Single-crystal Infrared Reflectance Spectrum of Potassium Tetraoxochromate(VI), and a New Reflectance Accessory

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The complete i.r. reflectance spectrum of potassium tetraoxochromate(VI) has been observed and analysed by the Kramers–Krönig method. All of the observable bands are assigned to their symmetry species. Together with previously reported single-crystal Raman data, this completes the assignment for this complex. The design of a near-normal-incidence reflectance accessory for the Perkin-Elmer 225 spectrometer is also described.

THE single-crystal Raman spectrum of potassium tetraoxochromate(VI) has recently resulted in reliable assignments for all of the complex Raman-active splittings evident in the tetramolecular cell.[1,2] Preliminary single-crystal i.r. spectra for the lattice-mode region have also been reported,[2] but the more-important high-frequency regions in which ν(Cr–O) and δ(OCrO) modes lie has not been studied other than by powder methods. We report the complete single-crystal i.r. spectrum of the title complex obtained for the principal crystallographic directions, thereby completing the vibrational assignment.

EXPERIMENTAL

Large single crystals of side several millimetres were grown by slow evaporation of aqueous solutions. Faces normal to the crystal axes were developed by grinding and were then polished. In the region 10—400 cm^{-1}, reflectance spectra were obtained using a Beckman-RIIC FS720 interferometer with the RS7F reflectance module. The range 200—1200 cm^{-1} was covered with a Perkin-Elmer 225 instrument, using the attachment described below. Perkin-Elmer wire-grid polarisers with AgCl or polyethylene substrates were used as appropriate.

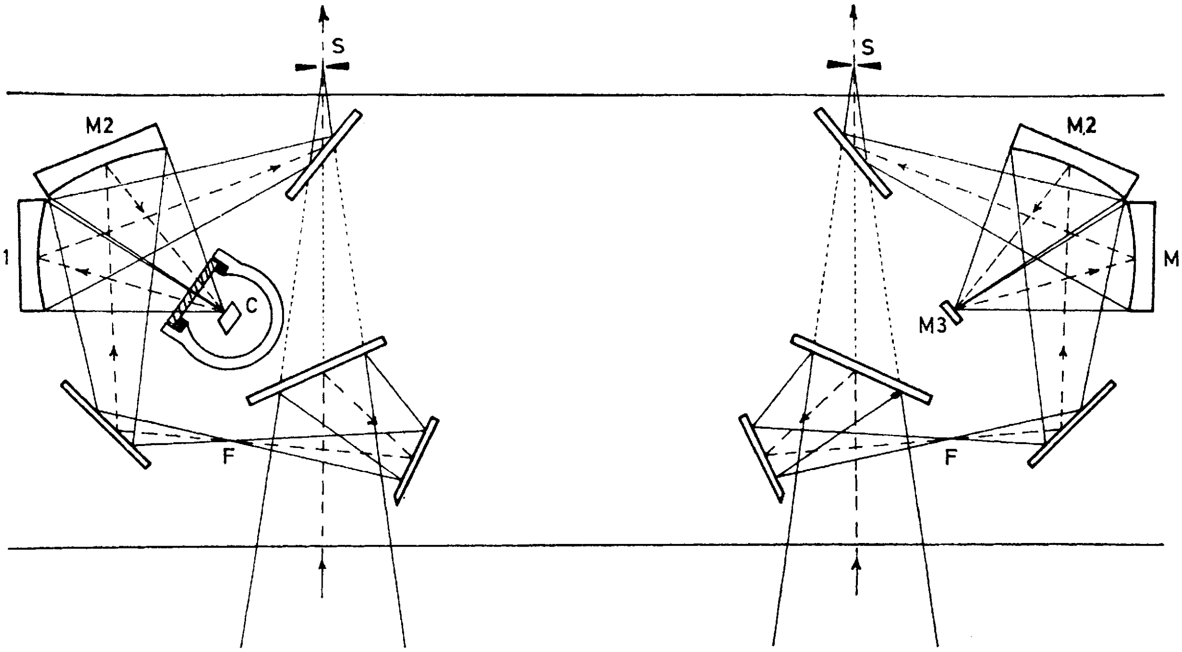

FIGURE 1 Optical diagram of reflectance accessory for the Perkin-Elmer 225 type instrument

In order to work with relatively small crystals it is necessary to reduce the size of the focus available in the Perkin-Elmer 225 instrument. Further, reflectivity measurements must be done at near-normal incidence.[3] Figure 1 shows the design of our accessory; M1 and M2 are of 4 cm focal length and size 4 × 5 cm^2. The plane mirrors are of sizes 4·5 × 6·5, 4 × 5, and 3 × 4 cm^2; relative dimensions are clear from the Figure. A small plane mirror, M3, serves as the reference sample. The crystal sample, C, is mounted inside an evacuated enclosure which can accept windows of KBr or CsI as appropriate. A cryostat is also available but was not used in these experiments. The entire optical train is mounted on a steel plate which is fixed to the instrument sample compartment, screwing into the tapped holes provided by the manufacturers. The only modification necessary to the instrument is to cut a rectangular hole in the lid of the sample compartment so that the cryostat can be inserted. Using the 2 : 1 reduced focus at C, sample heating can be a problem. This was amelio-

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[1] R. L. Carter and C. E. Bricker, *Spectrochim. Acta*, 1971, **27***A*, 569.

[2] D. M. Adams, M. A. Hooper, and M. H. Lloyd, *J. Chem. Soc.* (*A*), 1971, **946**.

[3] G. R. Wilkinson, 'Laboratory Methods in Infrared Spectroscopy,' 2nd edn., eds. R. G. J. Miller and B. C. Stace, Heyden, London, 1972, ch. 18.

rated by (*a*) running the source below normal operating temperature and (*b*) placing cut-off filters at position F.

RESULTS AND DISCUSSION

The real and imaginary parts of the dielectric constant, $\varepsilon = \varepsilon' - i\varepsilon''$, were obtained from the reflection spectra by Kramers–Krönig analysis.[3] Figure 2 shows the resulting spectra of ε which is related to the complex refractive index n by $\varepsilon = n^2$. The wavenumbers quoted are the maxima of ε''.

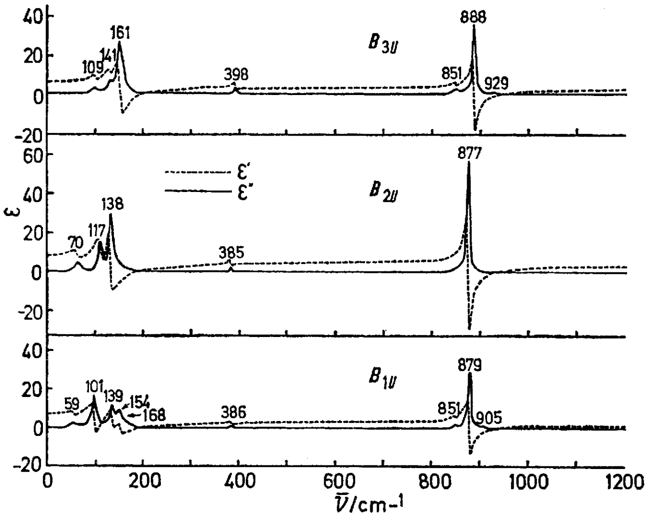

FIGURE 2 Real and imaginary dielectric parameters obtained by Kramers–Krônig analysis of the single-crystal i.r. reflectance spectrum of K_2CrO_4

Potassium tetraoxochromate(VI) has an orthorhombic cell of symmetry *Pnma* (D_{2h}^{16}) with $z = 4$. The factor-group analysis and mode-correlation scheme is to be found in a previous publication.[2] In the ν(Cr–O) region *ca.* 900 cm^{-1} we expect the following i.r.-active modes if full correlation coupling occurs:

$$\nu_3(t_2) \longrightarrow 2B_{1u} + 2B_{3u} + B_{2u}$$
$$\nu_1(a_1) \longrightarrow B_{1u} + B_{3u}$$

Our observations exactly fitted this pattern. We note that this result could not have been achieved other than by single-crystal reflectance; the absorption spectrum of a single crystal is complicated by the presence of combinations, and the presence of two coincident modes of different symmetry could only be shown using oriented specimens.

Splitting in the δ(OCrO) region *ca.* 390 cm^{-1} was slight in comparison with that for ν(Cr–O). The *e* species bend of CrO_4^{2-} becomes i.r.-active only by virtue of site splitting; it is too weak to appear in the reflectance spectra and only shows up as a very feeble absorption for powder samples. The three bands which we observed in the reflectance spectrum (at 385, 386, and 398 cm^{-1}) are therefore components of $\nu_4(t_2)$. In theory this should yield $2B_{1u} + B_{2u} + 2B_{3u}$, but it appears that the correlation field is too weak to show the full splitting possible for bending modes. In contrast, in the stretching region, correlation splitting of up to 20 cm^{-1} was observed. However, the major effect appears to originate in the site-symmetry splitting of the degenerate levels of each CrO_4^{2-} ion (see Table).

Combining translatory and rotatory lattice modes (since no experimental distinction can be made between them), factor-group analysis predicts $6B_{1u} + 4B_{2u} + 6B_{3u}$, to be compared with our observations of $5B_{1u} + 3B_{2u} + 3B_{3u}$. Since these lattice modes represent various symmetry-related ways of coupling translations of eight K$^+$ ions and rotations of four CrO_4^{2-} groups, it is rather remarkable that so many distinct bands were found. It might have been imagined that, as often seems to be the case, a smaller vibrational sub-cell of higher pseudosymmetry could account for the lattice modes, but this is evidently not the case. This work completes the vibrational assignment for K_2CrO_4. Results are summarised in the Table.

Vibrational assignment for K_2CrO_4 (internal modes of anion only) [a]

Raman (aqueous solution)	Crystal site symmetry	Raman (crystal)	I.r. (crystal)
T_d	C_s	D_{2h}	D_{2h}
884 (f_2)	2a' (914·5, 880) [b]	919 B_{2g}	929 B_{3u}
		905 A_g	905 B_{1u}
		884 B_{2g}	888 B_{3u}
		868 A_g	879 B_{1u}
	a'' (879)	881 B_{1g}	877 B_{2u}
		877 B_{3g}	A_u [c]
847 (a_1)	a' (851)	852 $A_g + B_{2g}$	851 B_{1u}
			851 B_{3u}
368 (f_2)	2a' (398, 387)	398 B_{2g}	398 B_{3u}
		397 A_g	B_{3u}
		388 B_{2g}	386 B_{1u}
		387 A_g	B_{1u}
	a'' (389)	393 B_{3g}	385 B_{2u}
		388 B_{1g}	A_u [c]
348 (e)	a' (349·5)	353 B_{2g}	
		347 A_g	
	a'' (349·5)	351 B_{3g}	
		348 B_{1g}	

[a] Raman solution data from H. Stammreich, D. Bassi, and O. Sala, *Spectrochim. Acta*, 1958, **12**, 403; Raman crystal data from ref. 2. [b] Values in parentheses were estimated from observed splittings. [c] A_u Modes are inactive.

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