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The Raman spectra of single crystals of $PbCl_2$ and $PbBr_2$

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RECENTLY the single crystal Raman spectrum of lead chloride was reported by Ozin[1]. This author makes an assignment of the normal modes with the help of polarization measurements. In this note we report our own results of a Raman study of a single crystal of lead chloride, because our data and assignment disagree with those of Ozin.

Previously Isupova *et al.*[2] have reported the Raman spectrum of powdered $PbBr_2$. The present study gives also the Raman frequencies of a lead bromide single crystal without assignment, because no polarization experiments were done on $PbBr_2$. These experiments will be performed in the future.

Single crystals with dimensions of a few centimeters long and a diameter of 1·5 cm were grown from the melt by a modified Bridgman technique[3]. From these optical transparent crystals, suitable cubic samples were cut, with the edges in the direction of the crystallographic axes.

Lead chloride and lead bromide crystallize in the orthorhombic system with space group D_{2h}^{16}, with four $PbCl_2$ or $PbBr_2$ molecules in the unit cell. The lead and halogen ions are each situated on the *xy* mirror planes.

An analysis based on the unit cell predicts 18 Raman active optical phonons, divided into modes of the following symmetry.

$$\Gamma_{vib} = 6\,A_g + 6\,B_{1g} + 3\,B_{2g} + 3\,B_{3g}.$$

Table 1.

Our results $PbCl_2$		Ozin $PbCl_2$		Our results $PbBr_2$	Isupova *et al.* $PbBr_2$
cm^{-1}	Type	cm^{-1}	Type	cm^{-1}	cm^{-1}
38	A_g	18	A_g	23	
60*	A_g	35	A_g	30	
62	A_g	156	A_g	36	34
148	A_g			55	54
160	A_g			75	74
182	A_g			87	
27?	B_{1g}	26	B_{1g}	89	88
88	B_{1g}	58	B_{1g}	109	108
131	B_{1g}	100?	B_{1g}	122	118
159*	B_{1g}	126	B_{1g}		
179*	B_{1g}	178	B_{1g}		
32	B_{2g}	35?	B_{2g}		
133	B_{2g}	86	B_{2g}		
179	B_{2g}	134	B_{2g}		
		156	B_{2g}		
27	B_{3g}	86	B_{3g}		
127	B_{3g}	156	B_{3g}		

*Weak or rather obscured lines.

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The polarizability components are as follows:

$$A_g: \alpha_{xx}, \alpha_{yy}, \alpha_{zz}; B_{1g}: \alpha_{xy}; B_{2g}: \alpha_{xz}; B_{3g}: \alpha_{yz}.$$

Our results, those of Ozin and those of Isupova *et al.* are summarized in Table 1; further details and polarized spectra will be published elsewhere.

Comparing our results with those of Ozin, we state that our results are in better accordance with the total number of the predicted normal modes. This is especially the case for the A_g modes.

The assignment of Ozin is based on the approximation, that there are modes involving mainly motion of lead ions and modes involving mainly motion of halogen ions. We shall test this approximation when the polarized Raman spectrum of $PbBr_2$ is also at our disposal.

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Kinetics of nitrogen uptake by Ruthenium(II) aquo species

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INTRODUCTION

THE ISOLATION of $[Ru(NH_3)_5N_2]BF_4$ by Allen and Senoff[1] and the subsequent preparation of a large number of molecular nitrogen complexes with transition metals[2] has generated considerable interest in such systems as possible models for nitrogen fixation. Many of these complexes have been formed in solution under mild conditions via the direct replacement of suitable ligands by nitrogen gas[3–6]

$$M\text{–}X + N_2 \longrightarrow M\text{–}N_2 + X \tag{1}$$

($X = H_2O$, H^-, Cl^-, THF). Reaction (1) might represent the first step in nitrogen fixation. However, apart from kinetic studies by Itzkovitch and Page[7] on the reaction between $[Ru(NH_3)_5(H_2O)]^{2+}$ and nitrogen, there is little quantitative data on the uptake of molecular nitrogen by metal complex substrates. This paper reports the kinetics of complex formation between nitrogen and the related ruthenium(II) complexes *cis*-$[Ru(A\text{–}A)_2(H_2O)_2]^{2+}$ ($A\text{–}A = (NH_3)_2$ ethylenediamine, ½ triethylenetetramine).

EXPERIMENTAL

Kinetic measurements

Weighed samples of *cis*-$[Ru(A\text{–}A)_2Cl_2]Cl\cdot H_2O$ were added to 100 ml of solvent (0·10M K_2SO_4,

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