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The Infrared Bands and Molecular Constants of HBr

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The fundamental band of HBr has been remeasured, and the harmonic band examined for the first time under high resolution. From the equations representing line positions the values $\nu_0 = 2649.74$ cm^{-1}, $I_0 = 3.2634 \times 10^{-40}$ g cm^2, and $r_0 = 1.4096 \times 10^{-8}$ cm are obtained. Resolution of the isotopic components was just possible in the fundamental band, and the observed separations agree with those computed from the isotopic masses of Br.

The fundamental band of HBr at about 4μ was first resolved by Randall and Imes[1] in one of the earliest studies of infrared absorption with high dispersion. It has not since been reexamined, though there have been great improvements in the sensitivity of the recording apparatus. The harmonic band was not observed at that time because of its low intensity, and until now it has not been studied in detail. For the following observations a standard prism-grating spectrometer was available, the grating having 7200 lines per inch. An absorption cell 25 cm long with windows of NaCl served admirably for the 4μ region, and at 2μ it was replaced by an iron tube 150 cm long with thin mica windows. HBr gas was generated by direct reaction of hydrogen and bromine in the presence of a catalyst, collected by freezing in liquid air and distilled into the evacuated cells to the desired pressure. In this way a high purity of gas was assured.

Curve *b* in Fig. 1 shows the fundamental band as observed with a slit 0.2 mm (0.4 cm^{-1}) in width and a pressure of 20 cm of HBr. The lines are well separated but show no signs of resolution into pairs. By reducing the slit width to 0.09 mm (0.18 cm^{-1}), deflections then being as small as permissible for trustworthy measurements, and advancing the grating by steps of only 10″ at a time, the separation indicated in curve *c* was obtained. Each of the four lines reproduced was defined by some fifteen or twenty points. The separations of the components are difficult to measure precisely due to overlapping of almost equally intense pairs, and it did not seem feasible to derive independent equations for the two isotopic bands. The expected displacements, as computed from the isotopic masses of Br, are indicated by pairs of vertical lines below the envelopes in curve *c* and it is clear that these agree very well with the experimental determinations.

The harmonic band, which is comparatively weak, appears in curve *a*, the gas pressure being atmospheric. The optical arrangement necessary for the accommodation of an absorption cell 150 cm long was not as advantageous as has since been devised,[2] and adequate deflections

TABLE I. *The fundamental band.*

m	Frequencies Observed	 Computed	Difference
+8	2675.36	2675.22	+0.14
+7	2662.60	2662.58	+0.02
+6	2649.38	2649.38	0.00
+5	2635.52	2635.64	−0.12
+4	2621.35	2621.37	−0.02
+3	2606.61	2606.58	+0.03
+2	2591.23	2591.29	−0.06
+1	2575.55	2575.52	+0.03
−1	2542.56	2542.54	+0.02
−2	2525.51	2525.37	+0.14
−3	2507.86	2507.76	+0.10
−4	2489.63	2489.73	−0.10
−5	2471.36	2471.28	+0.08
−6	2452.48	2452.44	+0.04
−7	2433.18	2433.22	−0.04
−8	2413.30	2413.62	−0.32

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[1] E. S. Imes, Astrophys. J. **50**, 251 (1919).

[2] Hardy, Barker and Dennison, Phys. Rev. **42**, 279 (1932).

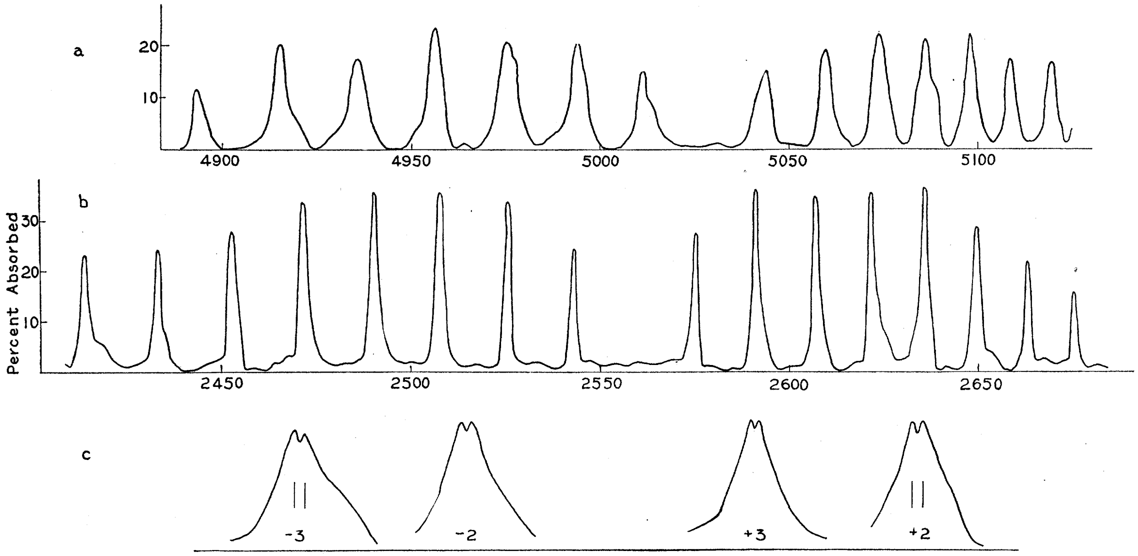

FIG. 1. Absorption bands of HBr. (*a*) First harmonic with slit width 1.2 cm^{-1}. (*b*) Fundamental slit width 0.4 cm^{-1}. (*c*) Four fundamental lines with higher resolution; slit width 0.18 cm^{-1}.

TABLE II. *The harmonic band.*

m	Frequencies Observed	Frequencies Computed	Difference
+7	5119.10	5118.88	+0.22
+6	5108.07	5108.85	−0.78
+5	5097.79	5097.81	−0.02
+4	5086.01	5085.78	+0.23
+3	5072.76	5072.77	−0.01
+2	5058.71	5058.81	−0.10
+1	5043.94	5043.92	+0.02
−1	5011.38	5011.40	−0.02
−2	4993.97	4993.81	+0.16
−3	4975.41	4975.37	+0.04
−4	4956.21	4956.08	+0.13
−5	4935.93	4935.95	−0.02
−6	4915.21	4915.03	+0.18
−7	4893.16	4893.30	−0.14

could be obtained only with relatively wider slits. Hence the definition is not as good and the isotopic separations, though greater than in the fundamental, were not observed. The positions of the rotation lines in the fundamental band are listed in Table I, together with corresponding values computed from the equation

$$\nu' = 2559.26 \pm 16.490m - 0.232m^2 \mp 0.0022m^3,$$

m being the ordinal number of any line counted outward from the center. Table II presents similar information regarding the harmonic band, for which the equation is

$$\nu'' = 5028.11 \pm 16.260m - 0.449m^2 \mp 0.0030m^3.$$

From these coefficients several of the molecular constants may be deduced, as indicated by Colby[3] in a study of HCl. (For definitions of *B* and *C*, and for comparison of the constants of HCl with those of HBr Colby's paper should be consulted.) The numerical values are as follows:

$\nu_0 = 2649.74\ \text{cm}^{-1}$, $B = 0.864 \times 10^{-5}$,
$I_0 = 3.2634 \times 10^{-40}\ \text{g cm}^2$, $C = 5.338$.
$r_0 = 1.4096 \times 10^{-8}\ \text{cm}$,

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[3] W. F. Colby, Phys. Rev. **34**, 53 (1929).