Electronic Spectra of Antimony Monobromide *

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Antimony monobromide was excited with the help of a microwave oscillator of 2450 mega cycles. Three new band systems in emission have been observed in the regions 2950—3020 Å, 3050—3340 Å and 4905—5340 Å; of which the first two have been discussed in this paper. All bands are degraded towards the red; they have been classified and attributed to the new molecule SbBr. Isotopic effects due to Br^{79} and Br^{81} have been observed in one of the systems.

Introduction

Although a few diatomic halides of V group elements e. g. NBr, PF, SbF, SbCl, BiF, BiCl, BiBr and BiI etc. have been spectroscopically studied by various workers, there remains a large number of these halides for which no spectra are known. One such halide is SbBr. FERGUSON and HUDES [1], while working on SbCl, made an attempt to excite the SbBr molecule also, by introducing $SbBr_3$ vapour in active nitrogen, but could not record any characteristic spectrum of this molecule. In the present investigation the SbBr spectrum could be recorded with the help of a 125 W Raytheon Diathermy Generator of 2450 mega cycles as a source of excitation. Preliminary results were briefly reported earlier [2].

Experimental Details

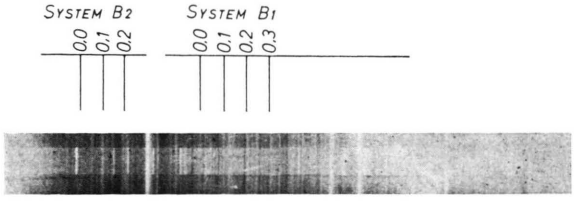
SbBr was excited by a 125 Watt Raytheon Microwave Diathermy Generator of 2450 mega cycles. The discharge tube used was an inverted L-shaped silica tube, sealed at the lower end. The upper open end was connected to a Cenco Hyvac oil pump. A bulb, containing P_2O_5, was connected to the discharge tube through a stop cock to absorb moisture. An auxiliary oscillator was necessary to initiate the discharge which could very well be maintained by the microwave generator. Solid $SbBr_3$ (Riedel) ** was kept at the lower sealed end of the discharge tube. The heat generated by the oscillator in the tube was not enough to vapourise the substance and therefore the tube had to be heated intermittently from outside. The pressure inside was regulated by a stop-cock connected to the Cenco Hyvac oil pump so that the characteristic brown yellow discharge of the SbBr molecule could be maintained. The spectrum was taken on a Zeiss Medium Quartz Spectrograph using Kodak II-O plates.

On the plates taken in the U-V region only one continuum is observed overlapping the bands. The troublesome effect of the overlapping continua along with OH bands in the U-V were minimised by adjusting the pressure inside the discharge tube and altering the time of exposure. Attempts were also made to photograph the bands on an E1 Quartz Littrow spectrograph; but due to long exposure time needed, it was not possible to get plates free from OH bands. Besides this a number of well known diffuse Br_2 bands [3] and SbO bands appeared with good intensity. It appears that $SbBr_3$ left with even traces of moisture for a long time, gives Sb_2O_3 and HBr, which themselves on dissociation give the SbO and Br_2 bands. It was, therefore, found impossible to photograph a pure SbBr spectrum with higher dispersion and resolution.

A copper arc was used as a standard in the ultraviolet region.

Experimental Results

A recorded spectrum is given in Fig. 1. These discrete bands appear to form two systems — one of them extends from 3340 – 3050 Å, hereafter de-



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[1] W. F. C. FERGUSON and I. HUDES, Phys. Rev. **57**, 705 [1940].

[2] N. L. SINGH and M. N. AVASTHI, Ind. J. Pure and Appl. Phys. **1**, 197 [1963].

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[3] P. VENKATESHWARLU, Proc. Ind. Acad. Sci. **25** A, 138 [1947].

signated as system B_1 and the other from 3020 – 2950 Å, designated as system B_2. A continuum without any pronounced maximum masks the B_1 system on its longer wavelength side. The spectrogram clearly shows that many faint and diffuse bands lie beyond 3340 Å, the longer wavelength limit up to which the bands were measured. These bands, in all probability form part of this system but could not be measured because of the difficulty in locating them, due to the overlapping continuum and their faint and diffuse appearance. The bands of both these U-V systems are degraded towards longer wavelengths. The bands of system B_2 are diffuse and those of system B_1 are partly comparatively sharp and partly diffuse.

Vibrational Analysis

While attempting to analyse the bands, a clue to the correct analysis was found in the isotopic shifts of the bands observed in system B_1. The isotopes Br^{79} and Br^{81} could be deciphered in bands involving higher vibrational quantum numbers. This, however, could not be observed in system B_2. As the assignment of the vibrational quantum numbers to the bands based on isotopic shifts was found to be comparatively easy, this system was analysed first.

The bands of this system can fairly well be represented by the equation

$$\nu = 32354 + (206.7\,v' - .85\,v'^2) - (242.3\,v'' - .60\,v''^2).$$

Isotopic Shifts

Bromine has two isotopes of nearly equal abundance with masses 79 and 81. The more abundant isotopes of antimony have the masses 121 and 123, their natural abundances being 57% and 43%. Therefore, in a naturally occurring compound SbBr, we can expect four isotopic SbBr molecules viz., $Sb^{121}Br^{79}$, $Sb^{121}Br^{81}$, $Sb^{123}Br^{79}$ and $Sb^{123}Br^{81}$, to participate in the emission spectrum. The band heads with the same quantum numbers for all the four species are expected to be of equal intensity. The isotopic shifts in wavenumbers for different isotopic molecules were calculated using the for-

Table 1. Band head data and vibrational analysis of the $B_1 - X$ system (3050 – 3340 Å of SbBr.

Wavelength in Å	Wavenumber in vacuum (cm^{-1})	Relative Intensity	v', v''	Wavelength in Å	Wavenumber in vacuum (cm^{-1})	Relative Intensity	v', v''	Wavelength in Å	Wavenumber in vacuum (cm^{-1})	Relative Intensity	v', v''
3051.3	32763	0	2,0	3143.9	31798	8	2,4	3242.1	30835	5	3,9
3059.3	32678	4	4,2	3153.2	31705	3	5,7	3245.2	30806	6	4,0
3062.6	32643	6	5,3	3156.2	31675	4	6,8	3248.5	30775	7	5,11
3065.7	32610	1	6,4	3160.1	31635	7	0,3	3251.5	30746	4	6,12
3068.9	32576	3	7,5	3167.4	31563	3	2,5	3254.4	30719	4	7,13
3070.4	32560	3	1,0	3169.6	31541	5	3,6	3258.8	30677	3	8,14
3073.9	32523	2	2,1	3172.1	31516	5	—	3263.6	30632	3	2,9
3077.9	32480	4	3,2	3173.1	31506	6	4,7	3266.7	30603	4	3,10
3081.4	32443	4	4,3	3176.2	31475	2	5,8	3269.8	30574	3	4,11
3084.9	32407	5	5,4	3183.6	31402	2	7,0	3272.9	30545	3	5,12
3089.9	32354	5	0,0	3184.4	31394	7	0,4	3279.1	30487	3	7,14
3093.3	32319	5	1,1	3188.0	31359	4	1,5	3286.0*	30423	2	9,16
3097.1	32279	5	2,2	3190.2	31337	3	2,6				1,9
3104,2	32205	1	4,4	3193.5	31305	4	3,7	3291.3	30374	3	3,11
3107.2	32174	2	5,5	3199.7	31244	4	5,9	3297.0	30322	2	5,13
3109.4	32151	4	—	3203.9	31203	1	6,0	3300.3	30292	1	6,14
3111.0	32135	1	6,6	3205.2	31190	2	—	3303.9	30259	2	7,15
3113.1	32113	6	0,1	3208.9	31154	4	0,5	3306.8	30232	1	8,16
3116.6	32077	5	1,2	3211.6	31128	4	1,6	3314.9	30158	0	3,12
3124.2	31999	2	3,4	3214.0	31105	5	2,7	3318.8	30123	0	4,13
3133.3	31906	3	6,7	3217.6	31070	8	3,8	3322.0	30094	1	5,14
3136.4	31874	10	0,2	3227.7	30973	6	6,11	3327.9	30040	0	7,16
3139.7	31841	8	1,3	3239.1	30864	4	2,8	3337,3	29956	2	2,12

* This band can be assigned two different places in the Deslandres table both by considerations of ΔG values and isotopic shifts; shifts being equal with quantum numbers (1.9) and (9.16).

mula:

$$\Delta\nu = (1-\varrho)\{\omega_e'(v'+\tfrac{1}{2}) - \omega_e''(v''+\tfrac{1}{2})\} - (1-\varrho^2)\{\omega_e' x_e'(v'+\tfrac{1}{2}) - \omega_e'' x_e''(v''+\tfrac{1}{2})\}$$

where $(1-\varrho)$ and $(1-\varrho^2)$ are Mulliken's isotopic displacement coefficients [4] and ϱ is $\sqrt{\mu/\mu_i}$, μ being the reduced mass. However, in the present work, it has been possible to detect the isotopic effect due to bromine isotopes only. The isotopic displacement due to the bromine isotopes, Br^{79} and Br^{81}, for the band (2, 12), is calculated to be 12 cm^{-1}. For other bands it is much less. For the same band (2, 12) the isotopic shift for the molecules Sb^{121} Br^{79} and Sb^{123} Br^{79} is calculated to be 8 cm^{-1} and it is nearly the same for the molecules Sb^{121} Br^{81} and Sb^{123} Br^{81}. This, as also the shifts of three or four bands which lie away from the system origin, could not be measured due to diffuseness of the bands. It was made still more difficult due to the overlapping continuum. For the majority of the bands the shift is much less than 5 cm^{-1} and therefore, the isotopic band heads due to antimony isotopes could not be resolved. Isotopic displacements due to bromine isotopes are given in Table 2.

Table 2. Isotopic shifts of some bands in the system B_1 (3340–3050 Å).

v', v''	ν in cm^{-1} for $SbBr^{79}$	$\Delta\nu$ Obs. in cm^{-1}	$\Delta\nu$ Calc. in cm^{-1}
2,12	29956	17	18
5,14	30094	17	16
7,15	30259	12	15
1,9 *	30423	19	16
9,16 *	30423	19	16
7,14	30487	14	15
1,5	31359	6	8
5,8	31475	10	7
3,6	31541	6	6

* This band can be fitted at two different places in Deslandres table, both by considerations of ΔG values and isotopic shifts, the shifts being the same with quantum numbers (1,9) and (9,16).

Table 3. Band head data and vibrational analysis of system B_2 (3020–2950 Å).

Wavelength in Å	Wavenumber in vacuum (cm^{-1})	Relative Intensity	v', v''
3023.0	33070	5	5,7
3017.5	33130	7	3,5
3011.1	33200	10	1,3
3007.5	33240	10	0,2
2999.4	33330	8	4,5
2996.5	33362	5	3,4
2992.9	33403	2	2,3
2986.1	33479	8	0,1
2978.9	33560	5	4,4
2971,8	33640	1	2,2
2968.3	33679	2	1,1
2964.8	33719	3	0,0
2962,4	33747	4	5,4
2958.7	33789	1	4,3
2950.9	33878	3	2,1
2947.2	33921	1	1,0

All the bands of system B_2 can fairly well be represented by the equation

$$\nu = 33719 + (200.7\,v' - .30\,v'^2) - (241.5\,v' - .75\,v''^2).$$

For both systems B_1, B_2 the ω_e values are correct within ± 3 cm^{-1} while the $\omega_e X_e$ values are accurate only to the first decimal place.

Agreement between the calculated and the observed probable isotopic shifts supports the correctness of the analysis. It further lends support to the identity of the emitter.

Discussion

Identification of the Emitter

The following observations lend support to the view that the present spectrum is due to the diatomic molecule SbBr:

(i) These bands appear only when the substance $SbBr_3$ is put into the discharge tube. In the empty discharge tube, in the radiation emitted under the same conditions of excitation, the bands characteristic of CO and OH molecules are only observed. This shows that the above spectrum is not due to an impurity in the silica discharge tube or other accessories employed.

(ii) A comparison with the spectra of commonly occurring impurities like CO, CO^+, N_2, CN etc. was made. Our measured band heads do not agree with the wavelengths of any of these molecules given in the table of the persistent band heads as it is given by PEARSE and GAYDON [5].

(iii) A sample of $SbBr_3$ prepared in the Department of Chemistry of this University, under excitation gave an identical spectrum. This proves that either the two samples carried exactly the same impurity responsible for the observed spectrum or

[4] R. S. MULLIKEN, Phys. Rev. **26**, 1 [1925].

[5] R. W. B. PEARSE and A. G. GAYDON, The Identification of Molecular Spectra, Wiley, New York 1965.

there was no impurity at all. The first possibility seems to be very much less probable than the second one.

(iv) The appearance of emission lines of the atoms of antimony, bromine and hydrogen alone further supports the view that the emitter is SbBr. A diatomic emitter can only be Sb_2, Br_2 and H_2 or any combination of any two of these. The observed spectrum cannot be due to a diatomic molecule having a hydrogen atom as one of its constituents as the hydride in general give rise to bands of open structure. A comparison of the bands recorded, with those of Sb_2, Br_2 shows no agreement.

(v) From the vibrational analysis of the two systems we obtain the lower state frequency, 242 cm^{-1} which is very near the expected value of the ground state of the molecule, as shown below on empirical considerations:

(1) The ratios of the ground state frequencies $\omega_e(X)$ of the analogous molecules are

$$\frac{\omega_e(X)_{SbF}}{\omega_e(X)_{BiF}} = \frac{614}{511} = 1.2$$

and

$$\frac{\omega_e(X)_{SbCl}}{\omega_e(X)_{BiCl}} = \frac{369}{308} = 1.2\,.$$

Hence, we can assume that for another set of analogous molecules,

$$\frac{\omega_e(X)_{SbBr}}{\omega_e(X)_{BiBr}} = \frac{\omega_e(X)_{SbBr}}{209} = 1.2$$

or

$$\omega_e(X)_{SbBr} = 250.8\ cm^{-1}\,.$$

(2) The ratios of the ground state frequencies $\omega_e(X)$ of the isoelectronic and similar molecules are

$$\frac{\omega_e(X)_{TeO}}{\omega_e(X)_{SbF}} = \frac{796}{614} = 1.3$$

and [6]

$$\frac{\omega_e(X)_{TeS}}{\omega_e(X)_{SbCl}} = \frac{472}{369} = 1.3\,.$$

Hence, as before, we will be justified to assume that,

$$\frac{\omega_e(X)_{TeSe}}{\omega_e(X)_{SbBr}} = \frac{318}{\omega_e(X)_{SbBr}} = 1.3$$

or

$$\omega_e(X)_{SbBr} = 245.0\ cm^{-1}\,.$$

(3) KRASNOV and MAKSIMOV [7] have suggested a method of calculating the ground state frequencies of the diatomic molecules of the XY type, where X belongs to one group of the Periodic Table and Y to another. They have shown that the ground state frequency of a diatomic molecule obeys

$$\omega_e(X) = A/\mu + B$$

where μ is its reduced mass and A and B are constants. For the elements of group V they found $A = 7793$ and $B = +74$. By this method, as stated by them, the calculated frequencies are in error by 4.9%. The value of $\omega_e(X)_{SbBr}$ as calculated in this way is 248.3 cm^{-1}.

These simple calculations not only support our view as to the identity of the emitter but also indicate that the observed frequency 242 cm^{-1} is the ground state frequency of the SbBr molecule.

(vi) The agreement between the observed and calculated values of isotopic shifts due to bromine isotopes, further indicates and confirms that in all probability the emitting molecule is none other than SbBr.

In the Deslandres scheme of representation, the bands of system B_1 are found to lie on a moderately wide parabola, as has been observed in the case of the Cu I molecule [4] for its C – X system. The vibrational frequencies of this system in the Cu I molecule are $\omega_e'' = 264.8\ cm^{-1}$ and $\omega_e' = 229.7\ cm^{-1}$. An analysis of the B_2 system gives $\omega_e'' = 242.3\ cm^{-1}$ and $\omega_e' = 206.7\ cm^{-1}$, which are nearly of the same order. Therefore, the Franck-Condon parabola is of the same type for this system. In the Deslandres table constructed for the system B_2 the bands again lie on a slightly wide parabola, just as for system B_1.

A comparison of $\Delta G''$ values of this system with coresponding values of system B_1 leads us to believe that both systems have a common lower state. The ω_e'' values of the two systems are very nearly the same. As a matter of fact, this was taken into account when v'' numbering of the bands of the system was done. Very probably the lower state of the system recorded in the visible region, designated as system A, is the same as that of the systems B_1 and B_2. This lower state, as shown above on empirical considerations, is taken to be the ground state of the molecule. Mostly the band systems of the various diatomic molecules involve the ground state of the molecule, and even in the case where the nature of the lower state is uncertain, as with some oxide

[6] H. MOHAN and K. MAJUMDAR, Proc. Phys. Soc. London **71**, 147 [1961].

[7] K. S. KRASNOV and A. I. MAKSIMOV, Optics and Spectroscopy **8**, 208 [1960].

emission spectra, it is in all probability the ground state. In comparatively few instances the excited states are found involved in more than one system. Accordingly, we believe that the lower state of all the three band systems A, B_1 and B_2 is the ground state of the molecule. Similar involvement of the ground states has been detected in the case of SbF and BiF molecules. However, a study of the spectrum of this molecule in absorption is desirable to confirm our statement.

From the similarity of the $\Delta G'$ and ω_e values of the two band systems B_1 and B_2, it seems probable at first sight that they together comprise a doublet system, but the even number of electrons in the molecule gives rise to a state of odd multiplicity, and the possibility of the existence of a third system cannot be ruled out. One may also be tempted to believe that the observed spectrum may be due to ionised SbBr molecule, which will give only even multiplicity. But in the present experiments, such a possibility is ruled out from energy considerations. If the molecule SbBr is the emitter then the third system, comprising a triplet with the observed two, is either too faint to be observed or lies outside the region photographed. Similar views have been expressed in respect to SbF by ROCHESTER [8].

Acknowledgement

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[8] G. D. ROCHESTER, Phys. Rev. **51**, 486 [1937].