A NEW BAND SYSTEM OF CuBr MOLECULE

BY P. RAMAKOTESWARA RAO

AND

K. V. S. R. APPARAO

(Spectroscopy Division, Atomic Energy Establishment, Trombay, Bombay)

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INTRODUCTION

THREE band systems are known to belong to the CuBr molecule—the A system (5050–4610 Å), the B system (4550–4190 Å) and the C system (4580–3930 Å). These have been investigated in considerable detail in absorption at high temperatures by Ritschl (1927). From vibrational analysis Ritschl has shown that the three systems involve the ground state of the molecule. Natural CuBr is a mixture of four isotopic species, $^{63}Cu\ ^{79}Br$, $^{63}Cu\ ^{81}Br$ $^{65}Cu\ ^{79}Br$ and $^{65}Cu\ ^{81}Br$, with approximate relative abundances of 7 : 7 : 3 : 3. Ritschl has recorded the isotope shifts in a number of bands. Based on thermochemical data, Terrien (1938) gave a value of 2·5 ev for $D_0°$, the dissociation energy in the ground state.

From a comparison of the known band systems of CuBr with those of CuCl, it appeared desirable to look for possible new band systems in the spectrum of CuBr. In the case of CuCl, microwave discharge (2450 Mc./sec.) in an electrodeless tube has been found to be an extremely intense source of the molecular spectrum (Ramakoteswara Rao and Brody, 1961). It was therefore decided to investigate the emission spectrum of CuBr excited by microwave oscillations in an electrodeless discharge tube.

As expected, this excitation has given rise to a very intense emission spectrum of CuBr. The spectrum showed, apart from some new bands in the B and C systems, a completely new band system in the 3700–4000 Å region. These are discussed in this paper.

EXPERIMENTAL

The method of preparation of the electrodeless discharge tube was identical with that described in detail elsewhere (Ramakoteswara Rao and Brody,

1961). The quartz discharge tube, about 1 cm. in diameter and 5 cm. in length, contained a few mg. of CuBr and was sealed off under vacuum after filling with neon to a pressure of 1 to 2 mm. E. Merck CuBr of Analar grade has been used; the spectrum obtained showed no impurity bands. The discharge tube was externally heated to about 500° C. and excited by a microwave, 2450 Mc./sec., oscillator operating at a power of 30 to 40 watts. The discharge in CuBr is considerably less stable than that in CuCl. The useful life of a CuBr discharge tube appeared to vary from about 10 minutes to one hour compared with 10 to 20 hours in the case of a CuCl tube.

The spectrum was photographed in the first order of a Jaco 3·4 meter, 15,000 l./inch grating spectrograph at a dispersion of 5 Å/per mm. With a view to obtain accurate isotope shifts in the 1–0 and 0–1 bands, the spectrum was also photographed in the second order of a 6·6 meter, 30,000 l./inch grating spectrograph at a dispersion of 0·6 Å per mm. The plates were measured on a Zeiss comparator. The sharp band heads are expected to be accurate to about $\pm 0{\cdot}05$ Å.

RESULTS AND DISCUSSION

Figure 1 shows a reproduction of the new band system photographed on the Jaco 3·4 meter grating spectrograph. The system consists of regular, well-separated band sequences characteristic of a typical diatomic molecule. The zero-zero band sequence could be readily identified by virtue of the marked sharpness of its members due to negligible isotope shifts.

The measured separation between the first bands of the $\Delta v = 0$ and $\Delta v = -1$ sequences is 312·7 cm.$^{-1}$, which agrees very well with $\omega_e'' - 2\,\omega_e'' x_e'' = 312{\cdot}4$ cm.$^{-1}$, where ω_e'' and ω_e'' refer to the ground state of CuBr. This provides ample evidence to conclude that the emitter of the new band system is the CuBr molecule and that the system has for its lower state the ground state of the molecule. This evidence is further corroborated by a comparison of the observed isotope shifts with those theoretically expected (Table II), as will be presently discussed.

The wavelengths, the wave-numbers and the vibrational assignments of the bands of the new system are given in Table I. The wave-numbers of the band heads can be represented by the formula:

$$\nu_H^{63,79} = 25538{\cdot}5 + 281{\cdot}9\,(v' + \tfrac{1}{2}) - 1{\cdot}35\,(v' + \tfrac{1}{2})^2 - 314{\cdot}4\,(v'' + \tfrac{1}{2}) + 0{\cdot}86\,(v'' + \tfrac{1}{2})^2. \quad (1)$$

Since the 0–2 band is overlapped by some bands of the C system, it was not possible *a priori* to locate its position precisely. It was therefore necessary to

use in equation (1) the value of $\omega_e'' x_e''$ (0·86 cm.$^{-1}$) from the known molecular constants of CuBr. All the other vibrational constants in equation (1) are derived from the band head data of this system. The last column of Table I shows the agreement between the observed values of the band heads and those calculated from equation (1).

The lack of definition and sharpness in the band heads, except of those of the $\Delta v = 0$ sequence, is due to isotope shifts. Accurate isotope shift measurements could not be made on spectrograms taken on the Jarrel Ash spectrograph. This is because the shifts involved are very small due to the low v' and v'' values of the bands recorded and the relatively small difference

TABLE I

*New band system in CuBr**

v'	v''	Rel. int.	λ in air Å	ν in vac. cm.$^{-1}$	ν obs. $-$ ν cal. cm.$^{-1}$
5	0	1	3718·40†	26885·6	−5·3
6	1	1	3724·74†	26839·9	−4·1
7	2	1	3730·39†	26799·2	+3·3
4	0	3	3754·91	26624·2	+1·6
5	1	3	3761·86	26575·0	−3·2
3	0	5	3793·67	26352·2	+0·7
4	1	4	3799·83	26309·6	−0·3
2	0	6	3833·61	26077·7	−0·1
5	3	4	3850·76	25961·5	+2·5
1	0	7	3874·67	25801·3	+0·1
3	2	5	3885·76	25727·6	−0·2
4	3	4	3891·46	25690·0	+0·4
0	0	8	3917·06	25522·1	0
1	1	7	3922·21	25488·6	0
2	2	7	3927·46	25454·5	+0·5
0	1	9	3965·31	25209·4	0
0	2	10	4015·25	24898·0	−0·4

* The measurements refer to ^{63}Cu ^{79}Br band heads.

† These bands are very diffuse and weak.

in the ω_e values of the two states involved—the few bands involving relatively high $\triangle v$ values are too weak for any accurate measurements. Since in the $\triangle v = +1, +2$, etc., sequences the band heads of the Cu^{63} Br^{79} molecule are in favourable positions, *i.e.*, at the shorter wavelength end of the red degraded isotopic band complex, the band head measurements given in Table I pertain to it.

Isotope shifts given in Table II are those obtained from spectrograms taken in the second order of the 6·6 metre grating. Figure 2 is a reproduction of a typical spectrum. It might be seen that the agreement between the measured isotope shifts and those expected theoretically is good. This provides an independent check on the identification of the emitter of the band system.

TABLE II

Isotope shifts in the new band system of CuBr*

Band \ Molecule	^{63}Cu ^{81}Br		^{65}Cu ^{79}Br		^{65}Cu ^{81}Br	
	$\triangle\nu$ obs. cm.$^{-1}$	$\triangle\nu$ cal. cm.$^{-1}$	$\triangle\nu$ obs. cm.$^{-1}$	$\triangle\nu$ cal. cm.$^{-1}$	$\triangle\nu$ obs. cm.$^{-1}$	$\triangle\nu$ cal. cm.$^{-1}$
1–0	−1·3	−1·4	−2·5	−2·2	−3·5	−3·7
0–1	+1·7	+1·8	+2·7	+2·8	+4·0	+4·7

* The isotope shifts, $\triangle\nu$, are measured with respect to the ^{65}Cu ^{79}Br molecule.

A few new bands belonging to the B and C systems of CuBr have been recorded in the present investigations. These are given in Tables III and IV. The vibrational assignments of these bands, made on the basis of the known band head formulae for the B and C systems, are confirmed by isotope shifts in all cases where the shifts have been measured. These bands involve high v'' values and were therefore not recorded by Ritschl in his investigation of the absorption spectrum of CuBr. In accordance with Ritschl's notation, this new band system in CuBr is designated as the D system.

The rotational structure of the CuBr band systems is under investigation and some inferences in this regard are probably not unwarranted even at this stage. The bands in the A and B systems of CuBr are double-headed bands, characteristic of $^1\Pi - {}^1\Sigma$ transition whereas those in the C and D

TABLE III

New bands in the B system of CuBr

v'	v''	Rel. int.	$^{63}Cu\ ^{79}Br$		$^{63}Cu\ ^{81}Br$			$^{65}Cu\ ^{79}Br$			$^{65}Cu\ ^{81}Br$		
			λ in air Å	ν in vac. $cm.^{-1}$	ν in vac. $cm.^{-1}$	Isotope shift $\Delta\nu^*$ in $cm.^{-1}$		ν in vac. $cm.^{-1}$	Isotope shift $\Delta\nu^*$ in $cm.^{-1}$		ν in vac. $cm.^{-1}$	Isotope shift $\Delta\nu^*$ in $cm.^{-1}$	
						Obs.	Cal.		Obs.	Cal.		Obs.	Cal.
5	8	10	4552·50	21959·8	21966·0	+6·2	+6·0	..	..	..	..	..	..
6	9	8	4558·82	21929·4	21935·3	+5·9	+6·1	..	..	..	..	..	..
7	10	6	4564·16	21903·7	..	..	+6·2	..	..	..	..	..	..
2	6	5	4598·29	21741·1	21748·4	+7·3	+7·2	..	..	+11·1	21759·2	+18·1	+18·5
3	7	4	4603·67	21715·7	21723·1	+7·4	+7·3	21726·5	+10·8	+11·3	21734·0	+18·3	+18·9
4	8	4	4609·24	21689·5	21696·7	+7·2	+7·5	21761·2	+11·7	+11·5	21708·3	+18·8	+19·2
5	9	3	..	..	21669·2	..	+7·6	21673·3	..	+11·8	..	..	+19·6
6	10	3	4621·24	21633·2	21640·8	+7·6	+7·8	21644·9	+11·7	+12·0	21652·2	+19·0	+20·0

* The isotope shifts, $\Delta\nu$, are measured with respect to the $^{63}Cu\ ^{79}Br$ molecule.

TABLE IV

New bands in the C system of CuBr

v'	v''	Rel. int.	^{63}Cu ^{79}Br		^{63}Cu ^{81}Br			^{65}Cu ^{79}Br			^{65}Cu ^{81}Br		
			λ in air Å	ν in vac. $cm.^{-1}$	ν in vac. $cm.^{-1}$	Isotope shift $\Delta\nu^*$ in $cm.^{-1}$		ν in vac. $cm.^{-1}$	Isotope shift $\Delta\nu^*$ in $cm.^{-1}$		ν in vac. $cm.^{-1}$	Isotope shift $\Delta\nu^*$ in $cm.^{-1}$	
						Obs.	Cal.		Obs.	Cal.		Obs.	Cal.
7	11	10	4522·73	22104·3	22113·4	+9·1	7·5	..	..	..	..	..	..
8	12	8	4526·87	22084·1	..	..	7·8	..	..	..	..	..	..
4	9	6	4573·15	21860·6	21869·2	+8·6	+8·8	21873·1	+12·5	+13·6	21881·7	+21·1	+22·8
5	10	5	4576·84	21843·0	..	..	+8·9	..	..	..	..	..	..
6	11	4	4579·78	21829·0	..	..	+9·0	..	..	..	..	..	..
7	12	3	..	..	21820·9	..	+9·1	..	..	..	..	..	..

* The isotope shifts, $\nu\Delta$, are measured with respect to the ^{63}Cu ^{79}Br molecule.

systems are single-headed bands, characteristic of $^1\Sigma - {}^1\Sigma$ transitions. In CuCl the ground state is a $^1\Sigma$ state and five of the six known excited states are shown to be either $^1\Pi$ or $^1\Sigma$ states (Asundi, Ramakoteswara Rao and Brody, 1961), *see* Fig. 3. Analogy suggests that probably in CuBr also the ground state is a $^1\Sigma$ state and the excited states involved in the A, B, C and D systems are $^1\Pi$, $^1\Pi$, $^1\Sigma$ and $^1\Sigma$ states respectively as indicated in Fig. 3.

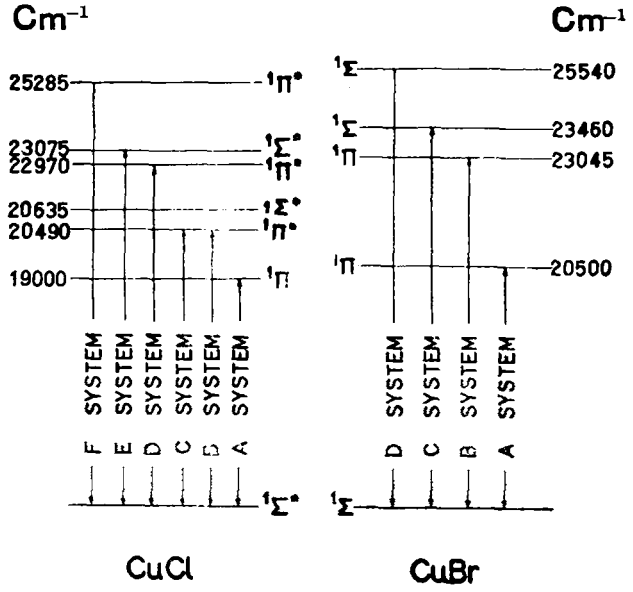

FIG. 3. Known electronic states in the CuCl and CuBr molecules. For states denoted by asterisks, the spectroscopic notation has been established by fine structure analysis, whereas for others it is suggested by the gross structure of the band systems.

SUMMARY

A new system of red degraded bands in the 3700–4000 Å region has been obtained in the spectrum of the CuBr molecule excited in an electrodeless discharge tube by a microwave oscillator. The band heads of this system are given by the formula:

$$\nu\,{}^{63}\mathrm{Cu}\,{}^{79}\mathrm{Br} = 25538{\cdot}5 + 281{\cdot}9\,(v' + \tfrac{1}{2}) - 1{\cdot}35\,(v' + \tfrac{1}{2})^2 - 314{\cdot}4\,(v'' + \tfrac{1}{2}) + 0{\cdot}86\,(v'' + \tfrac{1}{2})^2.$$

It has been found that the lower electronic state of this system is the same as the common lower state of the three known band systems, which is also the ground state of the molecule.

Some new bands recorded in the B and C systems are assigned vibrational quantum numbers.

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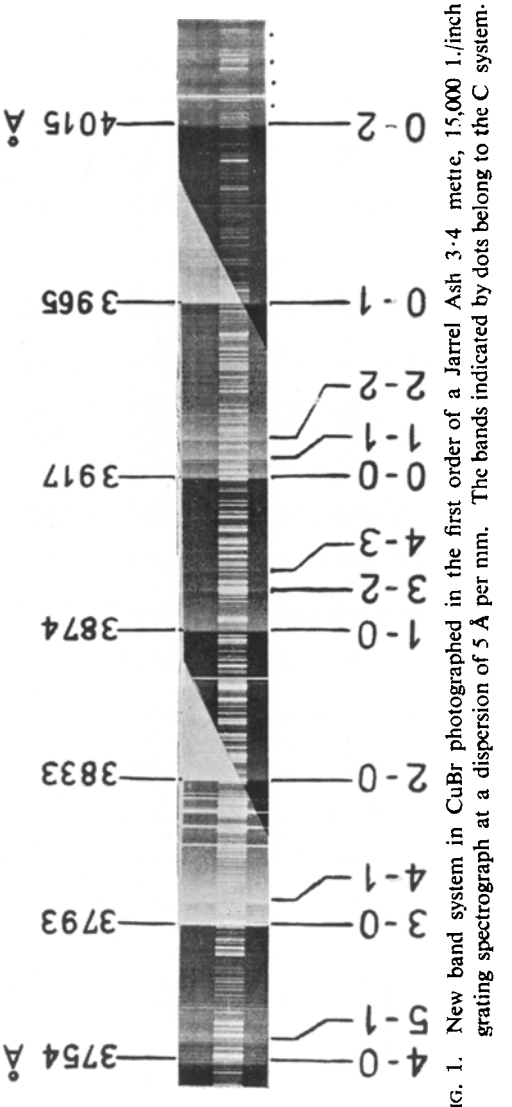

FIG. 1. New band system in CuBr photographed in the first order of a Jarrel Ash 3·4 metre, 15,000 l./inch grating spectrograph at a dispersion of 5 Å per mm. The bands indicated by dots belong to the C system.

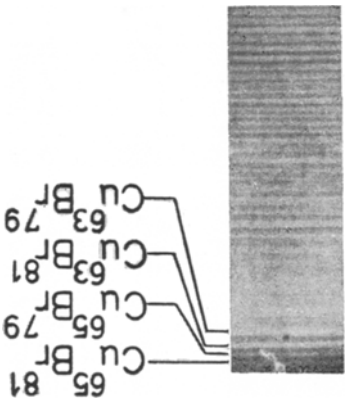

FIG. 2. The 0–1 band of the new system in CuBr photographed in the second order of the 6·6 metre, 30,000 l./inch grating spectrograph at a dispersion of about 0·6 Å per mm.