

TABLE II  
SPACINGS ( $d$ ) AND INTENSITIES FROM X-RAY DIFFRACTION PATTERNS FOR  $\text{BiCl}_3$  OBTAINED BY DIFFERENT WORKERS<sup>a</sup>

Gal'chenko, <sup>b</sup> kX	Petro and Shore, <sup>c</sup> Å	This work, <sup>d,e</sup> Å
		6.73 vvw
6.24 m	6.28 vw	6.27 m
5.96 m	5.95 vw	5.91 w
5.21 vw	5.19 m	5.20 m
		4.93 vvw
4.716 m	4.75 s	4.72 s
4.595 m		
4.521 m	4.55 s	4.50 s
4.328 vw		4.32 w
3.750 m	3.77 m	3.74 ms
3.709 w		
3.585 mw		3.56 w
3.518 w	3.48 w	3.49 m
3.456 w		
		3.29 vw
3.207 mw	3.21 vw	3.18 mw
		3.06 vvw
2.951 mw	2.97 m	2.95 ms
2.882 w	2.89 w	2.875 mw
2.790 m	2.81 s	2.796 s <sup>d</sup>

<sup>a</sup> Cu  $K\alpha$  radiation in each case. <sup>b</sup> See ref 7; 1.00202 Å = 1 kX. <sup>c</sup> V. P. Petro and S. G. Shore, *J. Chem. Soc.*, 336 (1964). <sup>d</sup> Eight further weak reflections were also recorded. <sup>e</sup> Samples sealed in 0.3-mm capillaries under dry nitrogen.

tional weak reflections. The spacings are also coincident with those of Gal'chenko with the exception of his 4.595 (m), 3.709 (w), and 3.456 (w) kX, which neither our nor Petro's sample shows. Two of these are weak, and in view of the close correlation of the remaining 13 spacings, it is overwhelmingly probable that all three samples were identical.

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## Raman Spectra of Solid Bismuth(III) Bromide and Chloride

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In the gas phase,  $\text{BiCl}_3$  and  $\text{BiBr}_3$  exist as discrete pyramidal molecules.<sup>2</sup> Largely owing to early photographic Raman evidence, a similar molecular structure has seemed likely for  $\text{BiCl}_3$  in the solid state. The reported Raman frequencies are four in number, as expected of  $C_{3v}$  pyramidal symmetry, but the two sets of data are not in complete agreement: Bhagavantam<sup>3</sup>

found Raman lines for solid  $\text{BiCl}_3$  at 290, 240, 130, and 90  $\text{cm}^{-1}$ , while Krishnamurti<sup>4</sup> found them at 288, 242, 169, and 153  $\text{cm}^{-1}$ . In addition, the far-infrared spectrum of solid  $\text{BiBr}_3$  dispersed in a polyethylene matrix exhibits four fundamentals at 196, 169, 104, and 89  $\text{cm}^{-1}$  consistent with  $C_{3v}$  symmetry for this molecule as well (the hygroscopic nature of  $\text{BiBr}_3$  prevented a Nujol mull from being used).<sup>5</sup>

A discrepancy arises, however, when the nuclear quadrupole resonance (nqr) spectra of  $\text{BiCl}_3$  and  $\text{BiBr}_3$  are examined. In the case of  $\text{BiCl}_3$ , the chlorine nqr spectrum reveals two nonequivalent positions for Cl in the unit cell, with approximately equal numbers of Cl atoms in each position.<sup>6</sup> For both  $\text{BiCl}_3$  and  $\text{BiBr}_3$ , the large asymmetry parameter of <sup>209</sup>Bi ( $\eta \sim 0.55$ ) indicates distortion from  $C_{3v}$  symmetry and has been interpreted in terms of cross bonding among the molecules in the solid.<sup>6,7</sup> The nqr studies rule out a formulation such as  $\text{Bi}_2\text{Cl}_6$  and eliminate a structure similar to that of  $\text{BiI}_3$ , in which Bi(III) is octahedrally surrounded by iodine atoms. The deviation from  $C_{3v}$  symmetry reportedly is greater for  $\text{BiBr}_3$  than for  $\text{BiCl}_3$ .

Available X-ray data for  $\text{BiCl}_3$  and  $\text{BiBr}_3$  are of uncertain value, as they consist only of powder patterns which indicate that the unit cells for both solids contain four molecules and are primitive cubic, the probable space group for both being  $P_{23}$ .<sup>8</sup>

To help clarify this structural question and determine accurate Raman frequencies for crystalline  $\text{BiCl}_3$  and  $\text{BiBr}_3$ , photoelectrically recorded Raman spectra were obtained for these solids.

### Experimental Section

Reagent grade anhydrous  $\text{BiCl}_3$  (Baker) and  $\text{BiBr}_3$  (Alfa) were dried *in vacuo* at ca. 55° for at least 2 days, while reagent grade  $\text{BiCl}_3 \cdot \text{H}_2\text{O}$  (Mallinckrodt) was used without further treatment. In order to reduce hydrolysis in a methanolic solution of  $\text{BiCl}_3$ , anhydrous methanol (Fisher) was refluxed over  $\text{CaH}_2$  and distilled. All solid samples were manipulated in a dry nitrogen-filled glove bag and the methanolic solution of  $\text{BiBr}_3$  was prepared and filtered under a stream of dry  $\text{N}_2$ .

The Raman spectra reported herein were obtained at 46° using a Cary Model 81 spectrophotometer, with 4358-Å Hg excitation for white, crystalline  $\text{BiCl}_3$  and  $\text{BiCl}_3 \cdot \text{H}_2\text{O}$  and 5461-Å Hg excitation for yellow, crystalline  $\text{BiBr}_3$  and the methanolic  $\text{BiBr}_3$  solution. The 5461-Å mercury line could be isolated using the green filter solution described previously,<sup>9</sup> although in the case of solid  $\text{BiBr}_3$  the spectrum was unchanged when this filter solution was not used. A sheet of Ozalid filter (General Aniline and Film), wrapped around the conical sample tube, served to remove the 4047-Å mercury line. The spectra of solid  $\text{BiCl}_3$  and  $\text{BiCl}_3 \cdot \text{H}_2\text{O}$  were examined up to 600  $\text{cm}^{-1}$  and that of solid  $\text{BiBr}_3$  to 330  $\text{cm}^{-1}$ . For all three solids, the anti-Stokes Raman spectrum was also obtained (using 5461-Å excitation) to rule out possible "instrument lines." In addition, spectra of solid  $\text{BiBr}_3$  and  $\text{BiCl}_3$  were recorded using a Spex Industries helium-neon laser Raman spectrophotometer (6328-Å excitation) and, except for improved resolution, were identical with those from the Cary

(4) P. Krishnamurti, *ibid.*, **5**, 116 (1930).

(5) T. R. Manley and D. A. Williams, *Spectrochim. Acta*, **21**, 1773 (1965).

(6) H. G. Robinson, *Phys. Rev.*, **100**, 1731 (1955).

(7) E. D. Swiger, *et al.*, *J. Phys. Chem.*, **69**, 949 (1965).

(8) G. M. Wolten and S. W. Mayer, U. S. Atomic Energy Commission Report NAA-SR-2939, 1958; *Acta Cryst.*, **11**, 739 (1958).

(9) R. P. Oertel and R. A. Plane, *Inorg. Chem.*, **6**, 1960 (1967).

(1) National Science Foundation Graduate Fellow, 1966-1968.

(2) H. A. Skinner and L. E. Sutton, *Trans. Faraday Soc.*, **36**, 681 (1940).

(3) S. Bhagavantam, *Indian J. Phys.*, **5**, 35 (1930).

81. The estimated accuracy of the reported frequencies is  $\pm 2$   $\text{cm}^{-1}$ .

### Results and Discussion

Raman spectra of solid  $\text{BiBr}_3$ ,  $\text{BiCl}_3$ , and  $\text{BiCl}_3 \cdot \text{H}_2\text{O}$  are shown in Figure 1, while the observed frequencies

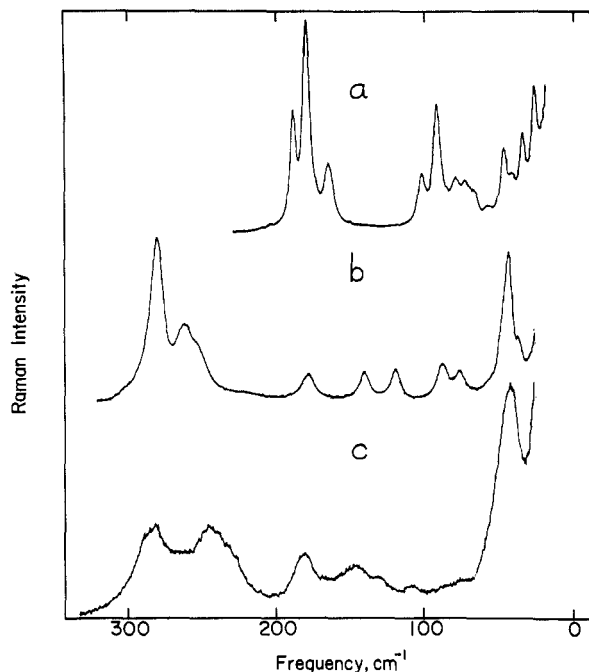


Figure 1.—Raman spectra of solid (a)  $\text{BiBr}_3$  (gain  $1.6 \times 50$ ), (b)  $\text{BiCl}_3$  (gain  $2 \times 100$ ), and (c)  $\text{BiCl}_3 \cdot \text{H}_2\text{O}$  (gain  $3 \times 200$ ). The Cary Model 81, 5461-Å Hg excitation for  $\text{BiBr}_3$ , and 4358-Å Hg excitation for  $\text{BiCl}_3$  and  $\text{BiCl}_3 \cdot \text{H}_2\text{O}$  were used. A single-slit width of 2  $\text{cm}^{-1}$ , Raman Dynode 3, and an Ozalid filter were employed for all three spectra.

and spectral features are listed in Table I. The multiplicity of lines observed in both the stretching and bending regions of these three solids can arise from several sources: (1) a crystalline site symmetry lower than  $C_{3v}$  pyramidal, (2) coupling between similar vibrations on different molecules in the unit cell, (3) splitting of degenerate molecular vibrations by crystal lattice modes,<sup>10</sup> and (4) a molecular symmetry lower than  $C_{3v}$  pyramidal in the solid state. The probable space group,  $P_{213}$ , leads to sites of  $C_3$  symmetry for the molecules in the crystalline phase, which alone cannot account for the observed multiplicity of bands. Intermolecular coupling and lattice interactions cannot be directly ruled out. The simplest interpretation, however, and the one which agrees with the nqr results is that the molecules do not possess  $C_{3v}$  pyramidal symmetry in the solid state. If the symmetry is lowered to  $C_3$ , for example, six Raman- and infrared-allowed bands will result. Since meaningful Raman polarization data are not possible for polycrystalline samples, tentative assignments must be based largely on relative intensity and position. From comparison with spectra of bromo- and chlorobismuthates,<sup>9</sup> it appears reasonable to ascribe the highest frequency band to the symmetric stretching ( $A'$ ) mode for both  $\text{BiBr}_3$  and  $\text{BiCl}_3$ . As-

(10) D. F. Hornig, *J. Chem. Phys.*, **16**, 1063 (1948).

TABLE I  
RAMAN FREQUENCIES<sup>a</sup> AND SPECTRAL FEATURES<sup>b</sup> OF SOLID  
 $\text{BiBr}_3$ ,  $\text{BiCl}_3$ , AND  $\text{BiCl}_3 \cdot \text{H}_2\text{O}$

$\text{BiBr}_3$	$\text{BiCl}_3$	$\text{BiCl}_3 \cdot \text{H}_2\text{O}$
21 m	37 w, sh	
27 ms	45 s	43 vs
35 m	58 w	
42 w	67 vw	
47 m	77 m	78 vw
57 vw	89 m	~88 vw (?)
68 w	120 m	110 w
75 m	141 m	130 mw, sh
81 m	180 m	143 m
88 vw, sh	225 vw	178 s
93 s	254 ms, sh	~225 w, sh
103 m	262 s	240 vs
166 ms	280 vs	281 vs
181 vs		
190 s		
205 vw		

<sup>a</sup> In  $\text{cm}^{-1}$ . <sup>b</sup> Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder.

signment of the two components ( $A'$ ,  $A''$ ) of the asymmetric stretching mode then follows directly, as shown below (in  $\text{cm}^{-1}$ ). The assignment of the Raman bands

$C_{3v}$	$A_1$	$E$		$A_1$	$E$	
$C_3$	$A'$	$A'$	$A''$	$A'$	$A'$	$A''$
$\text{BiBr}_3$	190	181	166	103	93	81
$\text{BiCl}_3$	280	262	254	?	?	?

in the bending region for solid  $\text{BiBr}_3$  follows from the reported infrared frequencies for supposed  $C_{3v}$  symmetry:  $A_1$ , 104  $\text{cm}^{-1}$ ;  $E$ , 89  $\text{cm}^{-1}$ .<sup>5</sup> Similar assignments for solid  $\text{BiCl}_3$  are not possible, owing to the complexity of this spectral region. The still lower frequency bands for both  $\text{BiBr}_3$  and  $\text{BiCl}_3$  are of uncertain origin, although at least some must be due to lattice modes. The inclusion of one water molecule in solid  $\text{BiCl}_3$  not only broadens the spectral bands but also causes drastic frequency shifts which must accompany a change in structure.

It is interesting to note that, for both  $\text{BiBr}_3$  and  $\text{BiCl}_3$ , the symmetric stretching frequency is substantially lower in the solid than in solution. Thus, a methanolic  $\text{BiBr}_3$  solution ( $[\text{Bi(III)}] = 0.54 M$ ,  $[\text{Br}^-]/[\text{Bi(III)}] = 3.0$ ) gives a strong, polarized symmetric stretching band at 200  $\text{cm}^{-1}$  and a weaker, depolarized band at 182  $\text{cm}^{-1}$ , while the bending region is obscured by intense Rayleigh scattering. We previously reported<sup>9</sup> that a methanolic  $\text{BiCl}_3$  solution ( $[\text{Bi(III)}] = 0.13 M$ ,  $[\text{Cl}^-]/[\text{Bi(III)}] = 3.1$ ) gives symmetric and asymmetric stretching bands at 305 and 268  $\text{cm}^{-1}$ , respectively, with bending activity near 120  $\text{cm}^{-1}$ . The Raman spectrum of molten  $\text{BiCl}_3$  shows bands at *ca.* 317, 267, and 121  $\text{cm}^{-1}$ .<sup>11</sup> In fact, the symmetric stretching frequency of solid  $\text{BiCl}_3$  (280  $\text{cm}^{-1}$ ) is as low as that of the species  $\text{BiCl}_5^{2-}$  both in solution and in the solid phase (280 and 276  $\text{cm}^{-1}$ , respectively).<sup>9</sup> This observed frequency difference between solid and solution for  $\text{BiBr}_3$  and  $\text{BiCl}_3$  is more than that normally encountered with

(11) J. T. Kenney and F. X. Powell, *J. Phys. Chem.*, **72**, 3094 (1968).

metal halide complexes and must be related to a change in structure between the two phases.<sup>12</sup> The spectrum of  $\text{BiCl}_3(\text{solv})$  has been interpreted in terms of  $C_{3v}$  pyramidal symmetry,<sup>9</sup> judging from the partial Raman spectrum of  $\text{BiBr}_3(\text{solv})$ , this molecule probably possesses  $C_{3v}$  symmetry in solution as well.

It is not difficult to understand why previous Raman and infrared studies failed to uncover the lower solid-state symmetry for  $\text{BiBr}_3$  and  $\text{BiCl}_3$ . First, the early photographic Raman technique applied to crystalline samples probably lacked the resolution necessary to detect the multiplicity of overlapping bands which can be observed photoelectrically. Based on the reported frequencies, it also appears as though the early workers might mistakenly have been investigating  $\text{BiCl}_3 \cdot \text{H}_2\text{O}$ , and not anhydrous  $\text{BiCl}_3$ . Second, since the polyethylene-matrix method used to obtain the far-infrared spectrum of  $\text{BiBr}_3$  was specifically designed to break down the intermolecular structure of related iodides, it could very well have isolated discrete  $\text{BiBr}_3$  molecules as well. The spectrum so obtained, then, was not that of crystalline  $\text{BiBr}_3$ ; in fact,  $196 \text{ cm}^{-1}$  in the infrared spectrum very closely matches  $200 \text{ cm}^{-1}$  in the Raman spectrum of the methanolic  $\text{BiBr}_3$  solution.

(12) P. J. Hendra, *Spectrochim. Acta*, **23A**, 2871 (1967).

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## The Crystal Structure of Potassium Perbromate<sup>1</sup>

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A description of the synthesis of perbromates has been published recently by one of us.<sup>2</sup>

The symmetry of  $\text{KBrO}_4$  is orthorhombic with  $a = 8.930$  (4),  $b = 5.921$  (4), and  $c = 7.488$  (4) Å. The extinctions are:  $0kl$  with  $k + l$  odd and  $hk0$  with  $h$  odd, which leads to space group  $C_{2v}^9$ - $\text{Pn}2_1a$  or  $D_{2h}^{16}$ - $\text{Pnma}$ . A pycnometric determination of the density gave a value of  $3.08$  (3)  $\text{g cm}^{-3}$ . The computed density, based on four molecules in the cell, is  $3.07 \text{ g cm}^{-3}$ .

### Experimental Section

Crystals of  $\text{KBrO}_4$  were grown by evaporation at room temperature of a saturated solution of the salt. All symmetry information was deduced from Weissenberg patterns obtained with each crystal axis serving as a rotation axis, using  $\text{Cu K}\alpha$  radiation. Cell dimensions and errors were determined from counter and diffractometric data after calibration of the instrumental settings with a sodium chloride crystal.  $\text{Mo K}\alpha$  radiation ( $\lambda(\text{K}\alpha) 0.71069$  Å) was used for this purpose and in the subsequent collection of diffraction information.

A spherical crystal of 0.021-cm diameter was used in the struc-

tural analysis. Intensity data were obtained by counter methods utilizing a single-crystal orienter mounted on a General Electric XRD-5 diffraction unit. One quadrant only was investigated because of the onset of radiation damage. The scattering angle was limited to  $2\theta = 50^\circ$ , for line intensities were quite reduced beyond this value.

Radiation damage was found to be very pronounced. In order to limit the exposure time of the crystal to irradiation and thereby reduce the radiation damage, the following data collection procedure was adopted.

The intensities of all reflections  $hkl$  within a quadrant were obtained rapidly with balanced filters based on a stationary crystal and counter technique and using 10-sec counting times for each filter. Examination of a number of reflections with a  $\theta$ - $2\theta$  scan indicated that the weak maxima, those with intensities less than approximately 1% of the value of the most intense ones, could be evaluated more reliably with the scan technique. Accordingly, data for the weaker reflections were obtained by scanning, with a scan interval of  $2^\circ$  on either side of the Bragg angle and a scanning rate of  $2^\circ/\text{min}$ . The intensity distribution was recorded on a chart recorder in order to obtain a visual display of line position, line width, and background and to permit evaluation of the intensity. Numerical values for the intensities were obtained with a planimeter. A diffraction line intensity observed as zero was given a value corresponding to our estimated lower limit of the measurement of the line above the background noise level of the tracing. The radiation damage was kept to a minimum by exposing the crystal to X-rays only long enough to obtain intensity readings. Reflections  $h00$ ,  $0k0$ , and  $00l$  served as standards, and curves displaying changes in intensities with time were used to deduce corrections to the intensities for all classes of reflections. Following the data collection, a number of reflections for which intensities had been obtained initially from the fresh nonirradiated crystal were re-examined. It was found that corrections so applied led to reasonable agreement with the initial values.

Spherical absorption corrections were applied based on a linear absorption coefficient of  $118.7 \text{ cm}^{-1}$ . This absorption correction is contained in our data reduction program. Following corrections for radiation damage and absorption, the data were scaled and the Lorentz and polarization corrections were applied in the usual manner.

Approximate K and Br positions, found by trial, gave  $\gamma$ -coordinate values near  $1/4$ , indicating the fourfold special positions of  $\text{Pnma}$ ,  $4c$ , but not necessarily eliminating the general positions of  $\text{Pn}2_1a$ .<sup>3</sup> Improvement of these trial coordinates, based on space group  $\text{Pnma}$ , was obtained with the Busing-Martin-Levy "Fortran Crystallographic Least-Squares Program." In these calculations, the scattering factors for K and Br were taken from ref 4. Two-dimensional Fourier syntheses were then computed with the signs of the coefficients determined from the improved K and Br coordinates. The electron density maps showed three sets of peaks corresponding to the oxygen positions—two in the special fourfold positions and one in the general eightfold position.

Refined coordinates for all atoms were obtained by a least-squares analysis on all atomic positions, using the oxygen-scattering curve reported by Tokonami.<sup>5</sup> In this and subsequent analyses, a total of 383 independent reflections was used. The final values for the coordinates are given in Table I. The conventional  $R$  factor for this refinement is 0.076.

The coordinates were then subjected to a new refinement based on the space group  $\text{Pn}2_1a$ , with no essential improvement in the  $R$  factor. We have therefore chosen space group  $\text{Pnma}$  as representing the symmetry of  $\text{KBrO}_4$ . The observed and calculated structure factors based on  $\text{Pnma}$  are presented in Table II.

(3) "International Tables for Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952.

(4) "International Tables for Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962.

(5) M. Tokonami, *Acta Cryst.*, **19**, 486 (1965).

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) E. H. Appelman, *J. Am. Chem. Soc.*, **90**, 1900 (1968).