

## The Infrared Spectrum and Molecular Constants of Hydrogen Iodide

ALVIN H. NIELSEN<sup>1</sup> AND HARALD H. NIELSEN, *Mendenhall Laboratory of Physics, Ohio State University*

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The fundamental and first overtone bands of hydrogen iodide have been measured under high resolution and the lines in the positive and negative branches in both bands have, respectively, been fitted to formulae of the form:

$$\nu = a + bm + cm^2 + dm^3.$$

The molecular constants  $\nu_0$ ,  $I_0$ ,  $B$  and  $C$  as defined by Colby depend directly upon the constants  $a$ ,  $b$ ,  $c$ ,  $d$  and have been determined from these measurements, their values being

$$\nu_0 = 2309.58 \text{ cm}^{-1}, \quad I_0 = 4.221 \times 10^{-40} \text{ g cm}^2, \quad B = 0.822 \times 10^{-5}, \quad C = 6.058.$$

THE vibration-rotation spectra of the hydrogen halides are extremely well known,<sup>2</sup> with the exception of hydrogen iodide which has never been investigated. It has seemed worth while also to measure this spectrum and to determine certain of the constants of the molecule from the information furnished by the fundamental and first overtone bands. A prism-grating spectrometer of a conventional design with a two-meter collimating mirror and a grating ruled by Wood with 3600 lines to the inch was available for these measurements. The cell used for containing the gas under investigation was a glass tube 30 cm long fitted with polished rocksalt windows. It was found that the same cell could be used for measurements on both the fundamental and the harmonic bands, for while the harmonic is much less intense than the fundamental, the galvanometer deflections there were many times greater than in the region of the fundamental so that the variation in deflections upon passing over a line was in both cases of the same order of magnitude. Also the recording instrument was extremely steady and the background quite free from atmospheric lines. The slit width in the region of the harmonic included about  $2.9 \text{ cm}^{-1}$  and readings were taken at intervals of  $1.2 \text{ cm}^{-1}$  along the curve. In the region of the fundamental the slit widths were equivalent to  $0.8 \text{ cm}^{-1}$  and here readings were taken at intervals of  $0.4 \text{ cm}^{-1}$ .

The cell was filled to atmospheric pressure with hydrogen iodide, prepared, quite free from impurities, by dropping hydriodic acid on phosphoric anhydride and subsequently trapping out all water and iodine vapor.

Curve (a), Fig. 1, which is a composite curve of a number of runs over this region, shows the lines of the fundamental band which has its center at  $4.5 \mu$ . The lines in the positive branch were somewhat falsified by overlapping with the strong carbon dioxide fundamental at  $4.3 \mu$ , but the transmission curve as here shown, has been rectified to take this into account. It is worthy of note that the lines in this band are extremely sharp, a characteristic to be expected since no isotopes of iodine are known. The lines in both branches may quite well be fitted to the formula:

$$\nu' = 2230.08 \pm 12.73m - 0.160m^2 \mp 0.0005m^3, \quad (1)$$

where  $m$  is the ordinal number of the line counted outward from the center. In Table I is given the

TABLE I. *The fundamental band.*

$m$	Observed $\nu$	Computed $\nu$	Difference
+6	2300.61	2300.59	+0.02
+5	2289.34	2289.67	— .33
+4	2278.34	2278.41	— .07
+3	2266.95	2266.82	+ .13
+2	2254.71	2254.90	— .19
+1	2242.59	2242.65	— .06
—1	2217.34	2217.19	+ .15
—2	2204.08	2203.98	+ .10
—3	2190.49	2190.46	+ .03
—4	2176.82	2176.63	+ .19
—5	2162.55	2162.49	+ .06
—6	2148.04	2148.05	— .01
—7	2133.29	2133.30	— .01

<sup>1</sup> Honorary Fellow in Physics, Ohio State University.

<sup>2</sup> Randall and Imes, *Phys. Rev.* **15**, 152 (1920); E. S. Imes, *Astrophys. J.* **50**, 251 (1919); Meyer and Levin, *Phys. Rev.* **34**, 44 (1929); Plyler and Barker, *Phys. Rev.* **44**, 984 (1933).

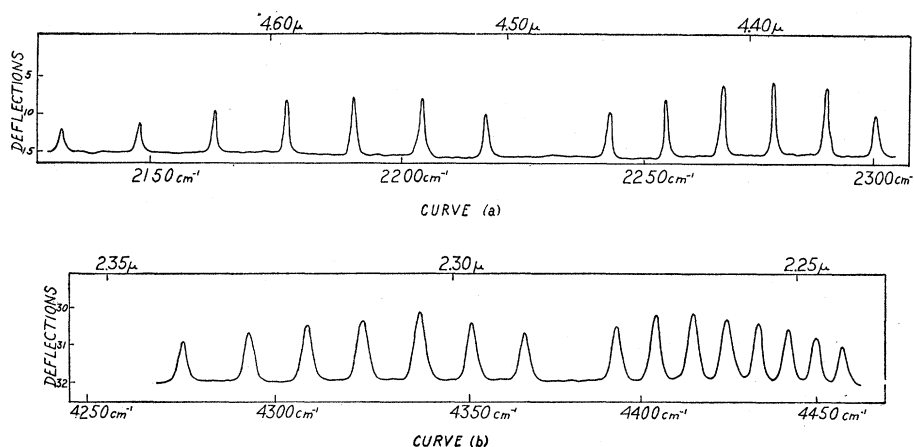


FIG. 1. Absorption spectrum of hydrogen iodide.

observed frequencies of the lines, the frequencies of the lines as calculated from (1) and the differences between the observed and calculated frequencies.

The harmonic band lies at  $2.3\mu$  and is shown in curve (b), Fig. 1, which again is a composite of the several runs made over this region. As in the case of the fundamental it has been possible to fit the lines in both branches to a formula

$$\nu' = 4380.71 \pm 12.54m - 0.370m^2 \mp 0.0005m^3, \quad (2)$$

where again  $m$  is the ordinal number of the line counted outward from the center. Table II gives

TABLE II. *The harmonic band.*

$m$	Observed $\nu$	Computed $\nu$	Difference
+8	4457.37	4457.35	+0.02
+7	4450.27	4450.19	+ .08
+6	4442.28	4442.53	- .35
+5	4433.66	4434.10	- .43
+4	4424.81	4424.92	- .11
+3	4414.81	4414.99	- .18
+2	4404.33	4404.31	+ .02
+1	4392.99	4292.88	+ .11
-1	4367.80	4367.80	.00
-2	4353.72	4354.15	- .43
-3	4339.09	4339.77	- .68
-4	4323.68	4323.66	- .02
-5	4308.13	4308.82	- .69
-6	4292.33	4292.25	+ .08
-7	4275.41	4274.97	+ .44

the observed frequency positions of the lines, the frequency positions as calculated from Formula (2), and the differences between the observed and calculated values.

It is now possible to determine the constants  $\nu_0$ ,  $I_0$  (and  $r_0$ ),  $B$  and  $C$  as defined by Colby<sup>3</sup> in his analysis of the bands in hydrogen chloride, these molecular constants depending directly upon the numerical constants in Formulae (1) and (2). The numerical values of these constants for hydrogen iodide as determined from the observed band data are

$$\begin{aligned} \nu_0 &= 2309.58 \text{ cm}^{-1}, & I_0 &= 4.221 \times 10^{-40} \text{ g cm}^2, \\ B &= 0.822 \times 10^{-5}, & C &= 6.058, \\ r_0 &= 1.600 \times 10^{-8} \text{ cm}. \end{aligned}$$

The value of  $\nu_0$  as here determined may be seen to differ from the value predicted by Ruark and Urey<sup>4</sup> by about  $40 \text{ cm}^{-1}$  while our value for  $I_0$  is in good agreement with the value  $4.3146 \times 10^{-40} \text{ g cm}^2$  given by Czerny<sup>5</sup> determined from measurements made on the pure rotation spectrum of HI.

<sup>3</sup> W. F. Colby, *Phys. Rev.* **34**, 53 (1929).

<sup>4</sup> Ruark and Urey, *Atoms, Molecules and Quanta*, McGraw-Hill Book Co., New York, p. 383.

<sup>5</sup> Czerny, *Zeits. f. Physik* **45**, 476 (1927).