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Depolarization of Raman Lines and Structure of Chlorate, Bromate and Iodate Ions

S. T. SHEN, Y. T. YAO AND TA-YOU WU
Department of Physics, National University of Peking, Peking, China

The Raman spectra of chlorate ClO_3, bromate BrO_3 and iodate IO_3 in solutions are examined under high dispersion and the degrees of depolarization of the Raman lines measured. It is shown that the strong line at 930 cm^{-1} of ClO_3 and that at 800 cm^{-1} of IO_3 in solutions, which are regarded as single lines in the literature, are each really composed of two lines. The presence of four lines in each ion in the Raman effect, together with the depolarization measurement, and the infrared data, shows that these ions have pyramidal structure. The valence force constants of these ions are calculated from the present data according to the equations of Lechner.

INTRODUCTION

IN the literature[1] it is assumed that the chlorate ClO_3, bromate BrO_3 and iodate IO_3 ions have symmetric, plane structure like the carbonate ion CO_3. A symmetric, plane structure belongs to the symmetry class D_{3h} and possesses four vibrations: one totally symmetric vibration which is active in Raman effect but inactive in infrared absorption; one asymmetric with respect to the plane of the molecule and active in the infrared but inactive in Raman effect; and two doubly degenerate vibrations which are active in both Raman effect and the infrared. An examination of the Raman spectrum of ClO_3 ions in solution revealed, however, that in addition to the two lines at 479 cm^{-1} and 610 cm^{-1}, the strong line at 930 cm^{-1} has a wing on the high frequency side (measured from the exciting line), which suggests the presence of a weak line at 982 cm^{-1}. It is of some interest to investigate this further; for the presence of four Raman line would point to a pyramidal structure for the ion rather than a plane structure. A symmetric pyramidal model belongs to the symmetry class C_{3v} and possesses two totally symmetric vibrations ν_1, ν_2 in which the change of the electric moment is along the axis of the pyramid, and two doubly degenerate vibrations ν_3, ν_4 in which the change of the electric moment is perpendicular to the axis. All four vibrations are active in Raman effect. As the line 930 cm^{-1} of ClO_3 cannot be resolved from the wing even with high dispersion (12A per mm), and as the corresponding line in IO_3 (800 cm^{-1}) is only barely resolved into two lines at 779 and 826 cm^{-1}, it is thought desirable to study the depolarization of the Raman lines of ClO_3, BrO_3 and IO_3 with a view (i) to decide whether the line 930 cm^{-1} in ClO_3 and its wing are really two lines by observing their difference in the degrees of depolarization, and (ii) to decide between the plane model and the pyramidal model by comparing the observed spectra and the depolarizations with the selection and depolarization rules for the two models.

EXPERIMENTAL

The experimental method is of the conventional type. A mercury arc 14 cm long irradiated the Raman tube at a distance of 2 cm through two slits, each 0.8 cm wide, one near the arc and the other near the Raman tube. The scattered radiation was focused by a lens one meter from the tube and 43 cm from the slit of a three-prism Steinheil spectrograph with glass optics. Arrangement for exact parallelism of the exciting radiation was not attempted for it would necessitate unduly long exposures. The radiation was analyzed by a method due to Hanle.[2] A thick calcite crystal decomposed the radiation into two components; one with electric vector parallel to that of the exciting radiation and perpendicular to the length of the slit of the spectrograph, and a depolarized component with electric vector perpendicular to that of the exciting radiation and parallel to the length of the spectrograph. A second thin, wedge-shaped calcite crystal, cut

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[1] C. Schaefer, F. Matossi and H. Aderhold, Zeits. f. Physik **65**, 289 (1930); C. Schaefer and F. Matossi, *Das Ultrarote Spektrum;* Cabannes, Ann. d. Physik **18**, 285 (1932), remarked in passing that in contrast with CO_3, ClO_3 has four Raman active frequencies but ν_3 could not be observed. We are indebted to Dr. H. C. Cheng for calling our attention to this remark. From x-ray studies and wave mechanical considerations, however, it is known that these ions ClO_3, BrO_3, IO_3 have pyramidal structure. See, for example, Slater, Phys. Rev. **38**, 325 (1931).

[2] W. Hanle, Zeits. f. Instrumentenk. **51**, 488 (1931).

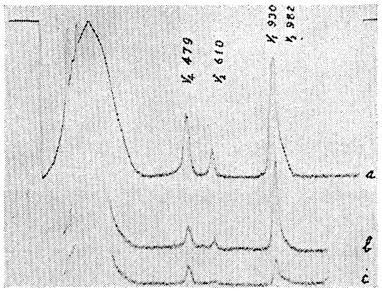

FIG. 1. ClO_3

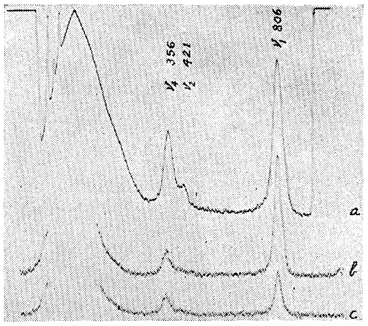

FIG. 2. BrO_3

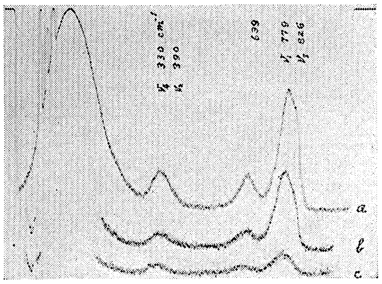

FIG. 3. IO_3

Raman spectra (a) without polarization, (b) polarized component, (c) depolarized component.

	ClO_3	BrO_3	IO_3
Concentration	10 N. $NaClO_3$	3 N. $NaBrO_3$	6.1 N. HIO_3
Slit width	0.06 mm	0.20 mm	0.06 mm
Exposure	250 hr.	230 hr.	210 hr.

with the optical axis in one face, was set with the axis at an angle of 45° with the slit to produce two images of depolarized light on the slit, so that difference in the loss of light due to reflections from the prism surfaces of the two components was eliminated. With this disposition, the two components were photographed simultaneously and exposures could be prolonged for the weak lines.

The comparison of the intensities of the two components of the Raman lines was made by the method of Thomson and Duffendack.[3] Intensity marks were put on the plate by means of a step-diaphragm. Intensity measurements were made on the microphotometer tracings of the line and the blackening-intensity curve at the position of the line.

In this study, excitation of the spectra was by means of the 4358 line. The jacket of the double-walled Raman tube contained a solution of sodium nitrite to filter off the line 4047 so as to eliminate the water band excited by it. This is necessary, for the broad water band falls in the region of the Raman lines of the ions excited by the line 4358 and would make intensity measurements very difficult. The Raman spectra of ClO_3, BrO_3 and IO_3 are represented in Figs. 1, 2, 3.

From Fig. 1, it is seen that the wing is more strongly depolarized than the line at 930 cm^{-1}, and it can be reasonably ascribed to a weak line with center at 980 cm^{-1}, though a decomposition of the intensity curve into two overlapping lines cannot be done entirely without arbitrariness. In BrO_3, the line at 421 cm^{-1} is observed for BrO_3 in solution for the first time. The strong line at 806 cm^{-1} is quite symmetrical, showing that the frequency ν_3 corresponding to the wing of the line 930 cm^{-1} in ClO_3 either is very close to $\nu_1 = 806$ cm^{-1} or is too weak to appear since the concentration of BrO_3 is low. In obtaining the curves *b* and *c*, the slit was opened up to 0.2 mm and the exposure was 210 hr. Even then the two components of ν_2 at 421 cm^{-1} were too weak to give an accurate value for the degree of depolarization. In IO_3,[4] the line at 330 cm^{-1} is broad and is due to two lines ν_4, ν_2 very close together. The line at 800 cm^{-1} is seen to be composed of two lines ν_1 and ν_3, the latter being more strongly depolarized than the former. Because of the overlapping of the two lines, an exact measurement of the intensity of the weak line ν_3 is impossible. However, by assuming a reasonable shape of the line ν_1 and by assuming that the half-width of the line is the same in the polarized and the depolarized components, a decomposition of the line into ν_1 and ν_3 may be performed

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[3] K. B. Thomson and O. S. Duffendack, J. Opt. Soc. Am. **23**, 101 (1933).

[4] The line at 639 cm^{-1} is present in the Raman spectra of HIO_3 crystals but is not found in KIO_3 crystals (Kohlrausch, *Smekal-Raman Effekt*, S. 351). By varying the concentration of the HIO_3 in the solution, we found that the intensity of the line 639 cm^{-1} relative to the line 800 cm^{-1} decreases with decrease of concentration. These facts seem to show that the line 639 cm^{-1} is due to the undissociated molecule HIO_3. Quantitative measurement on the variation of the relative intensities of the line 639, 800, 330 with the concentration will be published elsewhere.

graphically. The degree of depolarization was then calculated by means of the log blackening-intensity curve. The values of ρ's for ν_3 of IO_3 and ClO_3 obtained in this manner must be regarded as qualitative.

The results of this study are summarized in Table I, which includes the infrared data[5] for comparison.

Discussion of Results

The presence of four lines in the Raman spectra of ClO_3, BrO_3 and IO_3 shows that they are inconsistent with a plane model, but fit in quite well with a pyramidal model. According to the polarization rule of Placzek,[6] the two symmetric vibrations ν_1 and ν_2 are partially depolarized and the values of the degrees of depolarization ρ should be less than 6/7; while the two degenerate vibrations ν_3 and ν_4 are completely depolarized and $\rho = 6/7$ for natural light. It is seen from Table I that wherever ρ has been measured, it agrees with the theory, except for ν_3 of IO_3 in which case ρ cannot be determined accurately because of the closeness of ν_3 to ν_1.

Further evidence[7] for the pyramidal structure is furnished by the infrared absorption curves of these ions in crystals. For the ClO_3 ion, Schaefer, Schubert, Matossi and Laski[5] observed three bands at 23μ (434 cm^{-1}), 16μ (624 cm^{-1}) and 10.04μ (994 cm^{-1}). At low dispersion, the band at 10μ shows an asymmetry consisting of a wing on the long wave-length side. A comparison between the infrared curve and the Raman line drawn on the same scale is given in Fig. 4. It is seen that the wing in the infrared absorption curve corresponds to a weak band due to the parallel vibration ν_1 which appears strongly in Raman effect, and the wing in the Raman curve corresponds to the perpendicular vibration ν_3 which is strong in infrared absorption.

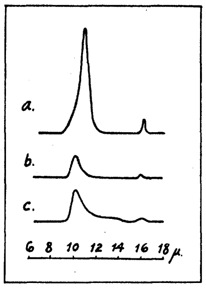

FIG. 4. (a) Raman lines of $NaClO_3$; (b) infrared curve of $NaClO_3$; (c) infrared curve of $KClO_3$.

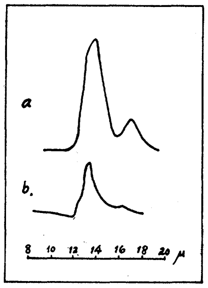

FIG. 5. (a) Raman lines of HIO_3; (b) infrared curve of KIO_3.

For BrO_3 two infrared bands at 23μ (434 cm^{-1}) and 12.2μ (820 cm^{-1}) are known, and a third at about 36μ (280 cm^{-1}) is obtained by extrapolation.[8] For IO_3, a band at 12.6μ (793 cm^{-1}) is observed, and one at 27μ (357 cm^{-1}) corresponding to ν_2 was obtained by extrapolation. A comparison between the infrared curve for the 12.6μ band and the Raman line at 800 cm^{-1} is given in Fig. 5.

Considering the low dispersion with which the infrared absorption curves were obtained, and

TABLE I. *The infrared and the Raman frequencies of ClO_3, BrO_3 and IO_3. The values in brackets are obtained by extrapolation only.*[5] *The values marked with an asterisk are taken from crystal data, Kohlrausch, "Smekal-Raman Effekt."*

		ν_1 ∥		ν_2 ∥		$\nu_3(2)$ ⊥		$\nu_4(2)$ ⊥	
		Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared
ClO_3	ν	930 cm^{-1}	950 cm^{-1}	610 cm^{-1}	624 cm^{-1}	982 cm^{-1}	994 cm^{-1}	479 cm^{-1}	434 cm^{-1}
	ρ	0.35		0.56		0.87		0.90	
BrO_3	ν	806	800	421	434	836*	820	356	(278)
	ρ	0.38						0.89	
IO_3	ν	779	780	390*	(357)	826	793	330	
	ρ	0.43				0.67		0.81	

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[5] C. Schaefer and M. Schubert, Zeits. f. Physik **7**, 309 (1921); C. Schaefer and Matossi, *Das Ultrarote Spektrum*, S. 328.

[6] Placzek, *Leipziger Vorträge*, 1931.

[7] An indirect reason against the plane model for these ions is that even if one neglects the presence of the line ν_2 in the Raman effect and proceeds to calculate the force constants of the ions, on the assumption of a plane model, using either the central force system of Dennison-Nielsen, Phys. Rev. **32**, 773 (1928), or the valence force system of Lechner, one is led to inconsistency in the equations giving the frequencies.

[8] C. Schaefer and F. Matossi, *Das Ultrarote Spektrum*, S. 328.

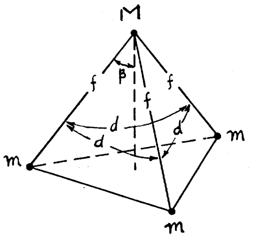

Fig. 6.

remembering that the long wave-length bands[8] were obtained by the Reststrahlen method of which the accuracy is very low, and that the infrared frequencies and the Raman frequencies were obtained for the ions in crystals and in solutions respectively, one feels that the agreement between the Raman data and the infrared data is as good as one would expect. It is desirable to examine the 10μ band of ClO_3 and the 12.6μ band of IO_3 in the infrared with higher dispersion, and to determine more accurately the positions of the long wave-length bands of these ions.

Assuming a pyramidal model, one can calculate the force constants of these ions. On the basis of a valence force system, Lechner[9] obtained the following equations for the four frequencies $\nu_i = \sqrt{\lambda_i}/2\pi$:

$$\lambda_1\lambda_2 = (f/m)(6d/m)2p\cos^2\beta/(1+3\cos^2\beta),$$

$$\lambda_1+\lambda_2 = (f/m)[1+(p-1)\cos^2\beta] + (6d/m)[p-(p-1)\cos^2\beta]2\cos^2\beta/(1+3\cos^2\beta),$$

$$4\lambda_3\lambda_4 = (f/m)(6d/m)[p+(2-p)\cos^2\beta]2/(1+3\cos^2\beta),$$

$$2(\lambda_3+\lambda_4) = (f/m)[p+1-(p-1)\cos^2\beta] + (6d/m)[1+(p-1)(1-\cos^2\beta)^2/2(1+\cos^2\beta)](1+\cos^2\beta)/(1+3\cos^3\beta),$$

where $p=(3m+M)/M$, and ν_1, ν_2 are the single frequencies and ν_3, ν_4 are the doubly degenerate frequencies.

By substituting the observed frequencies in these equations and so adjusting the values of the constants f, d and β that the two sides of the equations are closest to each other, we obtain the values of f, d, β for the ions given in Table II.

Table II. *Constants of the CLO_3, BrO_3, IO_3 ions.*

	$f\times10^{-5}$	$6d\times10^{-5}$	β
ClO_3	5.55	6.42	54°
BrO_3	5.25	3.52	53.5°
IO_3	5.35	3.19	53.3°

In conclusion, we wish to acknowledge our indebtedness to Dr. Ny Tzi-Zé, of the Institute of Physics, Peiping Academy, for the use of the microphotometer.

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[9] F. Lechner, Graz Dissertation, 1933; Monatshefte f. Chemie **61**, 385 (1932).

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The ${}^1\Sigma^*-{}^1\Sigma$ Band System of Ionized Cadmium Deuteride

R. V. Zumstein, J. W. Gabel and R. E. McKay
Mendenhall Laboratory of Physics, Ohio State University, Columbus, Ohio

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The ${}^1\Sigma^*-\Sigma$ bands have been photographed with a dispersion of about 1.3A/mm. Eight bands of the system, between λ2630 and λ2280 were analyzed. The isotopic coefficient ρ agrees with the value obtained from atomic weights. The electronic isotope displacement relative to Cd^+H appears to be 4.4 cm^{-1}. However, this value is somewhat uncertain as only three vibrational levels of the upper state and four of the lower state are available. The lines did not show a fine structure from the cadmium isotopes.

The band spectrum of the ionized cadmium hydride molecule has been investigated by Svensson and Tyrén[1] who give references to previous work. We have studied the similar spectrum obtained by substituting deuterium for hydrogen, thus providing additional experimental evidence concerning the problem of the electronic isotope effect.

Experimental

The spectrum was excited in an end-on discharge tube of fused quartz. The length of the

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[1] E. Svensson and F. Tyrén, Zeits. f. Physik **85**, 257 (1933).

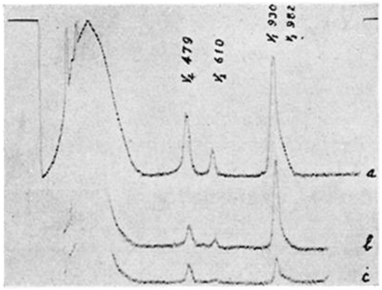

FIG. 1. ClO_3

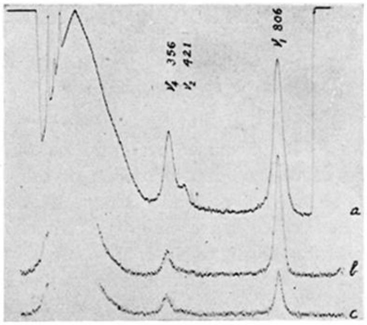

FIG. 2. BrO_3

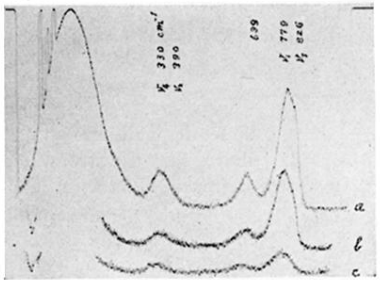

FIG. 3. IO_3

Raman spectra (a) without polarization, (b) polarized component, (c) depolarized component.

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Concentration	10 N. $NaClO_3$	3 N. $NaBrO_3$	6.1 N. HIO_3
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