SEPTEMBER 15, 1931 PHYSICAL REVIEW VOLUME 38

VIBRATIONAL QUANTUM ANALYSIS OF THE VISIBLE ABSORPTION BANDS OF BROMINE

By Weldon G. Brown
Department of Chemistry, University of California

(Received August 7, 1931)

Abstract

The absorption bands of bromine from 5100A to 7600A are classified into two band systems having a common lower level. One of these includes nearly all of the previously recorded bands of bromine while the other comprises a group of relatively weak bands lying in the extreme red. The upper level of the extreme red system differs from that of the main system in that it dissociates into normal atoms. Measurements of the vibrational isotope effect are given for a number of bands in the main system leading to a revision of the quantum numbering and of the vibrational constants.

Introduction

In THE vibrational analysis of the bromine bands by Kuhn,[1] which was carried out primarily for the purpose of obtaining the heat of dissociation, the isotope effect resulting from the existence of two isotopes of bromine, 78.93 and 80.93,[2] (atomic wt. 79.93) was not observed. The analysis did not include a large number of bands in the region 5300–5600A, and this omission lead to an inconsistent assignment of quantum numbers as Birge[3] discovered when recalculating the constants. Nakamura's[4] more numerous and more extensive measurements, when arranged in av', v'' matrix diagram show discordant G' and G'' differences. The present work was undertaken for the purpose of securing a more satisfactory vibrational analysis, utilizing, if possible, the isotope effect to obtain the true quantum numbering.

Experimental

Of photographs taken with a three prism Steinheil spectrograph, 10 and 21 ft. concave gratings, those taken in the first order of the 10 ft. grating (Paschen mounting; dispersion 5.4A/mm) were chosen as the best compromise between high dispersion and sharpness of band heads. With this dispersion the partial resolution of fine structure was quite troublesome but with the prism instrument the isotope shifts were hardly measureable and with the 21 ft. grating only those bands for which the isotope effect is negligibly small were distinct. Lines of the iron arc, second order where necessary, served as standards, and conversion from wave-lengths in air to wave numbers in vacuum was made by means of Kayser's "Tabelle der Schwingungzahlen." In general the measurements are not accurate to better than 2 cm^{-1}, and in cases where the isotope effect has not been identified the error is considerably greater.

---

[1] H. Kuhn, Zeits. f. Physik **39**, 77 (1926).

[2] F. W. Aston, Proc. Royal Society **115**, 487 (1927).

[3] R. T. Birge, International Critical Tables **V**, 411 (1929), and private communication.

[4] G. Nakamura, Mem. Coll. Sci. Kyoto Univ. **9**, 335 (1926).

Orthochromatic, panchromatic, and extreme red (kryptocyanine) plates were used to cover the visible and near infrared spectrum. Pyrex absorption tubes, from 10 cm to 4 m in length contained the bromine (Kahlbaum) at pressures determined by the temperature of attached bulbs. The absorbing vapor was at room temperature in all experiments except those designed to intensify certain members of the extreme red system. For these experiments the 4 m tube, containing excess liquid bromine, was heated to 50°C, thereby increasing the vapor pressure to about 600 mm.

TABLE I. *Frequencies of band heads in the main absorption system of bromine, in cm*$^{-1}$.

v'	′	0	1	2	3	4	5	$\Delta G'_{v+\frac{1}{2}}$
4	0					15185.5		149.6
5	1					15335.1		144.1
6	2			16113.4	15796.4	15479.2	15169.2	143.2
7	3			16255.4	15938.6	15624.6	15311.6	138.8
8	4			16394.5	16078.4	15762.6	15450.0	135.8
9	5			16530.6	16214.0	15898.8	15585.5	129.8
10	6			16660.4	16343.4	16029.4	15714.7	128.7
11	7			16789.1	16472.2	16156.4	15845.1	122.6
12	8			16912.9	16594.4	16278.9	15967.2	122.1
13	9		17353.3	17033.7	16718.7	16401.4		114.8
14	10		17467.1	17150.0	16831.5	16517.5		110.9
15	11	17901.2	17579.1	17259.8				108.5
16	12	18009.1	17688.0	17368.4				104.0
17	·	18113.2	17792.1	17472.1				99.7
18	·	18213.4	17890.9	17572.0				96.7
19	·	18310.9	17988.1	17667.6				90.9
20	·	18401.6	18077.8	17759.9				87.8
21	·	18490.4	18166.5	17845.8				81.9
22	·		18248.4					80.0
23		18650.2	18328.4					76.1
24		18725.9	18405.0					71.0
25		18796.4	18477.5					67.3
26		18865.2	18543.3					65.6
27		18928.8	18610.9					61.3
28		18990.1						55.5
29		19045.6						49.1
30		19094.7						52.3
31		19147.0						45.9
32		19192.9						44.4
33		19237.5						40.3
34		19275.8						36.9
35		19312.7						31.8
36		19344.5						30.3
37		19374.8						28.6
38		19403.4						25.7
39		19429.1						20.7
40		19449.8						20.5
41		19470.3						15.9
42		19486.2						13.3
43		19499.5						13.0
44		19512.5						11.8
45		19524.3						7.2
46		19531.5						10.7
47		19542.2						9.2
48		19551.4						
$\Delta G''_{v+\frac{1}{2}}$		321.6	319.3	316.9	315.4	312.4		

It is well known that the maximum intensity of absorption for bromine occurs in the region of continuous absorption at about 4100A. This can be observed with a very small quantity of absorbing vapor. On increasing the pressure the spectrum develops progressively toward longer wave-lengths and at the same time the region of continuous absorption widens. With the highest pressure employed the extreme red system appears with good intensity while below 6400A absorption is complete. This constitutes the only evidence of a continuum associated with the extreme red system.

VIBRATIONAL ANALYSIS

In Table I the frequencies of band heads in the main system are arranged in a v', v'' matrix showing G' and G'' differences. These are frequencies of the $Br^{79}Br^{81}$ molecule which is twice as abundant as either of the symmetrical molecules, Br_2^{79}, and Br_2^{81}. The $\bar{v}'$ numbering of column 2 is a provisional numbering adopted prior to the deduction of the v' numbering (column 1) from the isotope effect. This provisional numbering is identical with Kuhn's[1] v' numbering from 0 to 11 but differs by 5 units for higher states. There is no change in the v'' numbering.

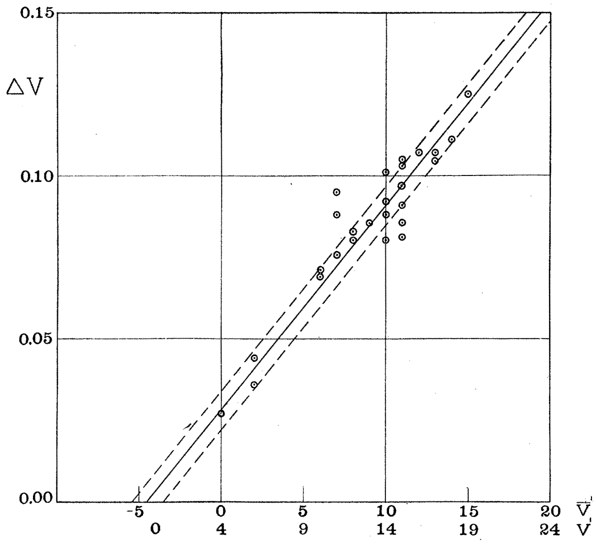

Fig. 1.

For the purpose of deriving the quantum numbering of the upper state use has been made of the following equations:[5]

$$\delta\nu = \delta G_v' - \delta G_v'' \tag{1}$$

$$\delta G_v'/\omega_v = \Delta v = (\rho - 1)(v' + \tfrac{1}{2}) \tag{2}$$

The correctness of the v'' numbering is assumed, so that for each observed

---

[5] G. E. Gibson, Zeits. f. Physik **50**, 692 (1928); J. Patkowski and W. E. Curtis, Trans. Faraday Society **25**, 725 (1929); R. T. Birge, Vibrational Isotope Effect, unpublished. Birge here suggests the use of δ to express an isotope displacement.

shift, $\delta\nu$, the value of $\delta G_v'$ may be found from equation (1), and the corresponding value of Δv from Eq. (2). These values of Δv, when plotted against an arbitrary numbering, $\bar{v}'$, should lie on a straight line of slope $(\rho - 1)$ and having an intercept on the $\bar{v}'$ axis equal to $\bar{v}' - (v' + \frac{1}{2})$.

TABLE II. *Observed isotope shifts and related quantities.*

v', v''	$\delta\nu$	$\delta G''$	$\delta G'$	w_v	Δv	$\bar{v}'$
5,4	4.8	8.82	4.0	147	0.027	1
6,4	3.7	8.82	5.1	144	0.036	2
6,4	2.5	8.82	6.3	144	0.044	2
6,5	4.4	10.70	6.3	144	0.044	2
11,3	4.2	6.90	11.1	126	0.088	7
11,3	5.0	6.90	11.9	126	0.095	7
10,2	4.2	4.97	9.2	129	0.071	6
10,2	3.9	4.97	8.9	129	0.069	6
11,2	4.2	4.97	9.2	126	0.073	7
14,3	3.5	6.90	10.4	113	0.080	10
14,3	3.0	6.90	9.9	113	0.088	10
12,2	3.4	4.97	8.4	123	0.069	8
12,2	4.9	4.97	9.9	123	0.080	8
14,2	4.1	4.97	9.1	113	0.080	10
15,2	4.4	4.97	9.4	110	0.086	11
13,1	7.2	3.00	10.2	119	0.086	9
14,1	8.4	3.00	11.4	113	0.101	10
18,2	5.9	4.97	10.9	98	0.111	14
15,1	7.1	3.00	10.1	110	0.092	11
15,1	8.6	3.00	11.6	110	0.105	11
19,2	6.8	4.97	11.8	95	0.125	15
16,1	8.4	3.00	11.4	106	0.107	12
17,1	7.9	3.00	10.9	102	0.107	13
17,1	8.6	3.00	11.6	102	0.104	13
15,0	10.3	1.01	11.3	110	0.103	11
15,0	7.9	1.01	8.9	110	0.081	11

TABLE III. *Frequencies of band heads in the extreme red system, in cm*$^{-1}$.

v'' v'	1	2	3	4	5	$\Delta G'_{v+\frac{1}{2}}$
0			13773.0	13457.2	13145.3	112.5
1			13885.3	13572.1	13257.9	103.5
2		14307.2	13989.3	13674.5	13361.0	95.4
3			14084.0	13769.9	13457.2	89.9
4		14490.6	14173.8	13859.7	13547.4	80.5
5		14570.3	14255.2	13940.4	13627.6	75.0
6		14647.3	14330.5	14013.9	13701.9	68.1
7		14714.3	14398.0	14084.0	13769.9	59.5
8		14775.5	14455.9	14143.1	13829.8	54.5
9		14828.5	14511.8	14197.7		50.0
10	15197.5	14877.5	14562.6	14247.9		44.1
11	15241.8	14922.4	14604.8			38.2
12	15280.9	14960.1	14643.7			35.4
13	15316.5	14996.2	14678.1			31.3
14	15347.1	15028.2				29.5
15	15376.6	15057.6				27.3
16	15403.4	15085.4				24.2
17	15427.6	15109.6				22.0
18	15450.0	15131.1				19.6
19	15470.0	15150.3				18.9
20		15169.2				16.3
21	15503.0	15185.5				
$\Delta G''_{v+\frac{1}{2}}$	319.2	316.5	314.5	312.6		

In this work the isotope shifts with respect to the $Br^{79}Br^{81}$ heads are considered. The two values of $(\rho - 1)$, though opposite in sign, are practically equal in magnitude: 0.00625. In Table II a few of the most reliable isotope shifts are given, together with the corresponding values of $\delta G_v'$, $\delta G_v''$, and Δv. The latter are plotted, as described above, in Fig. 1. The dotted lines correspond to $v' - \bar{v}' = 3$ and 5, while the v' numbering adopted differs from the arbitrary numbering by 4 units.

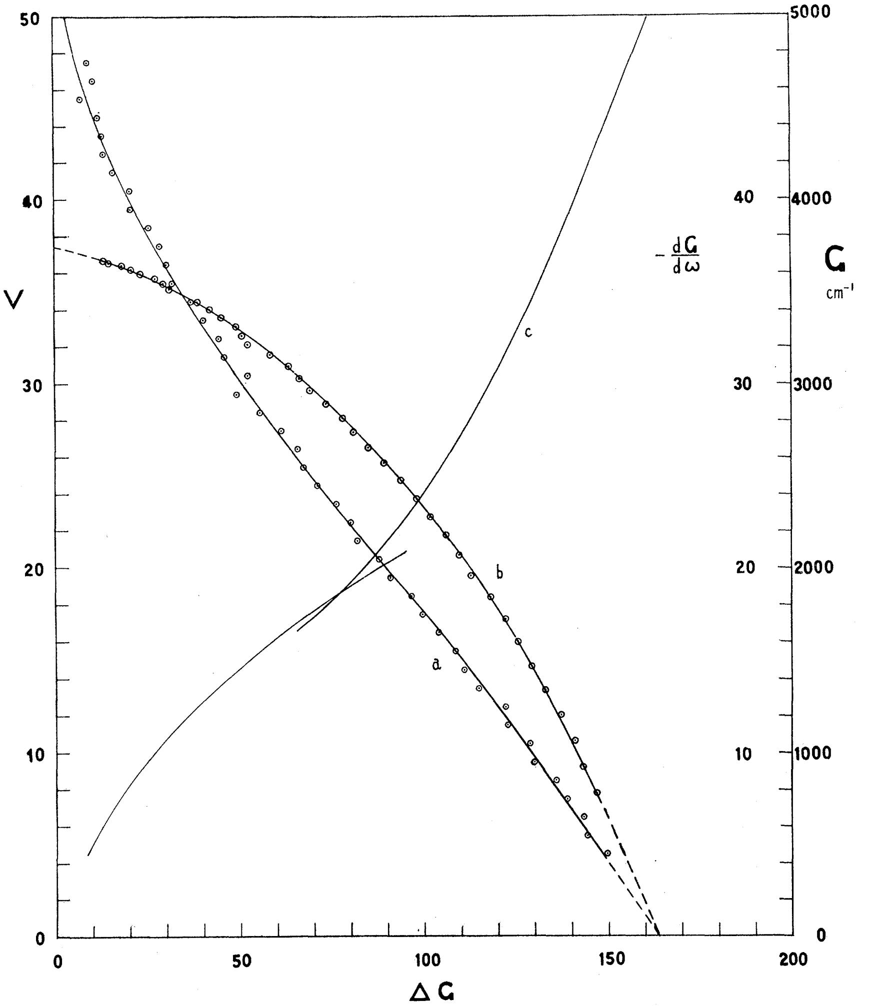

Fig. 2. (a) $\omega : v$, (b) $G : \omega$, (c) $dG/d\omega : \omega$ curves for the upper level of the main system of bromine.

The upper level of this system shows the features which Birge[6] has found to be typical of the halogens. Thus the $\omega : v$ curve (curve *a* of Fig. 2) exhibits a point of inflection at $v = 21 \pm 2$, while the vibrational energy, G, as a func-

---

[6] R. T. Birge, Trans. Faraday Society **25**, 707 (1929).

tion of ω is roughly parabolic. The derivative, $dG/d\omega$, plotted against ω as curve c, was calculated from least squares solutions over two separate portions of the data. The errors are such that it is difficult to decide whether this curve should be made up of two linear portions, but at any rate the curvature toward the origin at small values of ω is analogous to the behaviour of iodine[7] and is to be expected. For values of v' less than 21 the band heads may be represented by the formula:

$$\nu = 15{,}831.2 + (163.81v' - 1.59v'^2 - 0.0087v'^3) - (322.71v'' - 1.15v''^2)$$

The vibrational analysis of the extreme red system is given in Table III. The v'' numbering is based on the G'' differences, which agree well with those for the main system (cf. Table I), and on the heat of dissociation. No bands of the $v''=0$ progression could be detected. The intensities are distributed on a rather wide Condon parabola and the maximum intensity in this progression is to be expected at or near the convergence. This region of the spectrum is obscured by strong bands of the main system and by continuous absorption from higher progressions of the extreme red system.

No satisfactory measurement of the isotope effect in this system have been obtained and the v' numbering is, therefore, arbitrary. Evidence of qualitative nature indicates that this numbering should be increased by 4 ± 2 units. This evidence consists of observations of the point of sharpest band heads in each v' progression from which, by Eqs. (1) and (2), the true numbering can be obtained assuming that these are the points where the isotope effect changes sign. In the case of the main system preliminary observations of this kind gave a result in error by only one unit. The isotope effect changes much less rapidly in the extreme red system and such points do not appear well defined. In the higher progressions, $v''=5$, 4, and possibly 3, the relations between $\delta G'$ and $\delta G''$ are such that points of zero isotope shift are not to be expected but instead only a minimum.

The data for the upper levels are not capable of representation by a simple polynomial. From $v'=0$ to $v'=11$ the $\omega{:}v$ curve is approximately linear, or has slight positive curvature. In this interval the observed band heads may be expressed approximately by

$$\nu = 14734 + (112.8v' - 3.4v'^2) - (322.7v'' - 1.15v''^2).$$

Above $v'=11$ a pronounced positive curvature sets in but the curve later flattens out somewhat and a smooth extrapolation from the levels $v'=13$ to $v'=21$ results in the value 1.963 volts for the heat of dissociation. This is in excellent agreement with the value 1.961 volts calculated from the convergence of the main system. In this calculation the value, 3685 cm^{-1},[8] was used for the separation of the ^2P states of the bromine atom. This agreement, it need hardly be pointed out, affords satisfactory proof that the upper level of the extreme red system dissociates into two normal atoms. The probable error of the mean of these values for the heat of dissociation, 1.962 volts is

---

[7] W. G. Brown, Phys. Rev. **38**, 709 (1931).

[8] L. A. Turner, Phys. Rev. **27**, 397 (1926).

believed to be considerably less than the error given by Sponer,[9] whose value, 1.961 ± 0.008 volts, is derived from the measurements of Kuhn.[1]

No analysis of the fine structure of the bromine bands has been published. It may be worthwhile, therefore, to state here the result of a calculation of the moment of inertia from chemical data, namely the measurements by Bodenstein[10] of the dissociation of bromine at high temperatures. Using the equation of Gibson and Heitler,[11] modified slightly to take into account a small fraction of atoms in the $^2P_{1/2}$ state at the temperatures employed in the experiments, a value of I'' was calculated for each of eleven observations above 1400°K. These gave a mean value of 445×10^{-40} g·cm^2 and a probable error, based on internal consistency alone, of ±3 g·cm^2. The corresponding nuclear separation is 2.54A. Wierl[12] obtained 2.28A by the method of electron diffraction. In Fig. 3 the experimental values of log K for the reaction $Br_2 = 2$ Br are plotted against the reciprocal of the absolute temperature. The curve was drawn with the aid of the Gibson-Heitler equation using the value of I'' given above.

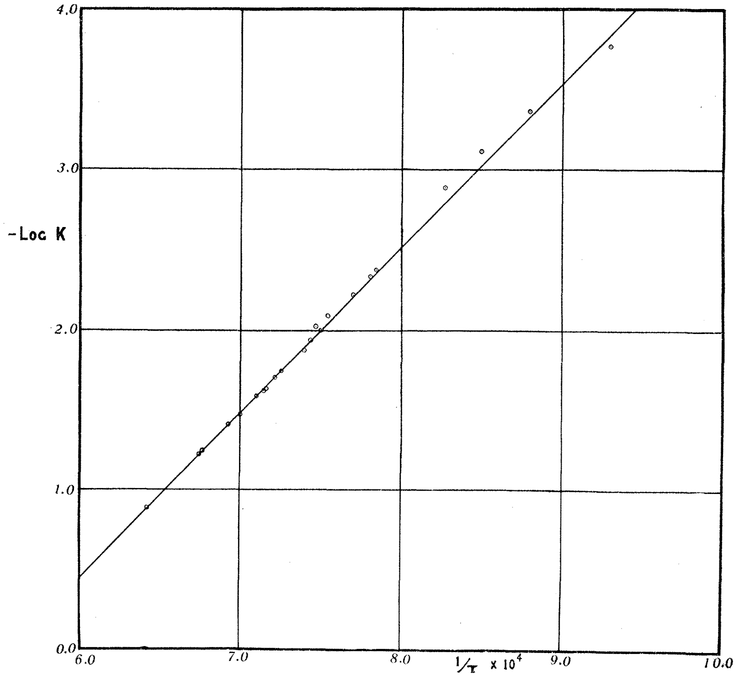

Fig. 3. Logarithm of the equilibrium constant for the dissociation of bromine plotted against the reciprocal of the absolute temperature. The curve was drawn with the aid of the Gibson and Heitler equation but is based on the experimental values at high temperatures.

---

[9] H. Sponer, Landolt-Bornstein Tabellen, Ergänzungsband. Values quoted by J. Franck, Naturwiss. **10**, 217 (1931).

[10] M. Bodenstein, Zeits. f. Elektrochemie **22**, 327 (1916).

[11] G. E. Gibson and W. Heitler, Zeits. f. Physik **49**, 465 (1928).

[12] R. Wierl, Ann. d. Physik **8**, 521 (1931).

In conclusion it might be pointed out that the existence of a separate band system in the red portion of the bromine absorption spectrum has been commented on by a number of investigators although no analysis has been given. Thus Nakamura[13] states that a second band system appears at high temperatures but the measurements given by him appear to be entirely measurements of higher progressions of the main system. Only a few correspond to the measurements of the extreme red system contained herein.

The writer is deeply indebted to Professor G. E. Gibson for his interest and advice, and to Professor R. T. Birge for the privilege of examining the manuscript of a paper to be published by him on the isotope effect.

---

[13] G. Nakamura, Footnote 4, References to earlier observations are given.