviving ion beam current upon chopping the laser beam at 1 kHz frequency. The apparatus can be considered as an optical-frequency counterpart of the Rabi-type molecular-beam radio-frequency resonance apparatus. A definite resonance intensity requires a nonzero difference in ion beam current and gas-target survival probability between the resonating states, as well as a nonzero laser-induced transition probability. Because the ion source operates at ambient temperature and the ions are extracted quickly after formation, many excited vibrational-rotational states are usually present in the ion beam. Vibrational and rotational deexcitation, if desired, can be enhanced by operation at the highest usable source-gas pressures.

Our high-precision technique entailed significant search problems because of the large uncertainties associated with the initial theoretical estimates. In our initial search procedure, the beam voltage was incremented in steps of 0.375 V (2.2 to 4.5 MHz, depending on beam voltage) with an integration time of 8 sec per step. A total frequency range of 300 GHz or 10 cm⁻¹ has been searched as of this writing. Typically a resonance (Fig. 1) yielded a signal-to-noise ratio of 10 in a total integration time of 10 min. Full widths at half maximum of the resonance signals ranged from 15 to 20 MHz. Major contributors to the observed linewidths are ion-kinetic-energy spread, laser-power broadening, and angular divergence of the two intersecting beams. Unresolved hyperfine-structure splittings are much less than 1 MHz.

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 70% confidence level). For all measurements, the laser was locked so as to oscillate on two longitudinal modes simultaneously, yielding enhanced frequency reproducibility. Nonetheless, the largest source of uncertainty (approximately 10 MHz) is the laser frequency, principally because of errors in the CO spectroscopic constants 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.

Table I also lists identifications and semiempirical theoretical frequencies for four transitions in the fundamental degenerate vibrational band. These results are based on an ab initio prediction by Carney and Porter of the vibrational-rotational Hamiltonian matrix. After

<table>
<thead>
<tr>
<th>¹²C¹⁶O–Laser transition</th>
<th>Assumed frequency (cm⁻¹)</th>
<th>D₃⁺ Transition</th>
<th>Observed frequency (cm⁻¹)</th>
<th>Theory (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v,N)ᵇ−(v',N')ᵇ</td>
<td>(J,K,v)ᵇ−(J',K',v')ᵇ</td>
<td>Spectroscopic notation</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

³P₃(2) A₁ 1757.4728 1757.508
³P₂(2) E 1759.2052 1759.208
³P₂(2) E 1761.7090 1761.866
³P₁(1) E 1802.7162 1802.706

³P₁(1) E 1810.483
³P₁(1) E 1810.9154
³P₂(2) E 1811.1320
³P₂(2) E 1811.6915

ᵃUpper state. ᵇLower state.
diagonalization of the matrix, Porter assigned the transitions provisionally and then made an adjustment of +8.9 cm⁻¹ in the vibrational frequencies and +1.6% in the rotational energies to obtain the best fit of the experimental values. The close agreement (0.03 cm⁻¹ maximum error) on all four assigned transitions confirms the assignments, in our judgment. The remaining four transitions appear to involve higher vibrational levels, higher rotational levels, or both. Unambiguous assignment was not possible because of the high density of candidates.

This Letter reports preliminary data for a few transitions. We expect that additional resonances will be found soon. Only about 4% of the infrared spectral region presently accessible to our experimental apparatus has been explored thus far. Such additional data would greatly facilitate transition identification. We hope that these results, combined with the results of Oka,¹ will lead to precise predictions of transitions observable in the interstellar medium in H₂⁺ and H₂D⁺. We also plan to search for the H₂D⁺ spectrum in the laboratory.

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Ab Initio Prediction of the Rotation-Vibration Spectrum of H₃⁺ and D₃⁺

G. D. Carney

Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973

and

R. N. Porter

Department of Chemistry, State University of New York, Stony Brook, New York 11794

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The first few lines in the P, Q, and R branches of the rotation-vibration spectra of the equilateral-triangle molecular ions H₃⁺ and D₃⁺, obtained by ab initio nonperturbative calculations, are reported. Comparison with observations indicates an accuracy better than 1% was obtained for both the infrared-active fundamental vibration frequency and the equilibrium internuclear distances.

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In this Letter we report the first results of an ab initio nonperturbative calculation of the rotation-vibration spectrum of a highly anharmonic, nonrigid polyatomic molecule. Our choice of system is H₃⁺ (and its deuterium analogue D₃⁺), an ion thought to play an important role in the forma-