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Polarized Raman Spectra of the Trigonal Crystal K_2ReF_6

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In two previous papers [1, 2], we reported the linearly polarized electronic absorption spectra of the trigonal crystal K_2ReF_6 at 4.2 K. Although it has been possible to locate all the eight intraconfigurational $t_{2g}{}^3 \leftrightarrow t_{2g}{}^3$ transitions, the assignment of the vibronic structure has not proved completely successful in the weak coupling limit. In particular, the presence of a substantial Jahn–Teller effect in the $\Gamma_8(^2T_{1g})$ and $\Gamma_8(^2T_{2g})$ electronic excited states could be ascertained by detecting the presence of progressions in the even non-total symmetric ν_2 and ν_5 vibrational modes split by the low symmetry crystal field. This has been partly done by using the frequencies of these modes as determined in a preliminary Raman experiment [2]. The present work aims to give the first detailed interpretation of the polarized Raman spectra of K_2ReF_6 in order to get more information on its vibrational properties and to lay the basis for a future elucidation of the vibronic structure superimposed on the electronic absorption transitions.

Experimental

Good quality K_2ReF_6 single crystals were grown as previously described [1]. Preliminary Raman spectra were taken both from powdered samples and single crystals at room temperature by using an Ar^+ laser (Spectra Physics model 165) operating at 60 mW, a double monochromator (Spex model 1401) and a RCA 31034 photomultiplier. The spectra were excited with the 488 nm line. The Raman spectra on the single crystals were measured in backscattering geometry with light propagating along the principal directions to avoid directional dispersion. The same crystals as for the electronic absorption measurements [1, 2] were used. The polarized spectra were recorded in four different orientations to minimize the effects of crystal misalignment. The scans with the propagation direction of the incoming light perpendicular to the optical axis were recorded in the range 50–1050 cm^{-1}, while the ones with the incident light propagating parallel to the optic axis were recorded in the range 20–270 cm^{-1}. The preliminary spectra covered the range 20–2000 cm^{-1}.

Results and Discussion

The crystal structure of K_2ReF_6 is of the K_2GeF_6 type (trigonal, space group $P\bar{3}m1$) [3]. The ReF_6 octahedra are compressed along the trigonal axis, yielding a local D_{3d} symmetry. The unit cell vibrational modes can be obtained by factor group analysis [1]. Seven of these modes $(3\alpha_{1g} + 4\epsilon_g)$ are Raman active, and seven peaks can be found in the Raman spectrum measured on the powdered sample.

In Figs. 1–3 we report the polarized and unpolarized Raman spectra in the various orientations. The unpolarized spectra (Fig. 1 and Fig. 3a) show seven peaks coincident with those present in the preliminary powder spectrum. The wavenumbers of the bands can be found in Table I. From comparison with studies on related octahedral compounds [4], it is possible to assign the peaks at 627 and 539 cm^{-1} and the twofold split band centered around 230 cm^{-1} as the octahedral ν_1, ν_2 and ν_5 octahedral intensity matrix elements for D_{3d} site symmetry [5]. The assignments are confirmed by the polarized spectra (Fig. 2), in which the 627 cm^{-1} band appears as α_{1g} and the one at 539 cm^{-1} as ϵ_g polarized, *i.e.* the correct trigonal symmetry. We point out that the ν_1 and ν_2 modes appear to have a normal intensity pattern, similar to that found in $PtF_6{}^{2-}$, but different from that observed in the Raman spectrum of $ReCl_6{}^{2-}$ [6]. The anomalous intensity pattern has been explained [6, 7] by taking into account the presence in the electronic ground state of a dynamical Jahn–Teller effect which does not seem to be operating in the present case.

The ν_5 band centered at 230 cm^{-1} is split by the trigonal field in two components peaking at 222 and 241 cm^{-1} of which the former is ϵ_g polarized and the latter is α_{1g} polarized (Fig. 2 and Fig. 3b and c). The splitting due to the low symmetry field is rather large (19 cm^{-1}) but similar to those found in the study of isostructural compounds [8, 9].

The remaining three bands below 200 cm^{-1} must be due to lattice modes. The band at 31 cm^{-1} is clearly α_{1g} polarized and is assigned, on the basis of the factor group analysis, to the lattice antitranslational $\nu_T(\alpha_{1g})$ mode. The peaks at 77 and 118 cm^{-1}

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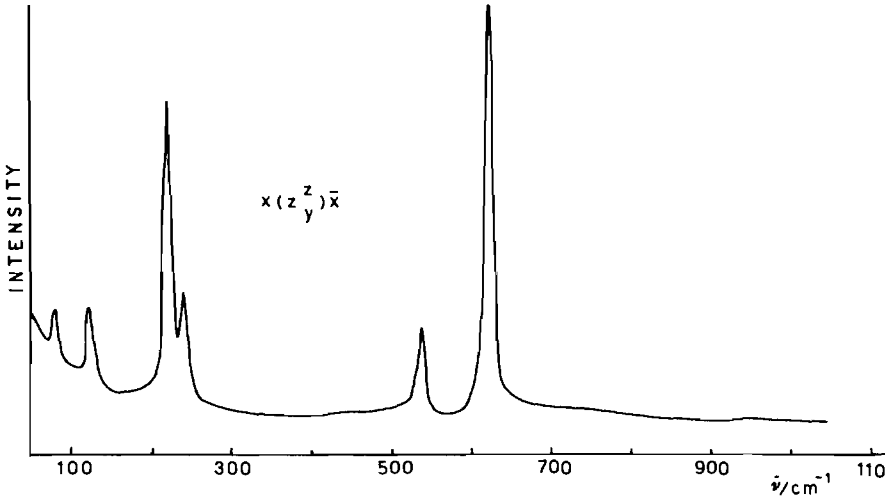

Fig. 1. Unpolarized Raman spectrum of a single crystal of K_2ReF_6. The incoming light was propagated perpendicular to the optical axis.

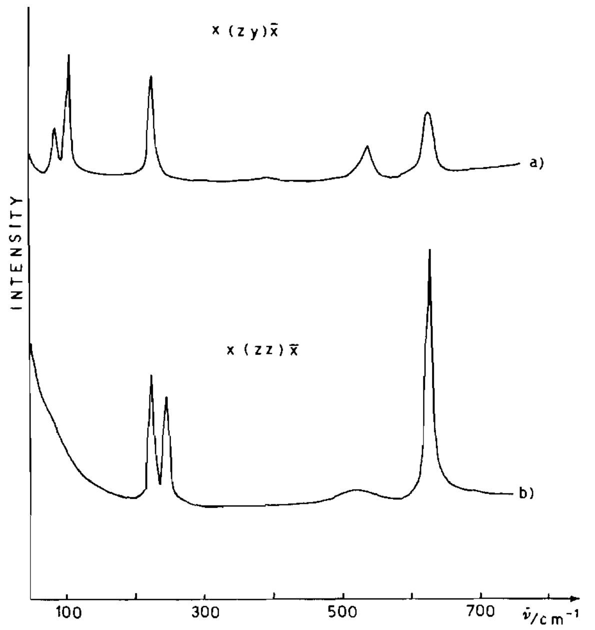

Fig. 2. Polarized Raman spectra of a single crystal of K_2ReF_6: (a) spectrum measured in the $x(zy)\bar{x}$ orientation, (b) spectrum measured in the $x(zz)\bar{x}$ orientation.

TABLE I. Raman Spectrum of K_2ReF_6

$\tilde{\nu}$ (cm^{-1})	Assignment
31 mw	$\nu_T(\alpha_{1g})$
77mw	$\nu_T(\epsilon_g)$
118m	$\nu_R(\epsilon_g)$
222s	$\nu_5(\epsilon_g)$
241m	$\nu_5(\alpha_{1g})$
539mw	$\nu_2(\epsilon_g)$
627vs	$\nu_1(\alpha_{1g})$

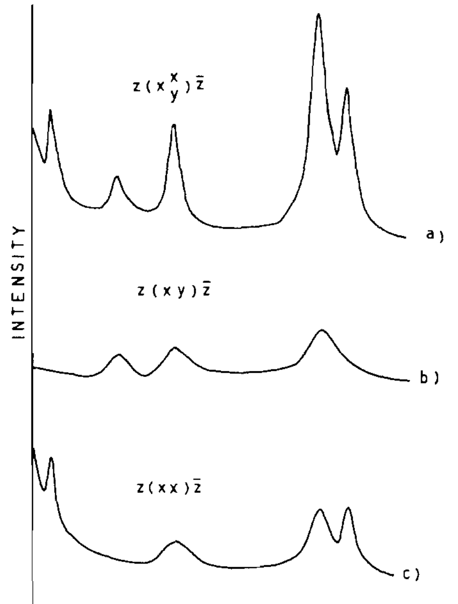

Fig. 3. Raman spectra of a single crystal of K_2ReF_6: (a) unpolarized spectrum with incident light parallel to the optical axis, (b) spectrum measured in the $z(xy)\bar{z}$ orientation, (c) spectrum measured in the $z(xx)\bar{z}$ orientation.

are both ϵ_g polarized and it is not possible, on the basis of the polarization characteristics alone, to determine their antitranslational or rotatory nature. We tentatively assign the former band as $\nu_T(\epsilon_g)$ and the latter as $\nu_R(\epsilon_g)$, taking as a guide the assignments in the lattice region given for the isostructural compound Cs_2TiF_6 (trigonal modification) [8].

As a conclusion, we have been able to assign the vibrational Raman spectrum of the trigonal crystal K_2ReF_6 on the basis of the polarization characteristics of the bands. The spectrum fits quite well with those of isostructural diamagnetic compounds and with the systematics of hexahalide complexes. There is no evidence of the presence of some degree of Jahn–Teller effect operating in the electronic ground state, contrary to what was found in the Raman spectrum of the isoelectronic compound IrF_6 [10], in which the broadenings, shifts and splittings of some bands could be attributed to this effect.

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