problem has to be solved, and finally the case of many electrons should be attacked within the framework of the Hartree-Fock method.

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[1] See, e.g., N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford Univ. Press, London, 1965).

[2] D. R. Bates and A. R. Holt, Proc. Roy. Soc. London, Ser. A 292, 168 (1966).

[3] D. R. Bates and R. McCarroll, Proc. Roy. Soc. London, Ser. A 245, 175 (1958); W. R. Thorson and J. B. Delos, Phys. Rev. A 18, 117, 135 (1978).

[4] G. Poots, U. Öpik, and D. R. Bates, Proc. Phys. Soc. London, Ser. A 66, 1173 (1953); H. Levy, II, and W. R. Thorson, Phys. Rev. 181, 244 (1969).

[5] R. Y. Cusson and J. A. Maruhn, Phys. Lett. B62, 134 (1976).

[6] R. Y. Cusson, R. K. Smith, and J. A. Maruhn, Phys. Rev. Lett. 36, 1166 (1976).

[7] S. E. Koonin, K. T. R. Davies, V. Maruhn-Rezwani, H. Feldmeier, S. J. Krieger, and J. W. Negele, Phys. Rev. C 15, 1359 (1977).

[8] K. T. R. Davies, V. Maruhn-Rezwani, S. E. Koonin, and J. W. Negele, Phys. Rev. Lett. 41, 632 (1978).

[9] R. Varga, *Matrix Iterative Analysis* (Prentice-Hall, Englewood Cliffs, 1962), p. 273.

[10] G. J. Lockwood and E. Everhart, Phys. Rev. 125, 567 (1962).

[11] D. R. Bates and D. A. Williams, Proc. Phys. Soc. 83, 425 (1964).

[12] I. M. Cheshire, D. F. Gallagher, and A. J. Taylor, J. Phys. B 3, 813 (1970).

Observation of Pure Rotational Transitions in the HBr^+ Molecular Ion by Laser Magnetic Resonance

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A molecular ion (HBr^+) has been observed for the first time by laser magnetic resonance spectroscopy. Pure rotational transitions have been detected with five different far-infrared laser lines. Assignment of the hyperfine patterns has produced values for the magnetic hyperfine constants.

Although optical emission spectra have been obtained for a fairly large number of molecular ions,[1] high-resolution spectroscopic techniques have been successfully applied to these species in only a few cases. H_2^+ was detected by Jefferts[2,3] in a rf-optical double-resonance experiment; several different isotopic forms of CO^+ (Ref. 4), HCO^+ (Ref. 5), and HNN^+ (Ref. 6) have been studied in live discharges with microwave spectroscopy by Woods and co-workers; Wing *et al.*[7] have observed vibration-rotation transitions in HD^+ by Doppler-tuning an ion beam into coincidence with an infrared laser; and, most recently, CO^+ (Ref. 8) and H_2O^+ (Ref. 9) have been detected by Carrington and co-workers, and O_2^+ by Tadjeddine *et al.*,[10] Moseley *et al.*,[11] and Carrington, Roberts, and Sarre[12] in the same manner using visible lasers. In this Letter we report the observation of pure rotational transitions for the HBr^+ molecular ion by far-infrared laser-magnetic-resonance (LMR) spectroscopy of a dc glow discharge contained inside the laser cavity.

The LMR spectrometer is similar to a previously described version[13] built in this laboratory. Briefly, it consists of a 7.6-cm-diam by 38-cm-long quartz far-infrared gain cell pumped transversely by a 2.3-m CO_2 laser with a 30-W output, and separated from the 5-cm-diam by 58-cm-long intracavity sample region by a 1.3-mm polypropylene beam splitter set at the Brewster angle. Instead of being located between the pole faces of a 15-in. magnet, as in Ref. 13, the sample region is centered inside the bore of a 5-cm-diam by 33-cm-long solenoid magnet cooled by liquid nitrogen, capable of providing field strengths up to 0.5 T with a homogeneity of 0.1% over a 15-cm length. The HBr^+ ions were generated within the laser cavity in a dc glow discharge through a flowing mixture of ~1% HBr in helium at 133-Pa (1-Torr) total pressure and near-ambient temperature. Pure rotational transitions in the paramagnetic $^2\Pi_{3/2}$ ground state of the ion were magnetically tuned into coincidence with the far-infrared laser frequency. The laser power within the cavity was monitored by coupling a fraction of it into a gallium-doped germanium bolometer cooled with liquid helium. The power absorbed by a transition shifted into coincidence with the laser frequency was modulated at 5 kHz by a solenoidal coil mounted concentrically inside the main solenoid. The resulting change in laser power was synchronously detected by a lock-in amplifier whose output was routed to a signal averager for processing and display. Since the magnetic field is directed along the laser axis, and is therefore always perpendicular to both the E and H fields of the laser, only σ-type ($\Delta M = \pm 1$) electric or magnetic dipole transitions can be observed. The capability of this new spectrometer to detect short-lived species has been demonstrated by our observation of spectra from ^3P O atoms[14] and metastable excited electronic states of CO($a^3\Pi$) and $O_2(a^1\Delta_g)$.[15]

An energy-level diagram for the $^2\Pi$ ground state of HBr^+ is given in Fig. 1. Two consecutive rotational transitions of HBr^+ in the $\Omega = \frac{3}{2}$ spin component and in the ground vibrational state, predicted from the optical constants of Barrow and Caunt[16] with the $^2\Pi$ Hamiltonian of Mizushima,[17] have been observed with three different laser lines. The $J = \frac{3}{2} \rightarrow \frac{5}{2}$ transition, shown in Fig. 2, was detected with both the 251.1-μm line of CH_3OH (Ref. 18) and the 253.7-μm line of CD_3OH (Ref. 19). The $J = \frac{5}{2} \rightarrow \frac{7}{2}$ transition was detected with the 180.7-μm line of CD_3OH,[19] as shown in Fig. 3. Each of the transitions was found very near the magnetic field values predicted from the optical data using first-order Zeeman theory, and the ratio of the energies (7:5) was consistent with that expected for these transitions in $a^2\Pi$ molecule. None of these spectra were observed when the discharge was shut off, or when the HBr was replaced by DBr. The spectra were found to disappear when small amounts of air, O_2, H_2, or H_2O were added to the discharge. An increase in the HBr concentration beyond a few percent also caused the lines to disappear. The optimum conditions for observing the spectra were obtained with currents of about 15 mA and total pressures near 133 Pa (1 Torr), using $a \sim 1\%$ HBr/He mixture. Under these conditions a signal-to-noise ratio of ~100/1 was observed on a single scan of one component of the 180.7-μm spectrum with a 1-sec time constant. Because of large mismatches between all three laser lines and the corresponding rotational transitions and a maximum field of 0.5 T, only the fastest-tuning Zeeman lobes were observed in each case ($M_J = -\frac{3}{2} \rightarrow \frac{1}{2}$ for 251.1 μm, $M_J = \frac{3}{2} \rightarrow \frac{1}{2}$ for 253.7 μm, and $M_J = \frac{5}{2} \rightarrow \frac{3}{2}$ for 180.7 μm). Three different magnetic components of the $J = \frac{5}{2}$

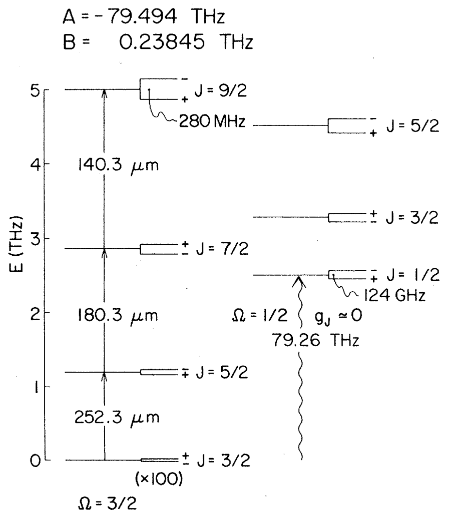

FIG. 1. Energy level diagram for the $^2\Pi$ ground state of HBr^+. The small lambda doubling in the $\Omega = \frac{3}{2}$ state (case A notation) is multiplied by 100; that in the diamagnetic $\Omega = \frac{1}{2}$ state is to scale. The molecular parameters used to calculate the energies are taken from Ref. 16.

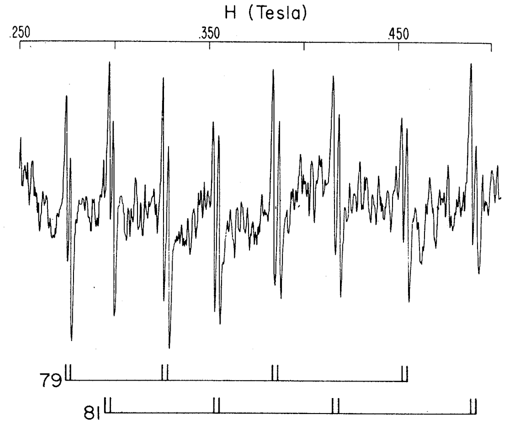

FIG. 2. The laser magnetic resonance spectrum of the $J = \frac{3}{2} \rightarrow \frac{5}{2}$ transition of HBr^+ observed at 251.1 μm (CH_3OH). This spectrum was recorded on a single scan with a 0.1-sec time constant in a glow discharge through 1% HBr in helium at a pressure of 133 Pa (1 Torr). The positions of the eight doublets represent the hyperfine splitting in the $M_J = -\frac{3}{2} \rightarrow -\frac{1}{2}$ Zeeman transition. The doublet splitting is due to the lambda doubling.

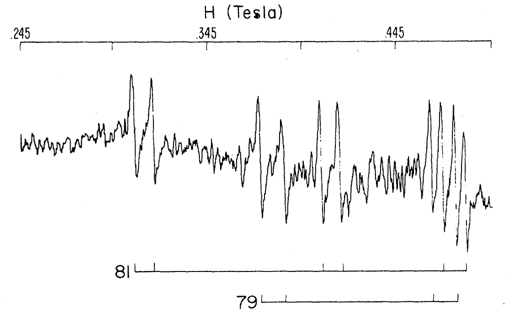

FIG. 3. The $J=\frac{5}{2}\rightarrow\frac{7}{2}$ transition of HBr^+ observed at 180.7 μm (CD_3OH) under the same conditions used in Fig. 2. Only the first eight hyperfine lines of the $M_J=\frac{5}{2}\rightarrow\frac{3}{2}$ Zeeman component could be reached with available magnetic fields.

$\rightarrow\frac{7}{2}$ transition of HBr^+ in the first excited vibrational state ($v=1$) were later detected at 186.2 μm (CH_3OH) with the same conditions used to observe the $v=0$ spectra. Finally, the $M_J=-\frac{3}{2}\rightarrow-\frac{1}{2}$ component of the $J=\frac{3}{2}\rightarrow\frac{5}{2}$ transition for DBr^+ in its ground vibrational state, predicted by scaling the molecular parameters according to their reduced-mass dependences, was observed with the 496.1-μm laser line of CH_3F, using isotopically enriched (99%) DBr.

Bromine has two stable isotopes of mass numbers 79 and 81 occurring in nearly equal natural abundance, both having nuclear spins of $\frac{3}{2}$. Because the reduced masses of these two forms of HBr^+ differ by only 0.03%, we simultaneously observe both species in each spectrum. The hyperfine pattern consists of eight lines, each of which is further split into a doublet by the small (ca. 30 MHz in HBr^+) lambda doubling in the $^2\Pi_{3/2}$ state. The proton hyperfine splitting is too small to resolve in this experiment (ca. 1 MHz, by comparison with the isoelectronic species HSe).[20] The hyperfine splittings resulting from each of the bromine nuclei are unsymmetrical because of both their large quadrupole moments and second-order magnetic hyperfine interactions. The complete pattern of sixteen lines was observed in the 251.1-μm spectrum, as is shown in Fig. 2. With use of first-order theory,[21] and neglect of parity-dependent terms, each line was assigned, and preliminary values of the magnetic and quadrupole hyperfine constants were obtained (Table I), assuming that the small asymmetry in the hyperfine splitting was due only to the quadrupole interaction. With these constants, the patterns for the 490.1, 253.7-, and 180.7-μm spectra were predicted, permitting these transitions to also be assigned to within the signs of M_I. Only the six, eight, and ten lines, respectively, occurring at the lowest fields are within reach of the magnet. The ratios of the magnetic hyperfine constants, $h=a+\frac{1}{2}(b+c)$, for the two isotopic species agree within 0.4% with the corresponding ratio of the nuclear g factors for the bromine nuclei.[22] The ratio of the quadrupole constants, eqQ, obtained in this manner does not agree well with the ratio of the nuclear quadrupole moments,[22] because the second-order effects of the magnetic hyperfine interactions, which are expected to be large, were not accounted for in this preliminary analysis. Therefore, while the values determined for h are probably good to within a few percent, those for the quadrupole constants are of dubious validity, and as such are not given here. A precise determination of the rotational constants B_0 and D_0, which is ultimately achieved in analyses of

TABLE I. Hyperfine parameters, rotational energies, and lambda splittings for HBr^+ determined from the 251.1-μm spectrum.

x	$h(^{79}Br^+)$ (MHz)	$h(^{81}Br^+)$ (MHz)		
h [a]	1460(30)	1580(30)	$h(79)/h(81)=0.924$	
Ratio of nuclear g-factors (Ref. 22)			0.9277	
			Average[a]	Ref. 16
E_{RFS}[b] ($J=3/2\rightarrow J=5/2$)	1 188 700(15)	1 188 660(15)	1 188 680(15)[c]	1 188 314
$\Delta\Lambda$[d] ($J=3/2\rightarrow J=5/2$)	39(5)	36(5)	37.5(5)[c]	35

[a] Only the average values for the two isotopes were observed in Ref. 16.

[b] E_{RFS} is the rotational-fine-structure energy difference.

[c] Uncertainties estimated from the uncertainties in the magnetic field measurements.

[d] Difference between lambda doublings in the two states.

LMR spectra, similarly was not done at this time, because this will require more data. However, rotational fine-structure (RFS) energies and lambda-doubling splittings determined in this experiment (Table I) are quite close to values calculated from the constants and formulas of Ref. 16. A detailed analysis of the spectra reported here as well as a search for new spectra are underway. When completed, these efforts will produce precise values for all of the parameters discussed.

In summary, we have identified spectra observed with five different laser lines as being due to isotopes of HBr^+ on the basis of substantial spectroscopic and chemical evidence as follows: The spectral patterns are observed near their predicted field values, with the correct isotope shifts and lambda doublings, for two consecutive rotational transitions in the ground state and one transition in $V=1$ of the hydrogen isotope, and for one transition in $V=0$ of the deuterium isotope. These transitions indicate that the molecule observed is linear and has a $^2\Pi$ ground state with a B value (and an α value) in agreement with that of HBr^+ as obtained from optical data.[16] The hyperfine patterns, ratios of hyperfine constants, and isotope shifts, and the fact that spectra assigned to HBr^+ disappear when HBr is replaced by DBr, indicate that the molecule contains H and Br. The observed chemistry is consistent with the known ion chemistry of HCl^+ in an afterglow.[23] From all the evidence, we cannot totally eliminate the remote chance that the species we are observing is of a more exotic nature, such as a metastable state of neutral HBr, or perhaps the negative ion HBr^-; however, the probability of identical rotational transitions occurring for these species is very slight. This first detection of an ion by laser magnetic resonance spectroscopy is significant because it makes the entire class of paramagnetic ions amenable to study by this technique. In particular, the similar ion HCl^+, which is of considerable astrophysical interest,[23] should be detectable by the same methods. Measurement of LMR spectra of HCl^+ and other ionic species will provide the accurate rest frequencies required to perform astronomical searches for these molecules in interstellar clouds. Furthermore, it will be of interest to compare spin densities, charge distributions, bond distances, and pressure-broadened linewidths obtained from LMR spectra with those of corresponding neutrals to ascertain the effects of a net charge on these properties.

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[1] G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, Princeton, New Jersey, 1950).

[2] K. B. Jefferts, Phys. Rev. Lett. 23, 1476 (1969).

[3] K. B. Jefferts, Phys. Rev. Lett. 20, 39 (1968).

[4] T. A. Dixon and R. C. Woods, Phys. Rev. Lett. 34, 61 (1975).

[5] R. C. Woods, T. A. Dixon, R. J. Saykally, and P. G. Szanto, Phys. Rev. Lett. 35, 1269 (1975).

[6] R. J. Saykally, T. A. Dixon, T. G. Anderson, P. G. Szanto, and R. C. Woods, Ap. J. 205, L101 (1976).

[7] W. H. Wing, G. A. Ruff, W. E. Lamb, and J. J. Spezeski, Phys. Rev. Lett. 36, 1488 (1976).

[8] A. Carrington, P. L. Milverton, and P. J. Sarre, Mol. Phys. 35, 1505 (1978).

[9] A. Carrington, D. R. Milverton, P. G. Roberts, and P. J. Sarre, J. Chem. Phys. 68, 5659 (1978).

[10] M. Tadjeddine, R. Abouaf, P. C. Cosby, B. A. Huber, and J. T. Moseley, J. Chem. Phys. 69, 710 (1978).

[11] J. T. Moseley, P. C. Cosby, J. B. Ozenne, and J. Durup, J. Chem. Phys. 70, 1474 (1979).

[12] A. Carrington, P. G. Roberts, and P. J. Sarre, Mol. Phys. 35, 1523 (1978).

[13] K. M. Evenson, D. A. Jennings, F. R. Petersen, J. A. Mucha, J. J. Jimenez, R. M. Charlton, and C. J. Howard, IEEE J. Quantum. Electron. 13, 442 (1977).

[14] R. J. Saykally and K. M. Evenson, to be published.

[15] R. J. Saykally and K. M. Evenson, in Proceedings of the Thirty-Third Annual Symposium on Molecular Spectroscopy, Columbus, Ohio, June 1978 (unpublished) paper No. FB-8.

[16] R. F. Barrow and A. D. Caunt, Proc. Phys. Soc., London, Sect. A 66, 617 (1953).

[17] M. Mizushima, *The Theory of Rotating Diatomic Molecules* (Wiley, New York, 1975).

[18] F. R. Petersen, K. M. Evenson, D. A. Jennings, J. S. Wells, Kenya Goto, and J. J. Jimenez, IEEE Quant. Electron. 11, 838 (1975).

[19] R. J. Saykally, K. M. Evenson, F. R. Petersen, and D. A. Jennings, to be published.

[20] H. E. Radford, J. Chem. Phys. 40, 2732 (1964).

[21] A. Carrington, D. H. Levy, and T. A. Miller, Adv. Chem. Phys. 18, 149 (1970).

[22] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill, New York, 1955).

[23] F. C. Fehsenfeld and E. E. Ferguson, J. Chem. Phys. 60, 5132 (1974).