Matrix-isolation Studies on Molecular K_2CrO_4, K_2MoO_4, and K_2WO_4 †

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The results of a matrix-isolation i.r. spectroscopic study on the vaporisation of the title compounds are described. When these materials are heated *in vacuo* and the products condensed in low-temperature matrices, the i.r. spectra obtained show the presence of the corresponding *molecular* species, together with a number of minor features. Oxygen-18 enrichment experiments establish a D_{2d} geometry for K_2WO_4, and high-resolution spectra on the isostructural species K_2CrO_4 and K_2MoO_4 provide an estimate of bond angles in these molecules from metal isotope frequency shifts.

CHROMIUM, molybdenum, and tungsten are elements of considerable metallurgical importance, but despite their widespread use in high-temperature processes little is known about the nature of vapour transport of these metals in oxidising atmospheres. As with many high-temperature systems, the existing literature is confusing, and sometimes contradictory. For example, one mass spectrometric report on the vaporisation of Na_2CrO_4 and K_2CrO_4 concludes that the parent molecular species are present in the vapour phase,[1] whilst a second study [2] on Na_2CrO_4 concludes that 'vaporisation of $[Na_2CrO_4]$ cannot be involved in the transport of chromium.' Electron-diffraction patterns for molecular Na_2CrO_4 have been interpreted assuming either C_{2v} (ref. 3) or D_{2d} (ref. 4) geometries, and although the corresponding alkali-metal molybdates and tungstates are common ternary species in high-temperature mass spectrometric studies [5] it is only fairly recently [6] that the D_{2d} structure has become accepted as the most likely geometry. One of the reasons for the difficulties encountered in the interpretation of electron-diffraction data is the large amplitudes of vibration which many of these species exhibit at high temperatures, and this has resulted in some ternary systems being described as exhibiting polytopic bonding.[7]

We are interested in the characterisation of high-temperature oxoanion salts using a combination of matrix isolation and vibrational spectroscopy. Here, the availability of ^{18}O isotope data frequently permits both an unequivocal identification of the ground-state molecular geometry, and also a definitive vibrational assignment. The approach has recently been used to characterise the molecular species KNO_3 [8] and $NaPO_3$,[9] and this paper describes the application of ^{16}O–^{18}O isotope patterns in establishing the shape of an M_2XO_4 species such as K_2WO_4.

During the course of this work we became aware of unpublished data on matrix-isolated Cs_2WO_4 by Atkins and Gingerich [10] and also of a concurrent study of chromates, molybdates, and tungstates by Spoliti *et al.*[11] However, these reports disagree over the position of the fundamentals of Cs_2WO_4, and in neither study were high-resolution data reported. In addition to establishing the D_{2d} geometry of K_2WO_4 using ^{16}O–^{18}O isotope patterns, the present paper therefore attempts to resolve these uncertainties, and also demonstrates how the *metal* isotope shifts which may be resolved for K_2CrO_4 and K_2MoO_4 provide an estimate of bond angles.

EXPERIMENTAL

The samples of K_2CrO_4 (AnalaR), K_2MoO_4 (reagent grade), and K_2WO_4 (>98%) used in this work were obtained from BDH, and high-purity nitrogen and argon (99.999%) were supplied by BOC. Vaporisation was accomplished from a platinum boat located inside an alumina holder heated inductively *via* a cylindrical tantalum susceptor, the whole being enclosed in a water-cooled glass vacuum jacket. Sample temperatures during deposition were monitored using an optical pyrometer, and matrix gas flows were regulated with a fine-control needle valve. Deposition times were typically *ca.* 1 h, and during this period the central CsI window in the cryostat was maintained at *ca.* 12 K. Spectra were recorded on a Perkin-Elmer 225 i.r. spectrometer (200—5 000 cm^{-1}) and calibrated using standard procedures. Further details of our apparatus are described elsewhere.[8]

The synthesis of ^{18}O-enriched K_2WO_4 was based on the method for Tl_2WO_4 described by Rastogi *et al.*[12] Tungsten powder (*ca.* 175 mg, 99.9%) was contained in a silica boat and heated in 90 atom % ^{18}O-enriched oxygen gas at a pressure of *ca.* 170 Torr.‡ At *ca.* 550 °C combustion was observed, and there was a rapid decrease in pressure. Reaction was completed by raising the temperature to *ca.* 800 °C for 1 h. The resulting red-orange powder became lemon-yellow on cooling, and the yield of WO_3 was essentially quantitative. This sample was then mixed with an equimolar amount of $K_2C^{16}O_3$ (AnalaR grade) in a platinum-lined alumina crucible, and heated *in vacuo*. As the temperature increased the mixture initially turned black and gas evolution (CO_2) began to take place. The reaction to give solid K_2WO_4 and CO_2 was complete after heating for 10 min at *ca.* 800 °C. On cooling, the product was an off-white powder. The theoretical final enrichment, assuming *no* ^{18}O incorporation in the CO_2, is *ca.* 67 atom %, whilst complete ^{18}O scrambling would result in *ca.* 48% enrichment.

Vibrational Analysis.—The quantitative interpretation of the spectroscopic data in this paper is based upon a simplified vibrational analysis of the D_{2d} M_2XO_4 structure in which only the X–O stretching modes are considered. For the free XO_4^{2-} ion (T_d), $\Gamma_{X-O} = A_1 + T_2$, and upon co-ordin-

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† Potassium chromate(VI), molybdate(VI), and tungstate(VI) respectively.

‡ Throughout this paper: 1 Torr = 101 325/760 N m^{-2}; 1 dyn = 10^{-5} N.

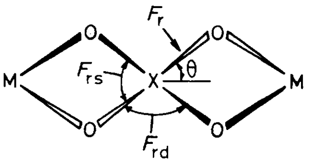
ation to give (I), the corresponding representation is $\Gamma_{X-O} = A_1 + B_2 + E$. If one assumes that these stretching modes are essentially uncoupled from the other fundamentals, the secular equations * for these vibrations may be shown to be as in (1)—(3) where M_O is the mass of oxygen, M_X is the

$$\lambda_{A_1} = 4\pi^2\omega^2 = (F_r + F_{rs} + 2F_{rd})(1/M_O) \qquad (1)$$

$$\lambda_{B_2} = 4\pi^2\omega^2 = (F_r + F_{rs} - 2F_{rd})[(1/M_O) + (4\cos^2\theta/M_X)] \qquad (2)$$

$$\lambda_E = 4\pi^2\omega^2 = (F_r - F_{rs})[(1/M_O) + (2\sin^2\theta/M_X)] \qquad (3)$$

mass of atom X, and the force constant parameters are defined as below. If one then assumes that anharmonicity corrections are small, and that observed transitions ν are a good approximation to zero-order frequencies ω, it is evident



(I)

that frequency data for two isotopic species M_X and M_X' may be used to estimate the bond angle 2θ. In particular, for the B_2 mode, equation (2) leads to the expression (4)

$$4\cos^2\theta = \frac{M_X M_X'}{M_O} \frac{[\nu^2 - (\nu')^2]}{[M_X'(\nu')^2 - M_X\nu^2]} \qquad (4)$$

where ν and ν′ are the observed B_2 frequencies for the two isotopically distinct species. This approach [13] to estimating bond angles has been shown to be satisfactory for many triatomics, and more recently for species such as CrO_2F_2, where the vibrational problem is similar [14] to that described here.

Finally, use may be made of the relative i.r. intensities of the three X–O stretching modes. Symmetry selection rules predict that only the B_2 and E modes will be i.r. active, and as these modes derive from a T_2 mode in free XO_4^{2-}, one might anticipate that very small perturbations from tetrahedral symmetry would result in a 1 : 2 intensity ratio for these bands. If the perturbation is more significant however, involving perhaps both a departure from tetrahedral bond angles, and significantly different interaction stretching constants F_{rs} and F_{rd}, then the more general expression (A) must be used.[15] Assuming that the changes in molecular

$$\Sigma I_k = \Sigma\left(\frac{\partial\mu}{\partial S_k'}\right)\cdot\left(\frac{\partial\mu}{\partial S_k''}\right) G_{k'k''} \qquad (A)$$

dipole, μ, may be adequately represented by changes in X–O bond dipoles, and that the above secular equations remain a useful approximation, it may then be shown that for the two i.r.-active X–O stretching modes in the D_{2d} XO_4 unit the relative intensities (I_k) are given by equation (5).

$$\frac{I_E}{I_{B_2}} = \tan^2\theta \frac{(M_X + 2M_O\sin^2\theta)}{(M_X + 4M_O\cos^2\theta)} \qquad (5)$$

RESULTS AND SPECTRAL INTERPRETATION

K_2CrO_4.—When samples of potassium chromate were heated to *ca.* 1 250 °C a greenish yellow sublimate was observed on the off-axis walls of the deposition system, and co-condensation of the vapour species with an excess of argon (typically >1 000 : 1) yielded a matrix i.r. spectrum (200—1 500 cm^{-1}) in which the principal features were an intense doublet at 893.4, 874.8 cm^{-1} and a prominent low-frequency band at 247.5 cm^{-1}. Several much weaker bands were also observed, and a typical spectrum is shown in Figure 1(*a*).

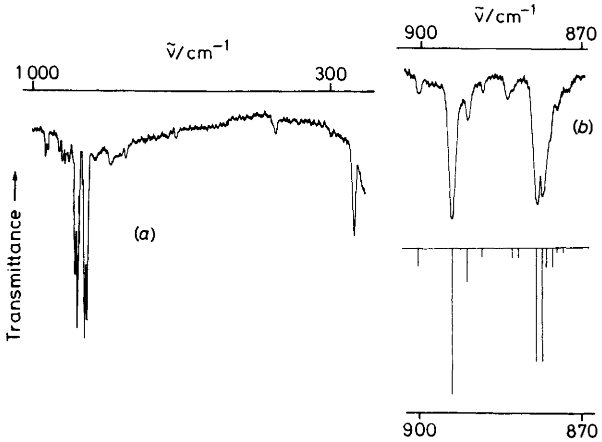


Figure 1 (*a*) Argon-matrix i.r. spectrum obtained after vaporisation of potassium chromate; (*b*) part of the corresponding nitrogen-matrix spectrum under high resolution, together with calculated spectrum

Comparison between experiments involving different deposition conditions indicated that a weak band at 429.3 cm^{-1} appeared to be associated with the more prominent features at 247.5 and 893.4, 874.8 cm^{-1}, but that the remaining low-intensity bands at 968, 964, 936, 928, 924, and 781 cm^{-1} were unrelated to the principal absorptions. In particular, they appeared relatively more intense under conditions of rapid spray-on, and are thus assigned to either polymer species, or, possibly, decomposition products such as $(CrO_3)_n$. The principal features are tentatively assigned to monomeric K_2CrO_4, although even under conditions of low resolution [*e.g.* Figure 1(*a*)], it is apparent that both components of the 893.4, 874.8 cm^{-1} doublet show unexpectedly extensive fine structure.†

Nitrogen matrices yielded similar spectra characterised by an intense doublet at 894.9, 878.1 cm^{-1} and a related weak feature at 420 cm^{-1}. Additional weak bands were also observed at 966, 934, 921, 828, and 816 cm^{-1} which did not appear to correlate with the main doublet. The overall spectrum, however, was now generally much cleaner than in argon, notably in respect of the intense 894.9, 878.1 cm^{-1} doublet, which showed no obvious fine structure under low resolution. This matrix material was therefore chosen as being more suitable for detailed studies. Table 1 summarises the principal bands assigned to monomeric K_2CrO_4 in both argon and nitrogen.

Figure 1(*b*) shows a nitrogen-matrix spectrum of the 894.9, 878.1 cm^{-1} ' doublet ' under high resolution. The

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* Equations derived using standard Wilson G–F matrix method.

† As a general observation, argon matrices are frequently found to give multiplet absorptions which are attributed to ' site effects.' Nitrogen matrices, however, often appear to exhibit only one trapping site.

higher-frequency component is seen to consist of a strong central band at 894.9 cm^{-1}, with satellites at 901.2, 891.9, and 889.0 cm^{-1}, whilst the lower-frequency absorption appears as a strong partially resolved doublet (878.7, 877.5 cm^{-1}) with additional shoulders. These bands all lie in the region of i.r.-active T_2 stretching mode [16] for CrO_4^{2-} (T_d) and are assigned as Cr–O stretching modes. In particular, the most intense spectral features at 894.9 and 878.1 cm^{-1} are attributed to the B_2 and E stretching modes in the D_{2d} molecular species $K_2{}^{52}CrO_4$ (^{52}Cr, 83.8% abundance). This preference for placing ν_{B_2} above ν_E comes from the probability that an E mode might show a partial lifting of degeneracy as a result of a low matrix site symmetry, and the lower component of this doublet indeed shows a splitting of *ca.* 1.2 cm^{-1}. The weaker satellites are then assigned to corresponding modes in the three less abundant species involving ^{50}Cr (4.5%), ^{53}Cr (9.4%), and ^{54}Cr (2.3%).

TABLE 1

Infrared bands (cm^{-1}) and assignments for matrix-isolated K_2CrO_4, K_2MoO_4, and K_2WO_4

K_2CrO_4			K_2MoO_4			K_2WO_4			Assignment	
Ar	N_2	(free ion) [16]	Ar	N_2	(free ion) [16]	Ar	N_2	(free ion) [16]	D_{2d}	(T_d)
893.4 ^{a}	894.9	890	839.3 ^{a}	842.0 ^{a}	837	834.4	835.9	838	B_2	$T_2[\nu(X–O)]$
874.8 ^{a}	878.1 ^{a}		827.1 ^{a}	832.0 ^{a}		827.4	830.8		E	
429.3	420.0	378	378.0	369.1	(317)	363.6	351.2	(325)	B_2	$T_2[\delta(X–O)]$
			317.6	320.6		304.0	306.0		E	
247.5			226.8			212.7			$\nu(K–O)$ (?)	

Metal isotope structure on B_2 $\nu(X–O)$ mode

	K_2CrO_4 ^{b}				K_2MoO_4 ^{c}						
	^{50}Cr	^{52}Cr	^{53}Cr	^{54}Cr	^{92}Mo	^{94}Mo	^{95}Mo	^{96}Mo	^{97}Mo	^{98}Mo	^{100}Mo
Obs.	901.2	894.9	891.9	889.0	846.1	844.0	843.0	842.2		840.2	838.3
Calc.	901.2	894.9	891.9	889.0	846.1	844.1	843.1	842.1	841.1	840.2	838.3

^{a} Centre of complex absorption. ^{b} Calculated assuming F_{B_2} ($= F_r + F_{rs} - 2F_{rd}$) = 4.87 mdyn Å^{-1} and $2\theta = 96° 16'$. ^{c} Calculated assuming F_{B_2} = 5.197 mdyn Å^{-1} and $2\theta = 98° 24'$. Overall frequency accuracy ±0.3 cm^{-1}.

Following the procedure outlined earlier, the isotope fine structure on the B_2 component, may be used [equation (4)] to estimate a bond angle $2\theta = 96° 16'$ for K_2CrO_4, whereupon the relative integrated intensities of the E and B_2 components may also be estimated. Application of equation (5) gives $I_E/I_{B_2} \approx 1.1$, and if one further assumes that the E mode is split into two equally intense bands it is then possible to simulate the observed spectrum. This is shown as a line diagram accompanying Figure 1(*b*). The satisfactory agreement between observed and calculated spectra provides convincing evidence for the D_{2d} structure of matrix-isolated K_2CrO_4, and it is also interesting to note that the T_2 stretching mode in the ' free ' anion lies between the B_2 and E components. The remaining bands assigned to matrix-isolated K_2CrO_4 lie at 429.3 and 247.5 cm^{-1} in argon, whilst in nitrogen an additional feature was observed at 420 cm^{-1}. Comparison with the bending modes of ' free ' CrO_4^{2-} (Table 1) indicates that the band at *ca.* 420 cm^{-1} is likely to correlate with the free-ion T_2 bend, and the remaining low-frequency argon feature is assigned to cation motion. This assignment is consistent with our earlier work on KNO_3,[8] where a band at 226 cm^{-1} was assigned to ν(K–O). Nitrogen matrices produce steeply sloping backgrounds between 200 and 250 cm^{-1}, and the corresponding mode could not be located with any confidence.

K_2MoO_4.—The vaporisation of solid K_2MoO_4 resulted in matrix i.r. spectra which corresponded closely to those described for K_2CrO_4. In argon matrices, the most intense features were a characteristic doublet at 839, 827 cm^{-1}, each component of which showed extensive fine structure, and a low-frequency band at 226.8 cm^{-1}. These are assigned to monomeric K_2MoO_4. Two weaker bands at 378.0 and 317.6 cm^{-1} also appeared to be associated with monomer absorptions, whilst additional weak features at 894, 888, 854, 776, and 737 cm^{-1} were assigned to small amounts of polymer or decomposition products.

Figure 2(*a*) shows the corresponding nitrogen-matrix spectrum obtained after deposition for 1 h from a sample heated to *ca.* 1 140 °C. The matrix ratio is well in excess of 1 000 : 1 and the features assigned to monomeric K_2MoO_4 are summarised in Table 1. By analogy with K_2CrO_4, the components of the intense doublet at 842.0, 832.0 cm^{-1} are assigned as the B_2 and E modes respectively of a D_{2d} MoO_4 unit, and this region of the spectrum is shown under high resolution in Figure 2(*b*). Molybdenum possesses seven naturally occurring isotopes with abundances: ^{92}Mo, 15.8; ^{94}Mo, 9.0; ^{95}Mo, 15.7; ^{96}Mo, 16.5; ^{97}Mo, 9.5; ^{98}Mo, 23.8, and ^{100}Mo, 9.6%, and the fine structure on these bands is attributed to molybdenum isotope effects. This structure is only partially resolved on the somewhat broad E component, but is better resolved on the upper B_2 mode, where

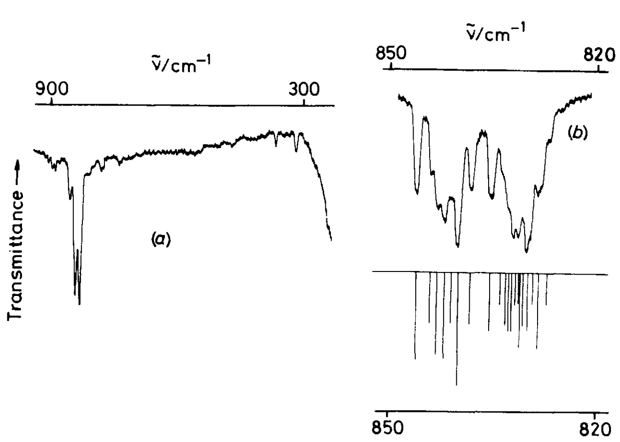

FIGURE 2 (*a*) Nitrogen-matrix i.r. spectrum obtained after vaporisation of potassium molybdate; (*b*) high-resolution spectrum of principal ' doublet ' in (*a*) together with calculated spectrum the outermost isotopic frequencies (^{92}Mo, 846.1; ^{100}Mo, 838.3 cm^{-1}) provide an estimate of $2\theta = 98° 24'$ from equation (4). This in turn leads to a predicted intensity ratio $I_E/I_{B_2} = 1.24$. The line diagram accompanying Figure 2(*b*) indicates the agreement between our observed and calculated spectra, assuming as before that the rather poor resolution on the E mode arises from two overlapping isotope patterns of equal intensity. Table 1 lists the frequencies of the resolved components on the B_2 mode.

Two of the remaining fundamentals assigned to K_2MoO_4 lie in the region of the T_2 bending mode in free MoO_4^{2-} (Table 1), and we arbitrarily place $\nu_{B_2} > \nu_E$ for these components. Finally, argon matrices reveal a prominent band at 226.8 cm^{-1} which is again assigned to cation motion. In nitrogen matrices, the corresponding mode would again be difficult to detect as a result of poorer i.r. transmission at this frequency, and was not observed.

K_2WO_4.—Figure 3(*a*) shows a typical nitrogen-matrix spectrum obtained from the vaporisation of potassium tungstate at *ca.* 1 150 °C. By analogy with the earlier molybdate spectra, the strong doublet at 835.9, 830.8 cm^{-1} and the weaker features at 351.2 and 306.0 cm^{-1} are assigned to molecular K_2WO_4, whilst weak, variable-intensity absorptions at 969, 910, 888, 859, and 785 cm^{-1} are attributed to polymers. Argon matrices yield corresponding monomer bands at 834.4, 827.4, 363.6, and 304.0 cm^{-1} and a further low-frequency feature at 212.7 cm^{-1} (Table 1). High-resolution studies on the intense doublet failed to reveal a tungsten isotope effect, but both the argon- and nitrogen-matrix spectra provided convincing evidence that for this system the T_2 degenerate stretching mode in the parent free ion also splits such that $\nu_{B_2} > \nu_E$. Figure 3(*b*) shows the nitrogen-matrix ' doublet ' under high resolution and it is evident that the lower-frequency component not only has a greater integrated intensity, but also shows a distinct asymmetry and broadening indicating a further lifting of degeneracy. Although there is no resolvable metal isotope structure on these bands, the intensity ratio I_E/I_{B_2} allows one to estimate the bond angle 2θ directly *via* equation (5). From Figure 3(*b*), this ratio is found to be 1.9 ± 0.2 which leads to a bond angle $2\theta = 108 \pm 3°$. The angular distortion of the XO_4 unit from regular tetrahedral geometry therefore appears to be smaller in K_2WO_4 than in K_2MoO_4 or K_2CrO_4. In an attempt to confirm this, and also to demonstrate the value of *oxygen* isotope substitution in characterising D_{2d} structures of this kind, high-resolution studies were carried out on ^{18}O-enriched K_2WO_4.

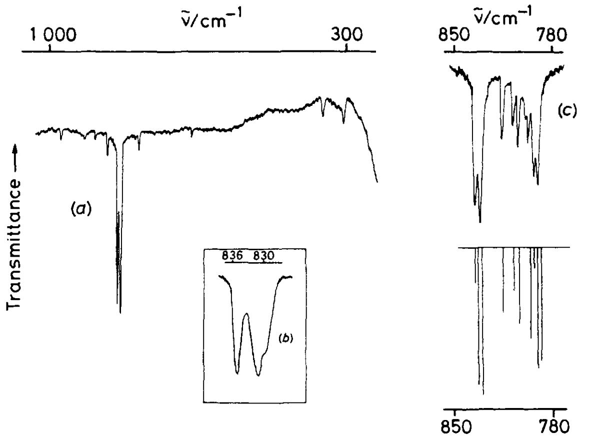

FIGURE 3 (*a*) Nitrogen-matrix i.r. spectrum obtained after vaporisation of potassium tungstate; (*b*) high-resolution spectrum of principal doublet in (*a*); (*c*) nitrogen-matrix i.r. spectrum obtained from ^{18}O-enriched potassium tungstate together with calculated spectrum

Oxygen isotope enrichment in molecular K_2WO_4. Partial ^{18}O enrichment in a D_{2d} M_2XO_4 structure leads to a maximum of six distinct isotopomers, and in four of these all vibrational degeneracy is removed. It is apparent that a mixture of these species will generate a complex i.r. spectrum, and using procedures developed in earlier studies on molecular nitrates [8] and carbonates [17] we have attempted to predict the spectrum which one would obtained for ^{18}O-enriched K_2WO_4.

First, the earlier approximations leading to equations (1)—(5) are assumed to be valid, and as the experimentally determined intensity ratio is close to 2.0 we assume initially that 2θ has the tetrahedral value of 109° 28'. The small $\nu_E - \nu_{B_2}$ separation is then attributed to a slight difference between the force-constant terms $(F_r - F_{rs})$ and $(F_r + F_{rs} - 2F_{rd})$. These two terms may be evaluated directly from our $K_2W^{16}O_4$ spectra, but in order to calculate the frequencies of the stretching modes for the less symmetrical isotopomers the three parameters F_r, F_{rs}, and F_{rd} must be independently determined, and a third equation is therefore required. The Raman spectrum of ' free ' $(W^{16}O_4)^{2-}$ shows a strong A_1 mode at 931 cm^{-1},[16] whilst in *solid* K_2WO_4 we observed a corresponding feature at 928.2 cm^{-1}. We therefore selected 930 cm^{-1} as a reasonable frequency for use in equation (1). Substitution of $\theta = 54° 44'$, and values of $\nu_{A_1} = 930$ cm^{-1}, $\nu_{B_2} = 835.9$ cm^{-1}, and $\nu_E = 830.8$ cm^{-1} into equations (1)—(3) leads to values of F_r, F_{rs}, and F_{rd} of 6.421, 0.598, and 0.562 mdyn Å^{-1} respectively, and these parameters were subsequently used to compute the W–O stretching frequencies of all the isotopic species. In order to simulate relative band intensities we further assumed that for $K_2W^{16}O_4$ and $K_2W^{18}O_4$ the ratio I_E/I_{B_2} is 2.0, whilst for a lower symmetry species such as $K_2W^{16}O^{18}O_3$ the intensity of the parent T_2 mode is distributed equally between the resulting $(2A' + A'')$ components.

Figure 3(*c*) shows the 780—850 cm^{-1} region of a nitrogen matrix spectrum obtained from a sample of ^{18}O-enriched K_2WO_4 prepared as described earlier, and it is accompanied by a line diagram showing the spectrum calculated for 48% ^{18}O enrichment. The agreement is clearly very satisfactory, supporting the proposed D_{2d} structure, and a comparison between the observed and calculated frequencies is included in Table 2. The frequency calculations were then repeated assuming the same basic $K_2W^{16}O_4$ data, but setting $2\theta = 100°$. The resulting spectral fit was only marginally less satisfactory, and in view of the simplifications in our vibrational analysis this difference could not be regarded as significant. Several sets of calculations were also carried out using more extensive force fields, and including thc WO_4 bending modes as constraints. These calculations also produced satisfactory isotope fits.

Oxygen-18 enrichment therefore proved to be of little value in establishing a precise bond angle, but regularly generated patterns which supported a basic D_{2d} geometry by virtue of the number, position, and relative intensity of the various components. For new systems, where the structural parameters are unknown, and where a complete set of vibrational fundamentals will only rarely be available, the *insensitivity* of these isotope patterns to these particular variables can be very useful.

Finally, it is interesting to note that the *intensity* pattern in Figure 3(*c*) corresponds very closely to 48% ^{18}O enrichment. This is the degree of enrichment expected for *complete* isotope scrambling in our WO_3–K_2CO_3 mixture, and points to the existence of molten salt equilibria. Subsequent examination of the CO_2 evolved from this system confirmed the presence of $C^{16}O^{18}O$ and $C^{18}O_2$.

TABLE 2

Observed and calculated i.r. bands (cm^{-1}) for isotopically labelled K_2WO_4 molecules

Observed (N_2 matrix)	Calculated [a]	Assignment		
835.9	835.9	B_2	$K_2W^{16}O_4$	(D_{2d})
834.6	834.3	A'	$K_2W^{16}O_3{}^{18}O$	(C_s)
	833.5 [b]	B	$K_2W^{16}O_2{}^{18}O_2$	(C_2)
830.8	830.8	E	$K_2W^{16}O_4$	(D_{2d})
	830.8	A''	$K_2W^{16}O_3{}^{18}O$	(C_s)
	830.8	B_1	$K_2W^{16}O_2{}^{18}O_2$	(C_{2v})
815.8	816.1	A'	$K_2W^{16}O^{18}O_3$	(C_s)
808.4	808.3	A_1	$K_2W^{16}O_2{}^{18}O_2$	(C_{2v})
804.3	803.6	A	$K_2W^{16}O_2{}^{18}O_2$	(C_2)
797.5	796.6	A'	$K_2W^{16}O_3{}^{18}O$	(C_s)
	793.0	B_2	$K_2W^{18}O_4$	(D_{2d})
792.8	791.2	A'	$K_2W^{16}O^{18}O_3$	(C_s)
	790.4 [b]	B	$K_2W^{16}O_2{}^{18}O_2$	(C_2)
790.1	788.1	E	$K_2W^{18}O_4$	(D_{2d})
	788.1	A''	$K_2W^{16}O^{18}O_3$	(C_s)
	788.1	B_2	$K_2W^{16}O_2{}^{18}O_2$	(C_{2v})

[a] These calculations assume $2\theta = 109° 28'$, and are based on force constants $F_r = 6.421$, $F_{rs} = 0.598$, and $F_{rd} = 0.562$ mdyn $Å^{-1}$. [b] These pairs of bands, which are predicted to be < 1 cm^{-1} apart, are represented by single lines in the computed spectrum accompanying Figure 3(*c*).

DISCUSSION AND CONCLUSIONS

The most significant conclusions to be drawn from these experiments are that, contrary to some earlier reports, the molecules K_2CrO_4, K_2MoO_4, and K_2WO_4 would all appear to be important high-temperature species under these conditions of vaporisation. High-resolution matrix-isolation i.r. spectroscopy allows one to confirm the D_{2d} geometries proposed for these species, and also to estimate bond angles using either relative intensity data or the angle dependence of isotope frequency shifts. Both methods involve a simplification of the vibrational problem, and before comparing this work with other studies on these systems it is important to assess how reliable these estimates might be.

First, it may readily be shown that an error of 0.2 cm^{-1} in the ^{50}Cr–^{54}Cr isotope shift for the B_2 mode in K_2CrO_4 will result in an error of *ca.* 2° in the bond angle 2θ, whilst in K_2MoO_4 a similar frequency error in the ^{92}Mo–^{100}Mo shift will produce a discrepancy in angle of *ca.* 3°. Our absolute frequencies for the appropriate fundamentals are quoted to ± 0.3 cm^{-1}, but we are confident that our isotope *shifts* are accurate to 0.2 cm^{-1}. Secondly, it is anticipated that the the use of observed transitions (ν) rather than zero-order frequencies may also lead to errors of a few degrees as a result of the neglect of anharmonicity, and that there may be an additional error associated with the separation of X–O stretching modes from the remaining fundamentals. The overall uncertainty in these cases is difficult to assess, but it is interesting to note that in a recent study of matrix-isolated CrO_2F_2 [14] the angles O–Cr–O and F–Cr–F estimated from chromium isotope shifts (102.5 and 124° respectively) are in fairly close agreement with those obtained from electron diffraction (102.1 and 118.9°).[18] For K_2WO_4, we rely on the relative intensities of the B_2 and E modes, and from an experimental viewpoint this method seems to be at least as precise. Using equation (5), it may be shown that a variation in O–W–O bond angle (2θ) from 104° to 110° is associated with a change in intensity ratio I_E/I_{B_2} of *ca.* 1.6 to 2.0, and this should not be difficult to measure. The errors introduced by the simplification of the secular equations and the additional approximations regarding the adequacy of the bond-dipole model are again difficult to assess. However, in ReO_3F, which has been studied both in low-temperature matrices [19] and by microwave spectroscopy,[20] the O–Re–O angle obtained from relative i.r. intensities is 110°, whilst microwave gives 109.5°. Both these routes would therefore appear to give satisfactory estimates of bond angles, and for the particular species considered here we estimate O–Cr–O and O–Mo–O in K_2CrO_4 and K_2MoO_4 as 96 ± 5 and 98 ± 5° respectively, with O–W–O in K_2WO_4 as 108 ± 4°. A direct comparison of these estimates with other studies cannot be made, as there appears to be little definitive structural data on molecular alkali-metal chromates, and the most reliable reports on tungstates and molybdates relate to the caesium salts.[6] For these species, electron diffraction gives bond angles (2θ) of O–Mo–O 105 ± 4° and O–W–O 104 ± 4° which in addition to being *less* than the tetrahedral angle are reasonably close to our estimates for K_2MoO_4 and K_2WO_4.

Finally, during the course of this work, we became aware of two other independent matrix i.r. studies on related systems. Atkins and Gingerich [10] carried out several experiments on matrix-isolated Cs_2WO_4, and assigned a prominent doublet at 835, 830 cm^{-1} in nitrogen as the E and B_2 modes respectively of the D_{2d} monomer. They also assigned weaker features at 908, 884, 767, and 662 cm^{-1} to a dimer $(Cs_2WO_4)_2$. Their spectra do not extend below 600 cm^{-1} but these higher-frequency features are similar to the weak bands noted in our K_2WO_4 spectra. The caesium tungstate system has also been studied by Spoliti *et al.*[11] as part of an overall investigation of the stretching modes of matrix-isolated M_2XO_4 species (M = alkali metal or Tl; X = Cr, Mo, or W). These authors report bands at 845 and 818 cm^{-1} for Cs_2WO_4 in nitrogen, which are significantly different from these found by Gingerich, although the overall conclusion regarding the D_{2d} shape of the monomer remains intact.

In an attempt to resolve this discrepancy we carried out a preliminary study on Cs_2WO_4, and found that in nitrogen matrices the intense monomer doublet appeared at 833.5, 828.5 cm^{-1} in close agreement with Gingerich. These frequencies are very similar to those found for K_2WO_4, and it is tempting to reverse Gingerich's assignment and place $\nu_{B_2} > \nu_E$. However, our Cs_2WO_4 bands were not sufficiently well defined to make this distinction.

It should however be possible to confirm the assignment of these components using ^{18}O enrichment. Here, the *E* mode should be readily identified by its reinforcement due to overlap with certain modes of the lower symmetry isotopomers (Table 2).

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REFERENCES

[1] C. A. Stearns, F. J. Kohl, R. A. Miller, and G. C. Fryburg, *NASA Tech. Memo.*, 1979, NASA-TM-79210, E-095.

[2] C. Hirayama and C. Y. Lin, *Nat. Bur. Stand.* (*U.S.*), *Spec. Publ.*, 561, 1979, 1539.

[3] V. P. Spiridonov, A. N. Khodchenkov, and P. A. Akishin, *Zh. Strukt. Khim.*, 1965, **6**, 634.

[4] V. P. Spiridonov and B. I. Lutoshkin, *Vestn. Mosk. Univ.*, *Khim.*, 1970, **25**, 509.

[5] See, for example, A. Buchler, J. L. Stauffer, W. Klemperer, and L. Wharton, *J. Chem. Phys.*, 1963, **39**, 2299; G. Verhaegen, R. Colin, G. Exsteen, and J. Drowart, *Trans. Faraday Soc.*, 1965, **61**, 1372; R. P. Burns, G. De Maria, J. Drowart, and M. G. Inghram, *J. Chem. Phys.*, 1963, **38**, 1035.

[6] V. V. Ugarov, Yu S. Ezhov, and N. G. Rambidi, *Zh. Strukt. Khim.*, 1973, **14**, 359.

[7] See, for example, R. A. Bowling, T. W. Lassiter, D. O. Vick, and G. K. Schweitzer, *Nat. Bur. Stand.* (*U.S.*), *Spec. Publ.*, 581, 1979, 771.

[8] I. R. Beattie, J. S. Ogden, and D. D. Price, *J. Chem. Soc., Dalton Trans.*, 1979, 1460.

[9] S. N. Jenny and J. S. Ogden, *J. Chem. Soc., Dalton Trans.*, 1979, 1465.

[10] R. A. Atkins and K. A. Gingerich, personal communication.

[11] M. Spoliti, L. Bencivenni, M. Maltese, and S. N. Cesaro, *J. Mol. Struct.*, 1980, **60**, 259.

[12] R. P. Rastogi, B. L. Dubey, L. Ishwar, and D. I. Ishwar, *J. Inorg. Nucl. Chem.*, 1977, **39**, 2179.

[13] See, for example, M. Allavena, R. Rysnik, D. White, G. V. Calder, and D. E. Mann, *J. Chem. Phys.*, 1969, **50**, 3399.

[14] I. R. Beattie, C. J. Marsden, and J. S. Ogden, *J. Chem. Soc., Dalton Trans.*, 1980, 535.

[15] See, for example, E. B. Wilson, J. C. Decius, and P. C. Cross, 'Molecular Vibrations,' McGraw-Hill, New York, 1955, p. 192.

[16] See, for example, K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds,' Wiley, New York, 1978, p. 142.

[17] J. S. Ogden and S. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1981, 456.

[18] C. D. Garner, R. Mather, and M. F. A. Dove, *J. Chem. Soc., Chem. Commun.*, 1973, 633.

[19] I. R. Beattie, R. A. Crocombe, and J. S. Ogden, *J. Chem. Soc., Dalton Trans.*, 1977, 1481.

[20] J. F. Lotspeich, A. Javan, and A. Englebrecht, *J. Chem. Phys.*, 1959, **31**, 633.