

## Absorption Spectrum of Iodine Bromide

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It is shown by means of a vibrational analysis that the absorption spectrum of iodine bromide is analogous to that of iodine chloride and that an interpretation similar to that recently proposed by the writer and Gibson for ICl is applicable. The infrared bands of IBr discovered by Badger and Yost are classified as a  ${}^3\Pi_1 \leftarrow {}^1\Sigma$  transition. The  ${}^3\Pi_0+ \leftarrow {}^1\Sigma$  system is observed as a faint set of bands in the red, not hitherto reported, which exhibit the same type of predissociation as the corresponding bands of ICl. Transitions to a state which originates at the maximum of the  ${}^3\Pi_0+$  state and which dissociates to yield normal iodine and excited bromine atoms are observed as a strong system of partially diffuse bands. Cordes' assignment of these bands to two systems is not confirmed. In the present work the vibrational quantum numbering for each system is deduced from measurements of the isotope effect due to bromine. The heat of dissociation of IBr is  $1.808 \pm 0.001$  volts. For the four molecules  $I_2$ , IBr, ICl, and  $Br_2$  it is shown that the separation of the  ${}^3\Pi_0+$  and  ${}^3\Pi_1$  states is roughly equal to two-thirds of the mean  ${}^2P$  multiplet widths of the constituent atoms. The total  ${}^3\Pi$  widths are then probably greater and the  ${}^3\Pi_2$  state somewhat lower than has been supposed.

### INTRODUCTION

THE close generic relationship between iodine bromide and iodine chloride furnishes good grounds for believing that their absorption spectra should be closely analogous. Thus, in accordance with the interpretation of the ICl spectrum recently proposed by the writer and G. E. Gibson,<sup>1</sup> one would expect to observe transitions from the normal  ${}^1\Sigma$  state to  ${}^3\Pi_1$  and  ${}^3\Pi_0+$  states, the latter exhibiting predissociation. A system of bands in the infrared is known from the work of Badger and Yost<sup>2</sup> who have shown that the dissociation products of the upper state are normal atoms. In this respect the system is like the strong visible system of ICl and is therefore probably the  ${}^3\Pi_1 \leftarrow {}^1\Sigma$  system. In the visible, according to Cordes,<sup>3</sup> there are two systems of diffuse bands, the upper levels of which dissociate to give normal iodine plus excited bromine ( $a'$ ) and normal bromine plus excited iodine ( $a''$ ). While one of these ( $a'$ ) may correspond to the peculiar  $0^+$  state of ICl, the other is quite unexpected, and transitions to the  ${}^3\Pi_0+$  state were not observed.

In the hope of making a detailed study of the spectrum, photographs of the visible and infrared regions were made with high dispersion (21' Rowland grating). Lack of sufficient resolution has hindered the fine structure analysis,

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<sup>1</sup> W. G. Brown and G. E. Gibson, Phys. Rev. **40**, 529 (1932). For the theory of the electronic states of the halogens, see R. S. Mulliken, Phys. Rev. **36**, 669, 1440 (1930); Rev. Mod. Phys. **4**, 17, 70 (1932).

<sup>2</sup> R. M. Badger and D. M. Yost, Phys. Rev. **37**, 1548 (1931).

<sup>3</sup> H. Cordes, Zeits. f. Physik **74**, 34 (1932).

however, and the following results are based on a study of the vibrational levels.

The strongest absorption bands are the partially diffuse bands in the visible which were studied by Cordes. At longer wave-lengths, in the red, a faint system of double headed bands is to be observed. This occurs in several  $v'$  progressions each of which terminates abruptly with an apparently diffuse band, and is obviously the  ${}^3\Pi_0+\leftarrow{}^1\Sigma$  system. The doublet nature of the heads is due to the equally abundant isotopes of bromine, 79 and 81. The infrared bands, as described by Badger and Yost, also appear in several  $v'$  progressions. A few members of the  $v''=0$  and  $v''=1$  progressions show the isotope effect sufficiently clearly for approximate measurement.

#### VIBRATIONAL ANALYSIS

Badger and Yost carried out a vibrational analysis of the infrared system but as a consequence of not having resolved the isotope effect their values of the vibrational constants for the normal state are only approximately correct and those for the upper state are without significance because of the arbitrary

TABLE I. *Infrared system.*

$v'$ \ $v''$	0	1	2	3	4	$\Delta G'$
9				12,464		103
10				567		96
11				663		94
12			13,021	757	12,496	88
13			107	845	584	86
14		13,459	194	931	670	79
15		537	275	13,010		73
16		609	348	084		68
17		677	414	155		65
18		745	478	219		59
19		806	537	275		54
20		858	593	330		51
21		906	645	382		46
22		953	691	427		43
23		995	734			40
24		14,038	771			34
25		071	806			36
26	14,373	107	842			29
27	404	135	871			30
28	434	165				25
29	459					23
30	482					22
31	504					21
32	525					19
33	544					19
34	563					16
35	579					14
36	593					12
37	605					10
38	615					9
39	624					9
40	633					8
41	641					5
42	646					4
43	650					4
44	654					

$v'$  numbering. As mentioned above, however, the isotope effect is observed only for a few members of the  $v''=0$  and  $v''=1$  progressions, and, because of the presence of a  $Q$  branch which tends to confuse the head formed by the  $R$  branch, it is not accurately measurable. Nevertheless, the data serve to determine the order of magnitude of the correction to be applied to the arbitrary  $v'$  numbering, and this turns out to be an increase of  $9 \pm 1$  units.

Some uncertainty in the value of  $\omega_e'$  is introduced by the long extrapolation from  $v'=9$ . In obtaining the value,  $\omega_e'=140 \pm 5 \text{ cm}^{-1}$ , we are guided to some extent by the assumption that the  $\omega:v$  curve will have the same general shape as the corresponding curve for ICl which is known over its entire course. The heat of dissociation, on the other hand, can be determined with high precision, and the extrapolation gives for the convergence of the  $v''=0$  progression the value  $14,660 \pm 5 \text{ cm}^{-1}$ , or  $D''=1.808 \pm 0.001$  volts. This is somewhat higher than the Badger and Yost value,  $1.801 \pm 0.007$ , but within their limit of error. The new value introduces a small discrepancy between the spectroscopic value for the heat of formation of IBr from  $\text{I}_2$  and  $\text{Br}_2$  and the thermal value determined by Yost and McMorris,<sup>4</sup> but is nicely confirmed by the convergence of the system III bands.

The analysis of the infrared bands given in Table I, from low dispersion measurements, undoubtedly confirms that of Badger and Yost who have not yet published their data, and is given here for the sake of completeness. Table II contains the measurements of the isotope shifts, from photographs taken in the first order of the 21' grating.

TABLE II. *Isotope shifts, infrared system.*

$v', v''$	$\nu^*$	$\delta\nu$ obs.	$\delta\nu$ calc.	$v', v''$	$\nu$	$\delta\nu$ obs.	$\delta\nu$ calc.
26,1	14,106.8 103.2	3.6	3.7	29,0	14,459.2 454.0	5.2	4.8
27,1	137.8 134.2	3.6	3.5	30,0	482.3 477.5	4.8	4.5
28,1	165.2 162.4	2.8	3.2	31,0	503.9 499.9	4.0	4.3
26,0	373.3 357.6	5.7	5.7	32,0	525.1 521.6	3.5	4.1
27,0	404.4 398.3	6.1	5.5	33,0	544.3 540.0	4.3	4.0
28,0	433.6 427.0	6.6	5.2	34,0	563.4 560.2	3.2	3.8

\* First given in each pair is the IBr<sup>79</sup> head.

More accurate data for the normal state are provided by the visible  ${}^3\Pi_0^+ \leftarrow {}^1\Sigma$  bands, the analysis of which is given in Table III. The  $v''$  numbering is fixed with reference to the infrared system and the  $v'$  numbering is that obtained from the isotope shifts in the usual way. Only bands with sharp heads

<sup>4</sup> D. M. Yost and J. McMorris, J. Am. Chem. Soc. **53**, 2625 (1931).

are included in the table; in addition, bands with  $v' = 6$  have been observed in each progression. These bands are approximately  $100 \text{ cm}^{-1}$  distant from the corresponding  $v' = 5$  bands, and like the  $v' = 4$  bands of the corresponding ICl system, appear diffuse but with widely spaced series of lines superimposed.

TABLE III.  ${}^3\Pi_0+\leftarrow{}^1\Sigma$  systems.

$v' \backslash v''$	3		4		5		6		7	
2					15,053.4					
					15,062.8					
						125.1				
						123.1				
3			15,438.7	260.2	15,178.5	257.0	14,921.5			
			15,444.4	258.5	15,185.9	256.5	14,929.4			
								115.1		
			116.8		116.5		115.1			
			116.3		116.1		116.1			
4	15,817.2	261.7	15,555.5	260.5	15,295.0	258.4	15,036.6	257.1	14,779.5	
	15,820.7	260.0	15,560.7	258.7	15,302.0	256.5	15,045.5	255.0	14,790.5	
										106.7
										107.1
										107.7
										108.4
										108.0
5	15,925.8	262.0	15,663.8	260.4	15,403.4	259.1	15,144.3	258.1	14,886.2	
	15,929.1	260.8	15,668.3	258.3	15,410.0	257.4	15,152.6	255.0	14,897.6	

Since the data provide only three values of  $\omega_{v'}$ , which are not quite linear in  $v'$ , the extrapolation to  $v' = -\frac{1}{2}$  is again somewhat uncertain, the value of  $\omega_e'$  being  $\sim 140 \text{ cm}^{-1}$ . Thus, as nearly as can be determined, the  ${}^3\Pi_0+$  and  ${}^3\Pi_1$  states have the same value of  $\omega_e$ . An extrapolation to the point of dissociation is much more uncertain but it is obvious that too low a value will be obtained. Even a linear extrapolation from the observed levels, which in most cases yields too high a value for the heat of dissociation, falls short of the limit  $\text{I}({}^2P_{3/2}) + \text{Br}({}^2P_{1/2})$  by  $1000 \text{ cm}^{-1}$ . Clearly such an extrapolation is without significance except insofar as it shows the abnormality of the levels.

The remaining visible bands, which have their analogy in the system III bands of ICl, are remarkable not only for their intensity but also for the anomalous appearance of certain bands ( $v' = 8$  and 11). These bands are assigned in the analysis (Table IV) in a way that may seem arbitrary, for, unlike all other bands in this system, they possess sharp heads showing the isotope effect clearly. Attempts were first made to consider them as members of an independent system, that is, as successive members in  $v'$  progressions instead of differing by three in quantum number. This possibility was rejected for two reasons, first, there are no additional bands of like character to support such an assignment, and secondly, the isotope shifts calculated on this basis do not agree with the observed values. Supporting their assignment in Table IV is the observation of the intervening levels, 9 and 10, although these bands are totally different in appearance and are so ill-defined that they are not measurable.

TABLE IV. System III,  $0^+ \leftarrow 1^-\Sigma$ .

$v'' \backslash v'$	0	1	2	3	4
8		{16,947.8 265.1 16,947.3 263.5	{16,682.7 263.7 16,683.8 261.7	{16,419.0 262.0 16,422.1 260.5	{16,157.0 58 16,161.6 58
9		17,002* 256 54 68	16,746* 257 63 60	16,489* 271 66 55	16,218* 66
10		17,070* 264 61	16,806* 262 59	16,544* 260 57	16,284* 57
11		17,131 266	16,865.3 263.7 262.2	{16,601.6 262.5 16,603.1 260.1	{16,339.1 57 16,343.0 60
12		17,188* 263 49	16,925 263 53	16,662 263 57	
13		17,237 259 54	16,978 259 56	16,719* 259	
14		17,291 257 67	17,034 257 59		
15		17,358 265 53	17,093 264 58	16,829 264	
16		17,411 260 51	17,151 260 42	(continued)	
17		17,462 269 44	17,237 269 44	$v'' \backslash v'$	
18		17,506 265 50	17,237 265 54	0	1
19		17,556 265 47	17,291 265 50	28	18,157 264 17,893 30 26
20		17,603 262 42	17,341 262 43	29	18,187 268 17,919 22 23
21		17,645 261 35	17,384 261 40	30	18,209 267 17,942 20 19
22	17,942 262	17,680 256 46	17,424 256 38	31	18,229 268 17,961 19 22
23	17,983 257	17,726 264 42	17,462 264 38	32	18,248 265 17,983 15 15
24	18,029 261	17,768 268 33	17,500 268 33	33	18,263 15
25	18,068 267	17,801 268 29	17,533 268 32	34	18,278 17
26	18,101 271	17,830 265 33	17,565 265 34	35	18,295 12
27	18,130 267	17,863 264 30	17,599 264 28	36	18,307 8
28	18,157 264	17,893 266	17,627 266	37	18,315

\* Cordes' measurements.

Cordes has described the bands of this system as diffuse, but in reality they are only partially so. Fine structure appears throughout and in certain regions is remarkably sharp. It is true, however, that the heads are not sharp, except for those with  $v' = 8$  and 11, and cannot be measured at all accurately as the combination differences of Table IV will show. The sharpness of the heads varies greatly, improving somewhat at high quantum numbers, and also, bands with  $v' = 15$  and 20 are somewhat sharper than their neighbors.

No evidence has been obtained for the existence of a second band system in this region, as reported by Cordes. The bands assigned by Cordes to this second system fit, within the experimental error, in the  $v', v''$  matrix of Table IV.

The dissociation products of the upper state are obviously normal iodine and excited bromine atoms, since, by a short extrapolation, we obtain the value,  $18,345 \pm 15 \text{ cm}^{-1}$ , for the convergence of the  $v''=0$  progression. Subtracting the  $^2P$  separation of bromine,  $3685 \text{ cm}^{-1}$ , gives for the heat of dissociation  $D'' = 14,660 \text{ cm}^{-1}$ , in fortuitously good agreement with the value obtained from the infrared bands.

In attempting to determine the value of  $\nu_e$  or of  $\omega_e'$  we are again confronted with the uncertainty of a long extrapolation, as the lowest observed level is  $v'=8$ . There is some evidence for a maximum in the  $\omega:v$  in this case

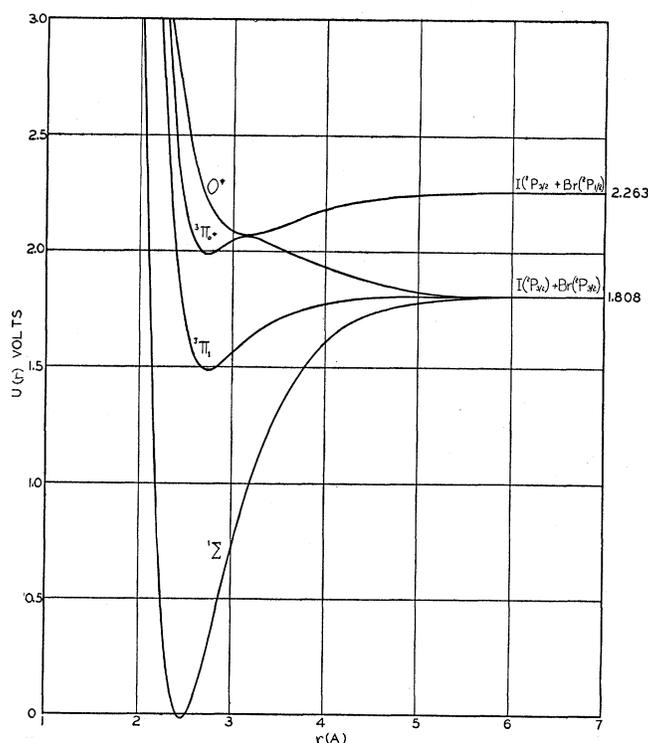


Fig. 1. Approximate potential energy curves for IBr. The  $r_e$  value for the normal state is assumed to lie midway between those for  $I_r$  and  $Br_r$ .

as well as in ICl. Assuming that  $\omega$  does not change with  $v'$  up to  $v'=8$ , the origin of the upper state would lie approximately at the height of the  $^3\Pi_0^+$   $v=5$  level, or perhaps  $50 \text{ cm}^{-1}$  higher if the  $\omega:v$  curve actually has a maximum. The latter position is required by the interpretation. The fact that the upper state originates in the neighborhood of the last  $^3\Pi_0^+$  level lends strong support to the interpretation, since it was not possible to prove this in the case of ICl.

It seems reasonable to suppose that the phenomena are essentially similar to those in iodine chloride, and that the upper state of system III arises in the same way, namely, by interaction of a repulsive  $O^+$  state derived from

normal atoms and the  ${}^3\Pi_0^+$  state with the resultant formation of a quantized set of levels at the intersection. This state being formed from two  $0^+$  states also has the  $0^+$  character, and leads to dissociation into normal iodine and excited bromine atoms. The situation is illustrated in Fig. 1 by means of approximate potential energy curves for the various states. To interpret the character of the bands and the irregular fine structure we must suppose a certain degree of communism between the new  $0^+$  state and the  ${}^3\Pi_0^+$  state so that transitions only to certain limited ranges of rotational quantum numbers, varying from level to level, can give rise to sharp lines. In some cases, as for  $v = 8$  and 11, the range of quantum numbers will be so low that a sharp head will be formed. In others the range will be higher so that the band appears shifted to the red and the progression accordingly irregular. Thus it can be seen that the interpretation proposed to account for the structure of the ICl bands provides a qualitative explanation for the unusual appearance of this system of IBr. It is unfortunate that on account of the overlapping of bands, the large mass of molecule, and the equally abundant isotopes of bromine, a detailed study of the structure is a problem of extreme difficulty.

Likewise, the relative intensities of the transitions  ${}^3\Pi_1 \leftarrow {}^1\Sigma$  and  ${}^3\Pi_0^+ \leftarrow {}^1\Sigma$  are very much the same as in ICl when the Franck-Condon effects are taken into consideration. This involves the interpretation of the various regions of continuous absorption, and, because of the uncertainty as to the exact form of the potential energy curves, it is difficult to make an unambiguous assignment. The work of Cordes shows the existence of two regions of continuous absorption, with maxima at 4050A and 4950A, the latter being stronger. As drawn in Fig. 1 the potential energy curves indicate that transitions from the level  $v'' = 0$  to the  ${}^3\Pi_1$  state would be strongest in the region of the latter's discrete states but at high quantum numbers, while transitions to the  ${}^3\Pi_0^+$  state would account for the strong maximum at 4950A. (Since the energy of this radiation is slightly more than enough to give excited bromine atoms on dissociation, a decision as to which path the  ${}^3\Pi_0^+$  state actually follows, that is, whether normal or excited bromine atoms are the result, cannot be made.) The maximum at 4050A is then to be attributed to transitions to the  $0^+$  state, in harmony with the fact that iodine bromide does not exhibit a region of continuous absorption in the ultraviolet corresponding to that of iodine chloride.<sup>5</sup> The continuous absorption associated with the infrared system is probably that underlying the  ${}^3\Pi_0^+ \leftarrow {}^1\Sigma$  bands. According to this interpretation the  ${}^3\Pi_0^+ \leftarrow {}^1\Sigma$  system is actually very much stronger than the  ${}^3\Pi_1 \leftarrow {}^1\Sigma$  transition, just as in ICl, although a comparison of transitions to discrete levels would yield an opposite conclusion.

#### VIBRATIONAL CONSTANTS

In obtaining the vibrational constants for the normal state, data from the three systems have been combined, the normal state being common, and selected to include only measurements of bands for which the isotope effect

<sup>5</sup> H. Cordes and H. Sponer, *Zeits. f. Physik* **63**, 338 (1930).

has been measured. The theoretical relations between the constants for isotopic molecules have also been taken into consideration. Owing to the long extrapolations the  $\omega$  values for the  ${}^3\Pi$  states are too uncertain to differentiate between the isotopic species.

TABLE V. *Vibrational constants.*

State	$\nu^{e1}$	$\omega_e$	$\omega_e x_e$	$D_0$ (volts)
${}^1\Sigma$	0	{268.4 266.4}	{0.78 0.77}	1.808
${}^3\Pi_1$	12,230	140		0.31
${}^3\Pi_0^+$	16,240	140		
$O^+$	16,880	60		0.19

 ${}^3\Pi$  MULTIPLET WIDTHS

Unfortunately the  ${}^3\Pi_2$  and  ${}^3\Pi_{0-}$  states cannot be observed in absorption since transitions to these states from the normal state are not allowed according to the selection rules,<sup>6</sup> and, therefore, one cannot determine the total multiplet width from the absorption bands alone. However, Van Vleck<sup>7</sup> has shown that the splitting of the  $0^+$  and  $0^-$  levels at moderate values of  $r$  is small compared to the multiplet width, though not negligible. It may be assumed then that the separation of the  $0^+$  and 1 states gives an approximate measure of the half width of the multiplet and it is of some interest to consider how the values obtained in this way are related to the  ${}^2P$  atomic separations.

Data are available for the four molecules,  $I_2$ ,  $I\text{Br}$ ,  $I\text{Cl}$ , and  $\text{Br}_2$ . The value for  $\text{Br}_2$  is based on new measurements of the isotope effect in the infrared system according to which the arbitrary  $\nu'$  numbering used by the writer<sup>8</sup> is to be increased by 6 units. Unfortunately, the  $\nu'$  numbering in the infrared system of iodine cannot be determined in this way as there are no isotopes of iodine. If one assumes that, as in  $I\text{Br}$ ,  $I\text{Cl}$ , and  $\text{Br}_2$ , the  ${}^3\Pi_{0^+}$  and  ${}^3\Pi_1$  states of iodine have the same value of  $\omega$ , a reasonable extrapolation can be made from the observed  ${}^3\Pi_1$  levels,<sup>9</sup> and a value for the separation obtained. The data are given in Table VI, together with the mean  ${}^2P$  widths in the atoms.

TABLE VI.

Molecule	Mean ${}^2P$ width	${}^3\Pi_{0^+} - {}^3\Pi_1$ obs.
$I_2$	0.94	$0.68 \pm 0.05$
$I\text{Br}$	0.70	0.50
$I\text{Cl}$	0.53	0.44
$\text{Br}_2$	0.46	0.27

<sup>6</sup> R. Schlapp, Phys. Rev. **39**, 806 (1932).

<sup>7</sup> J. H. Van Vleck, Phys. Rev. **33**, 484 (1929); **40**, 544 (1932).

<sup>8</sup> W. G. Brown, Phys. Rev. **38**, 1179 (1931).

<sup>9</sup> W. G. Brown, Phys. Rev. **38**, 1187 (1931).

The proportionality is obvious, the  $0^+, 1$  width being approximately two thirds the atomic multiplet width.

These results indicate that the total width of the  ${}^3\Pi$  multiplets is greater by one-third than the mean  ${}^2P$  separations in the atoms, or approximately twice the width estimated by Mulliken.<sup>10</sup> If true, this implies that the  ${}^3\Pi_2$  state lies considerably lower than has been supposed. For  $I_2$  this supposition of equal spacing of the components places the  ${}^3\Pi_2$  component about 0.6 volts above the normal state. It would then be low enough to affect the dissociation equilibrium at high temperatures whereas Gibson and Heitler<sup>11</sup> have found very close agreement between the experimental values and those calculated by considering the normal state alone. It seems likely, therefore, that for the heavier halogens, at least, there is a considerable departure towards case  $c$  so that the spacing of the multiplet is no longer the usual equal spacing of molecular (case  $a$ ) multiplets.<sup>12</sup>

<sup>10</sup> R. S. Mulliken, Phys. Rev. **36**, 1413 (1931).

<sup>11</sup> G. E. Gibson and W. Heitler, Zeits. f. Physik **49**, 465 (1928).

<sup>12</sup> R. S. Mulliken, Interpretation of Band Spectra, Part IIc, Rev. Mod. Phys. **3**, 117 (1931).