dence of $<Y_4{}^0>$ (not shown) shows that $A_2{}^0$ production is very small [see also W. Beusch *et al.*, Phys. Lett. 60B, 101 (1975)] and can be safely ignored in the analysis to follow.

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Observation of the Infrared Spectrum of the Hydrogen Molecular Ion HD^+

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The vibration-rotational spectrum of the hydrogen molecular ion HD^+ has been observed by means of a new ion-beam laser-resonance method employing Doppler-effect tuning and collisional detection. Six transition-frequency groups between 1642 and 1869 cm^{-1}, exhibiting partially resolved hyperfine structure, have been measured to ± 1 ppm. The accuracy exceeds that of present theoretical calculations of HD^+ energy levels.

The hydrogen molecular ion is the simplest molecule in nature, consisting of two nuclei and a single electron. It has been the subject of numerous theoretical treatments, which begin with the solutions of the nonrelativistic, one-particle, two-center problem, one of the few separable problems in quantum mechanics.[1] In the physical molecule, the constituents vibrate and rotate about the center of mass. Tables of adiabatic vibration-rotational energy levels in the $1s\sigma\,{}^2\Sigma_g{}^+$ electronic ground state (including nuclear-motion terms diagonal in the electronic basis) have been prepared most recently by Hunter, Yau, and Pritchard.[2] Nonadiabatic (nonrelativistically exact) calculations have also been made for a few low-lying levels.[3,4] In the electronic ground state, a heteronuclear isotope of the ion will interact strongly with optical radiation fields because its mass asymmetry and net charge lead to a substantial electric-dipole transition moment. A homonuclear ion will interact weakly via its electric-quadrupole transition moment.[5]

Spectroscopically, however, the molecule has remained elusive. While spectra of most common molecules have been measured with accuracies of a few parts per million, the optical absorption or emission spectrum of the hydrogen molecular ion has not been seen heretofore. Past searches for the spectrum have been frustrated by the gas-phase reaction $H_2{}^+ + H_2 \rightarrow H_3{}^+ + H$, which proceeds rapidly for all isotopes in thermal plasmas of appreciable density, keeping $H_2{}^+$ concentrations too low for conventional spectroscopic techniques. At present the most accurate observational information on energy levels is derived from vacuum-ultraviolet absorption studies[6] of Rydberg-series limits in the isotopes of molecular hydrogen with uncertainties of a few parts per ten thousand. At this level the calculations and data are in agreement. Experimental data of greater accuracy would make it possible to test a more realistic molecular model incorporating a relativistic wave equation and the effects of quantum electrodynamics.

We have observed infrared transitions between electronic-ground-state vibration-rotational levels of the heteronuclear hydrogen molecular ion HD^+, using a new ion-beam laser-resonance method. A schematic diagram of the experimental apparatus is shown in Fig. 1. In a region of constant electrostatic potential an ion beam of several keV energy crosses at a small angle (≈ 11 mrad) the beam from an infrared molecular laser. The accelerating potential is adjusted to Doppler shift an ion transition into resonance with a nearby laser line. The ions then pass through a gas target where they are partially neutralized by charge exchange (and, to a lesser extent, dissociated and scattered), and are collected in a Faraday cup.

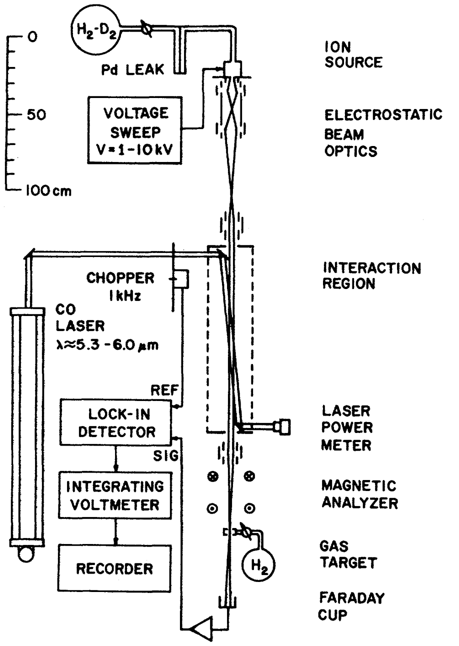

FIG. 1. Apparatus layout. Not shown are four electrostatic-deflection-plate pairs for ion-beam alignment, two long-coil pairs to cancel transverse components of the laboratory magnetic field, and laser-beam optics. Both beams come to focal waists 2–3 mm in diameter at the interaction-region center. Voltages on all electrostatic elements track the ion-beam supply voltage to maintain focusing and alignment. Interaction-region pressure is $\approx 10^{-6}$ Torr. Signals have been seen using N_2, Ar, and H_2 target gases.

At resonance the laser stimulation results in a net population transfer between vibrational-rotational states because the electron-bombardment ionization in the source produces unequal initial-state populations. In addition, cross sections for the various beam-attenuating collisions commonly differ by a few percent between the ions' vibrational states. Consequently the resonant population transfer *changes* beam charge survival in the gas target and, hence, the current into the Faraday cup. Since the change is rather small (typically 3×10^{-6} of the beam current), the laser beam is chopped at 1000 Hz and the resonance signal is synchronously detected. The beam noise is nearly shot-effect limited. With a beam current of 10^{-7} A, the resonances have a signal-to-noise ratio typically 2.5:1 for a 1-sec averaging time, and are not difficult to find.

We use a stable 1-W, cw, sealed-off, grating-controlled, single-mode, $^{12}C^{16}O$ laser designed by Freed.[7] Its intensity is sufficient to saturate and broaden the HD$^+$ transitions. For ion-beam accelerating potentials of 1 to 10 kV the Doppler tuning range of mass-3 ions is ± 1.5 to 5 cm^{-1} from the laser frequency. This is enough to match most of the lower-vibrational-state HD$^+$ transitions with lasing CO transitions[8] in the range 5.3–6.0 μm (1900–1600 cm^{-1}, or 60–50 THz); in some cases several possible matches exist.

Ions are extracted axially from a small hole in the anode of a convergent spherical-cathode electron gun. Gas is supplied to the hole radially. This arrangement minimizes gas-phase reactions and multiple electron impacts, which would tend to equalize level populations. Vibrational populations are given by Franck-Condon factors, and rotational populations roughly by Boltzmann factors for the parent molecules at the anode temperature (≈ 320°K). The source gas is made by passing an equal mixture of H_2 and D_2 through a hot palladium leak. Typically the ion beam contains 40% HD$^+$ ions.

We have found six groups of transitions, involving states having vibrational quantum numbers v, v' in the range 0 to 3 and rotational quantum numbers N, N' in the range 0 to 2. The results are summarized in Table I. There and in the text we use the notation $(v, N) - (v', N')$ for all transitions. The observed resonances obey the electric-dipole harmonic-oscillator selection rule $|v - v'| = 1$ and spherical-harmonic selection rule $|N - N'| = 1$. Each transition exhibits structure due to hyperfine interactions. Typically there are two or three strong components, which are apparently blends of several individual hyperfine resonances, and one to four weak ones, with separations ranging from 0.0004 to 0.0015 cm^{-1} or 12 to 45 MHz. A trace of the relatively intense HD$^+$ transition group (1, 1)–(0, 2) is shown in Fig. 2.

The HD$^+$ molecule contains four interacting magnetic moments associated with the rotational angular momentum $\vec{N}$, the electron spin $\vec{S}$, and the proton and deuteron spins $\vec{I}_1$ and $\vec{I}_2$. In addition the deuteron's electric-quadrupole moment interacts with the gradient of the molecular electric field at its site. By scaling corresponding experimental[9] and theoretical[10] H_2^+ interaction strengths we conclude that the structure in Fig. 2 results primarily from the $\vec{S}\cdot\vec{N}$ interaction and from the variation of the $\vec{S}\cdot\vec{I}_1$ interaction strength with vibrational state.

The ion kinetic energy spread of around 0.5 eV contributes the greatest part of the resonance widths. A kinematic compression of the velocity

TABLE I. Summary of first results on HD$^+$ vibration-rotational transitions. The (1,0)−(0,1) HD$^+$ transition has been observed using two separate laser lines. Ion-beam kinetic energies are in the range 1500–4000 eV.

$^{12}C^{16}O$ laser transition		HD$^+$ transition			
$(v,N)-(v',N')$	Assumed frequency[a] (cm^{-1})	$(v,N)-(v',N')$	Observed frequency[a] (cm^{-1})	Theory[b] (cm^{-1})	Difference[b] (cm^{-1})
(9,15)−(8,16)	1872.231	(1,0)−(0,1)	1869.134	1869.21	−0.07
(8,21)−(7,22)	1872.331	(1,0)−(0,1)	1869.134	1869.21	−0.07
(10,20)−(9,21)	1826.214	(1,1)−(0,2)	1823.533	1823.59	−0.06
(9,18)−(8,19)	1859.820	(2,1)−(1,0)	1856.778	1856.82	−0.04
(12,23)−(11,24)	1763.535	(3,1)−(2,0)	1761.616	1761.48	0.14
(12,14)−(11,15)	1800.399	(3,2)−(2,1)	1797.522	1797.41	0.11
(17,22)−(16,23)	1644.293	(3,1)−(2,2)	1642.108	1641.98	0.13

[a] Assigned uncertainty is ± 0.002 cm^{-1} (see text).

[b] Nonadiabatic calculation (Ref. 3).

distribution occurs on acceleration, giving a Doppler breadth $\Delta\nu/\nu \approx 1.2\times10^{-7}$ for 3000-eV ions. Additional smaller linewidth contributions arise from laser power broadening and from the angular spreads of the two intersecting beams. Observed linewidths range from 7 to 25 MHz.

To obtain the results listed in Table I we have averaged the frequencies of the strong hyperfine components, using relativistically computed Doppler shifts. The values should be accurate to ±0.002 cm^{-1} or 60 MHz. The largest errors arose from voltage calibration, contact potentials, effects of extractor field leakage into and space charge within the electron-gun anode hole (all of order 0.5 V), and laser tuning.

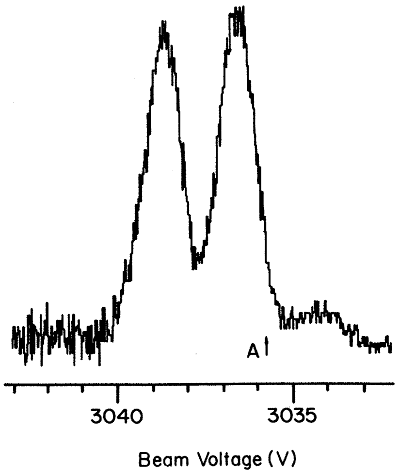

FIG. 2. Trace of the (1,1)−(0,2) HD$^+$ resonance. Two strong hyperfine features and one weak one may be seen. The strong-feature splitting is 0.0010 cm^{-1}. The integrating time per step was 2 sec for voltages above point A, 8 sec for those below.

Table I also lists theoretical transition frequencies obtained from the nonadiabatic energy levels of Hunter and Pritchard.[3] The experimental-theoretical differences range from −0.07 to +0.14 cm^{-1}. Differences of comparable size result if the theoretical adiabatic energies[2] are used instead, with the theoretical frequencies always larger in this case. The quantum-electrodynamic (QED) frequency shifts of −0.006 to −0.013 cm^{-1} from Gersten's calculation[11] are too small to alter the situation materially.

From the results and error estimates of Takezawa and Tanaka's vacuum-ultraviolet absorption experiment[6] in HD we have computed the value 1869.2 ± 0.7 cm^{-1} for the (1, 0)−(0, 1) transition frequency, which is consistent with our value 1869.134 ± 0.002 cm^{-1}.

It is appropriate to speculate briefly on possible future results of this program research. Our present 1-ppm data will allow a test of QED effects in HD$^+$ to ≈ 20% if the non-QED theory is improved. In view of the 0.2–0.5 ppm linewidths and present line-center reproducibility of 0.02 ppm, substantial further refinement appears possible. Measurements with absolute accuracies at such levels will become useful, if the theory is correspondingly further refined, in determining the several fundamental constants that set the overall molecular energy scale. Of these the least well known is the electron-proton mass ratio, now uncertain to ±0.4 ppm.[12]

Based on our results, the theoretical energies should serve as an adequate guide in infrared searches for the hydrogen molecular ion in extraterrestrial sources.

We expect that additional transitions, involving higher vibrational and rotational quanta, will be found shortly. HD$^+$ pure rotational spectra $(v=v')$ and overtone spectra $(|v-v'|\geq 2)$ may appear in other laser frequency ranges. It also seems likely that the equipment can be used to study other molecular ions possessing adequate oscillatory dipole moments, as well as the vibrational-state dependence of molecular-ion collision processes.

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He(3^3P) States Excited in 1.5- and 3.0-keV He$^+$-H$_2$ Charge-Transfer Collisions[*]

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The linear polarization of 3889-Å radiation in coincidence with scattered neutral particles has been measured for 1.5- and 3.0-keV He$^+$-H$_2$ collisions at selected scattering angles. At one scattering angle the measurements show a stronger polarization than is presently observed in He$^+$-He at any scattering angle; this is surprising in view of the many final states available to the recoiling H$_2^+$ ion.

The introduction of coincidence techniques to atomic collision measurements has focused attention on processes where one determines the maximum information concerning the state of the entire collision system, for example the excitation of He atoms by electron impact when the emitted radiation is detected in delayed coincidence with the scattered electrons.[1] Such measurements are known to deal with pure atomic states, i.e., states represented by a density matrix which has only one nonzero diagonal element of unit magnitude in a representation of eigenstates. On the other hand, collisions with complex targets generally produce excited atoms or ions in mixed states because of the averaging over a large number of degrees of freedom of the target. The excited He atoms resulting from collisions of He ions with a tilted foil, as first measured by Berry and Subtil,[2] are a noteworthy example of such mixed states. Although the excited He atoms from the foil were oriented and aligned, the relative magnitudes of these parameters demonstrated that the atoms were in mixed states as would be expected of atoms interacting with a complex system.

The excitation of atoms by diatomic molecules, however, represents a case of intermediate complexity, even though the averaging over all orientations of the molecule would indicate the production of mixed states. In this note we report mea-