Infrared Emission Spectroscopy of HBr

V. BRAUN AND P. F. BERNATH[1]

Centre for Molecular Beams and Laser Chemistry, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

The vibration–rotation emission spectrum of HBr was recorded with a Fourier transform spectrometer. Line positions for the 1–0 and 2–1 bands were measured for both $H^{79}Br$ and $H^{81}Br$. A pure rotation emission spectrum of HBr was also obtained, and rotational lines for $v = 0$ were measured. The two sets of data, when combined with previously measured submillimeter-wave pure rotational transitions, yielded a set of improved rotational constants for $H^{79}Br$ and $H^{81}Br$. © 1994 Academic Press, Inc.

1. INTRODUCTION

In three previous papers (*1–3*) we have reported on the thermal emission spectra of HF and HCl. For HF and HCl, both pure rotational transitions and vibration–rotation transitions were measured in infrared spectra recorded for other purposes. In this paper, we report on the analogous results for $H^{79}Br$ and $H^{81}Br$. Although HF, HCl, and HBr have been studied by numerous previous workers, our measurements provide data of improved precision.

The spectra of hydrogen halides are important as absolute wavenumber standards. The hydrogen halides are observed in the stratosphere, where they play a role in the depletion of the ozone layer (*4*). HBr is of theoretical interest for the determination of Dunham constants and corrections to the Born–Oppenheimer approximation (*5–8*).

There have been numerous previous measurements of the pure rotational transitions of HBr. Pure rotational spectra were measured in the far-infrared region by Hansler and Oetjen (*9*). Submillimeter-wave spectra of HBr have been obtained for the $J = 1 \leftarrow 0$ transition in the 500-GHz region by Jones and Gordy (*10*) and at a higher resolution by Van Dijk and Dymanus (*11*). De Lucia *et al.* (*12*) carried out further submillimeter-wave work on the hydrogen halides to provide precise values for the centrifugal distortion constants. Dabbousi *et al.* (*13*) obtained hyperfine structure constants, electric dipole moments, and magnetic properties. The most recent work was completed by Di Lonardo *et al.* (*4*), who recorded the pure rotational submillimeter-wave spectrum of HBr using a tunable far-infrared laser spectrometer. They observed transitions up to $J = 9 \leftarrow 8$ and $J = 7 \leftarrow 6$ for $H^{79}Br$ and $H^{81}Br$, respectively, and resolved the hyperfine structure.

The vibration–rotation spectra of HBr are also well known. James and Thibault (*14*) analyzed the 1–0, 2–1, and 3–2 bands in emission, obtaining a set of rotational and vibrational constants. Rank *et al.* (*15*) recorded the infrared absorption spectra of HBr and measured lines in the 1–0, 2–0, and 3–1 bands. Bernage *et al.* (*16–19*)

obtained data for many overtone bands with measurements up to $v = 7$. In addition to these vibrational transitions, numerous electronic transitions are known in the vacuum ultraviolet region (see, for example, Refs. (20–22)).

In this paper, we report on the high-resolution infrared emission spectrum of HBr. Vibration–rotation line positions were measured for the 1–0 and 2–1 bands. The $v = 0$ pure rotational lines were observed in a separate experiment, and were combined with the vibration–rotation data and the pure rotational transitions of Di Lonardo et al. (4) to obtain sets of molecular constants for both $H^{79}Br$ and $H^{81}Br$.

2. EXPERIMENTAL DETAILS

The rovibrational HBr lines were recorded during the measurement of the infrared spectrum of the pyrolysis products of $CHBr_3$ with the Fourier transform spectrometer located at the McMath Solar Telescope on Kitt Peak. A slow flow of $CHBr_3$ was maintained through a stainless steel tube furnace at 1000°C at a total pressure of 5 Torr.

The Fourier transform spectrometer was operated with InSb detectors and a CaF_2 beamsplitter. Eight scans were co-added in 45 min at a resolution of 0.015 cm^{-1}. The spectral range was 1850–5000 cm^{-1}, with the upper wavenumber limit set by a wedged Ge filter and the lower limit by the detector. Vibration–rotation absorption and emission lines were observed for both $H^{79}Br$ and $H^{81}Br$.

In a separate experiment, the pure rotational emission spectrum of HBr was recorded while trying to measure the infrared spectrum of AlBr. The spectrum was obtained

TABLE I

Pure Rotational Line Positions for $v = 0$ of HBr (in cm^{-1})

Assignment	$H^{79}Br$	$H^{81}Br$
R(0)	16.70068453(0)[a, b]	16.69552177(3)[a, b]
R(1)	33.39310763(-3)[b]	33.38278716(-15)[b]
R(2)	50.06901350(-10)[b]	50.05354547(-53)[b]
R(3)	66.72015756(-21)[b]	66.69955731(-105)[b]
R(4)	83.33831208(-28)[b]	83.31260033(-133)[b]
R(5)	99.91527181(-4)[b]	99.88447483(-54)[b]
R(6)	116.4428596(0)[b]	116.4070095(0)[b]
R(8)	149.3173845(100)[b]	-
R(25)	410.58410(55)[c]	410.46428(84)[c]
R(26)	424.49346(49)[c]	424.37028(90)[c]
R(27)	438.19628(16)[c]	438.06980(62)[c]
R(28)	451.68665(12)[c]	451.55695(54)[c]
R(29)	464.95818(31)[c]	464.82500(28)[c]
R(30)	478.00358(-31)[c]	477.86785(-3)[c]
R(31)	490.81836(-9)[c]	490.67927(-50)[c]

[a] Observed - calculated values are in parentheses.

[b] Ref. (4), see text.

[c] This work.

TABLE II

Vibration–Rotation Line Positions for $H^{79}Br$ (in cm^{-1})

Line	Observed	Line	Observed	Line	Observed
			$v = 1\text{-}0$		
P(23)	2074.57866(-31)[a]	P(1)	2542.21265(-5)	R(12)	2730.91199(-9)
P(21)	2123.81714(23)	R(0)	2575.15048(32)	R(13)	2740.40528(-14)
P(20)	2148.01126(-40)	R(1)	2590.91498(14)	R(14)	2749.32885(7)
P(19)	2171.91230(-41)	R(2)	2606.19932(1)	R(15)	2757.67513(-27)
P(18)	2195.51105(-67)	R(3)	2620.99548(-6)	R(16)	2765.43875(9)
P(9)	2392.91024(0)	R(4)	2635.29555(-3)	R(17)	2772.61281(82)
P(8)	2413.02038(38)	R(5)	2649.09137(-21)	R(18)	2779.18854(-44)
P(7)	2432.73327(-18)	R(6)	2662.37559(-20)	R(20)	2790.52505(-359)
P(6)	2452.04173(-26)	R(7)	2675.14019(-36)	R(21)	2795.27795(-96)
P(5)	2470.93691(-16)	R(8)	2687.37875(46)	R(22)	2799.40591(-218)
P(4)	2489.41016(2)	R(9)	2699.08164(4)	R(23)	2802.91199(212)
P(3)	2507.45281(9)	R(10)	2710.24337(24)	R(24)	2805.78088(234)
P(2)	2525.05633(-3)	R(11)	2720.85571(5)		
			$v = 2\text{-}1$		
P(16)	2158.76466(86)	R(5)	2555.84478(5)	R(13)	2643.55085(14)
P(4)	2400.78245(-22)	R(6)	2568.67377(-15)	R(14)	2652.02614(-70)
P(3)	2418.35880(42)	R(7)	2580.98504(8)	R(15)	2659.92647(-4)
P(2)	2435.49581(-25)	R(8)	2592.77026(-1)	R(16)	2667.24426(142)
R(0)	2484.19942(122)	R(9)	2604.02238(7)	R(17)	2673.96878(-29)
R(1)	2499.50065(-68)	R(10)	2614.73304(-63)	R(18)	2680.09854(-5)
R(2)	2514.32541(-9)	R(11)	2624.89664(-37)	R(19)	2685.62309(-176)
R(3)	2528.66275(3)	R(12)	2634.50670(162)	R(21)	2694.84252(22)
R(4)	2542.84478(-30)				

[a] Observed - calculated values are in parentheses.

with the Bruker IFS 120 HR Fourier transform spectrometer at the University of Waterloo. $AlBr_3$ was placed in an alumina tube and heated to $1000°C$ by a commercial CM Rapid Temp furnace. The tube was pressurized with argon gas to prevent condensation of material on the polyethylene windows. Reaction with water, which is present as an impurity in the system, gave HBr as a product.

The emission spectrum was recorded at a resolution of $0.0098\ cm^{-1}$ over the spectral range 300–780 cm^{-1} with a liquid-helium-cooled Si:B detector and a 3.5-μm Mylar beamsplitter. Nine scans were co-added. The lower wavenumber limit was set by the beamsplitter, and the upper limit by a cold red-pass optical filter. Pure rotational lines for $v = 0$ were observed for both HBr isotopomers.

3. RESULTS AND DISCUSSION

The line positions were measured using the spectral analysis program PC-DECOMP written by Brault, which fits the peaks with Voigt lineshape functions. Seven pure rotational lines for $v = 0$ were observed for each isotopomer, ranging from $J = 26$–25 to 32–31. These lines were calibrated using the impurity H_2O lines present in the

TABLE III

Vibration–Rotation Line Positions for $H^{81}Br$ (in cm^{-1})

Line	Observed	Line	Observed	Line	Observed
			v = 1-0		
P(23)	2074.35843(72)[a]	P(1)	2541.83357(1)	R(12)	2730.48202(15)
P(21)	2123.57803(-65)	R(0)	2574.76109(19)	R(13)	2739.97356(-2)
P(20)	2147.76515(11)	R(1)	2590.52089(7)	R(14)	2748.89576(17)
P(19)	2171.65695(-81)	R(2)	2605.80086(12)	R(15)	2757.24105(-10)
P(18)	2195.24636(-218)	R(3)	2620.59270(5)	R(16)	2765.00334(-28)
P(9)	2392.57558(-364)	R(4)	2634.88854(-7)	R(17)	2772.17668(26)
P(8)	2412.68393(162)	R(5)	2648.68089(13)	R(18)	2778.75331(17)
P(7)	2432.38872(-56)	R(6)	2661.96094(-43)	R(19)	2784.72696(-46)
P(6)	2451.69149(-4)	R(7)	2674.72235(-45)	R(20)	2790.09152(-150)
P(5)	2470.58048(-1)	R(8)	2686.95849(100)	R(21)	2794.84365(-12)
P(4)	2489.04760(-4)	R(9)	2698.65825(23)	R(23)	2802.47686(27)
P(3)	2507.08446(-3)	R(10)	2709.81719(14)	R(24)	2805.34650(-17)
P(2)	2524.68259(1)	R(11)	2720.42752(15)		
			v = 2-1		
P(16)	2158.50663(-270)	R(4)	2542.12713(-14)	R(13)	2643.15170(127)
P(14)	2202.51239(153)	R(5)	2555.46360(12)	R(14)	2651.62600(68)
P(4)	2400.44743(26)	R(6)	2568.28935(-10)	R(15)	2659.52240(-167)
P(3)	2418.01770(48)	R(7)	2580.59761(8)	R(16)	2666.83948(-34)
P(2)	2435.14914(-32)	R(8)	2592.38000(-9)	R(17)	2673.56711(124)
R(0)	2483.83930(259)	R(9)	2603.62919(-44)	R(18)	2679.69249(-316)
R(1)	2499.13576(38)	R(10)	2614.33752(-121)	R(19)	2685.21644(-625)
R(2)	2513.95478(-56)	R(11)	2624.50022(19)	R(21)	2694.44356(-9)
R(3)	2528.28842(-20)	R(12)	2634.10581(-51)		

[a] Observed - calculated values in parentheses.

spectrum (*23*) and are reported in Table I. For completeness, the previously measured line positions of Di Lonardo *et al.* (*4*) are included in Table I. In order to correct for the effects of hyperfine structure, these transitions are, in fact, calculated values obtained using the constants reported by Di Lonardo *et al.* (*4*).

A filter-fitting routine available in PC-DECOMP was used to measure the rovibrational lines because of the ringing in the spectrum caused by the sin x/x lineshape function of the Fourier transform spectrometer. Line positions were measured for the 1–0 and 2–1 bands of both isotopomers. Many of the *P*-branch lines of HBr were obscured by impurity CO emission lines which were used for absolute calibration of the wavenumber scale (*24*). The observed lines for $H^{79}Br$ and $H^{81}Br$ are reported in Tables II and III, respectively. Curiously the low-*J* transitions (*J* < 8) of the 1–0 band appeared in absorption, while all other lines appeared in emission. Presumably the cooler HBr molecules near the cell windows appeared in absorption, while the hot HBr molecules in the center of the tube at 1000°C appeared in emission.

For each isotope, the pure rotational and rovibrational lines were combined and fitted to the usual energy expression

BRAUN AND BERNATH

TABLE IV

Rotational Constants of $H^{79}Br$ and $H^{81}Br$ (in cm^{-1})

$H^{79}Br$

Constant	v = 0	v = 1	v = 2
T_v	-	2558.913 382(81)	5027.337 57(16)
B_v	8.351 030 806(19)	8.119 071 3(32)	7.887 684 6(39)
$10^4 D_v$	3.442 872(29)	3.413 16(31)	3.387 45(21)
$10^9 H_v$	7.796(13)	7.57(12)	6.669(29)
$10^{13} L_v$	-3.314(97)	-5.0(11)	-

$H^{81}Br$

Constant	v = 0	v = 1	v = 2
T_v	-	2558.529 082(76)	5026.596 50(20)
B_v	8.348 448 996(18)	8.116 589 2(28)	7.885 327 3(58)
$10^4 D_v$	3.440 715(33)	3.410 43(22)	3.385 78(33)
$10^9 H_v$	7.770(12)	7.421(56)	6.735(33)
$10^{13} L_v$	-3.188(89)	-4.04(45)	-

$$E(v, J) = T_v + B_v J(J + 1) - D_v[J(J + 1)]^2$$
$$+ H_v[J(J + 1)]^3 + L_v[J(J + 1)]^4 \quad (1)$$

The rotational constants obtained from these fits are reported in Table IV. We were able to improve the ground-state constants of Di Lonardo et al. (4), as well as provide improved values for the rotational constants of the $v = 1$ and $v = 2$ vibrational levels of $H^{79}Br$ and $H^{81}Br$.

REFERENCES

1. R. B. LE BLANC, J. B. WHITE, AND P. F. BERNATH, J. Mol. Spectrosc. 164, 574–579 (1994).
2. H. G. HEDDERICH, K. WALKER, AND P. F. BERNATH, J. Mol. Spectrosc. 149, 314–316 (1991).
3. H. G. HEDDERICH, C. I. FRUM, R. ENGLEMAN, JR., AND P. F. BERNATH, Can. J. Chem. 69, 1659–1671 (1991).

4. G. DI LONARDO, L. FUSINA, P. DE NATALE, M. INGUSCIO, AND M. PREVEDELLI, *J. Mol. Spectrosc.* **148,** 86–92 (1991).
5. J. F. OGILVIE, *J. Mol. Spectrosc.* **69,** 169–172 (1978).
6. P. NIAY, P. BERNAGE, AND C. COQUANT, *Can. J. Phys.* **55,** 1829–1834 (1977).
7. J. A. COXON AND P. G. HAJIGEORGIOU, *J. Mol. Spectrosc.* **150,** 1–27 (1991).
8. P. BERNAGE AND P. NIAY, *Can. J. Phys.* **55,** 1016–1024 (1977).
9. R. J. HANSLER AND R. A. OETJEN, *J. Chem. Phys.* **21,** 1340–1343 (1953).
10. G. JONES AND W. GORDY, *Phys. Rev. A* **136,** 1229–1232 (1964).
11. F. A. VAN DIJK AND A. DYMANUS, *Chem. Phys. Lett.* **4,** 170–172 (1969).
12. F. C. DE LUCIA, P. HELMINGER, AND W. GORDY, *Phys. Rev. A* **3,** 1849–1857 (1971).
13. O. B. DABBOUSI, W. L. MEERTS, F. H. DE LEEUW, AND A. DYMANUS, *Chem. Phys.* **2,** 473–477 (1973).
14. T. C. JAMES AND R. J. THIBAULT, *J. Chem. Phys.* **42,** 1450–1457 (1965).
15. D. H. RANK, U. FINK, AND T. A. WIGGINS, *J. Mol. Spectrosc.* **18,** 170–183 (1965).
16. P. BERNAGE, P. NIAY, H. BOCQUET, AND R. HOUDART, *Rev. Phys. Appl.* **8,** 333–335 (1973).
17. P. BERNAGE, P. NIAY, AND R. HOUDART, *C.R. Acad. Sci. Paris Ser. B* **278,** 235–238 (1974).
18. P. BERNAGE AND P. NIAY, *C.R. Acad. Sci. Paris Ser. B* **282,** 243–245 (1976).
19. P. BERNAGE AND P. NIAY, *J. Quant. Spectrosc. Radiat. Transfer* **18,** 315–325 (1977).
20. D. S. GINTER AND M. L. GINTER, *J. Mol. Spectrosc.* **90,** 152–176 (1981).
21. M. A. BAIG, J. HORMES, J. P. CONNERADE, AND W. R. S. GARTON, *J. Phys. B* **14,** L147–L151 (1981).
22. R. CALLAGHAN, Y.-L. HUANG, S. AREPALLI, AND R. J. GORDON, *Chem. Phys. Lett.* **158,** 531–534 (1989).
23. J. W. C. JOHNS, *J. Opt. Soc. Am. B* **2,** 1340–1354 (1985).
24. A. G. MAKI AND J. H. WELLS, "Wavenumber Calibration Tables from Heterodyne Frequency Measurements," U.S. Government Printing Office, Washington, DC, 1991.