Matrix Isolation Studies on $Cs_2[CO_3]$, $Rb_2[CO_3]$, and $K_2[CO_3]$. The Shape of Molecular $K_2[CO_3]$

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This paper describes the results of a matrix isolation i.r. spectroscopic study on the vaporisation of the alkali-metal carbonates $Cs_2[CO_3]$, $Rb_2[CO_3]$, and $K_2[CO_3]$. When these materials are heated *in vacuo* and the products condensed in nitrogen matrices at low temperatures, the i.r. spectra obtained show the presence of the *molecular* carbonates together with CO_2 and a number of minor features. With the aid of ^{18}O enrichment, it is suggested that $K_2[CO_3]$ has a C_{2v} structure with characteristic i.r. bands at 1 471.6 (B_2), 1 317.4 (A_1), 1 010.1 (A_1), 869.8 (B_1), and 696.7 (B_2) cm^{-1}.

ALKALI-METAL carbonates have been studied extensively in the solid state and in aqueous solution, and recent years have also seen developments in the characterisation of the species present in molten carbonates and in carbonate–chloride eutectics.[1-3] However, despite the widespread occurrence of potassium carbonate in several high temperature chemical systems (*e.g.* blast furnaces), relatively little is known about the stability or molecular parameters of vapour phase alkali-metal carbonates. The high-temperature mass spectrometric studies on $K_2[CO_3]$ reported by Simmons *et al.*[4] and related work on $K_2[CO_3]$ and $Cs_2[CO_3]$ by Gorokhov[5] have provided unequivocal evidence for the existence of $M_2[CO_3]$ vapour species, but in that work the parent ion was found to be only a minor feature in the spectrum, and it was concluded that vaporisation was accompanied by extensive decomposition to CO_2, O_2, and alkali metal.

We are currently studying a wide range of molecular oxoanion salts with the aim of establishing their vibrational fundamentals and shapes using a combination of high-temperature vaporisation, matrix isolation, and i.r. spectroscopy,[6,7] and this paper describes our recent work on caesium, rubidium, and potassium carbonates.

EXPERIMENTAL

The samples of $Cs_2[CO_3]$, $Rb_2[CO_3]$, and $K_2[CO_3]$ used in this work were all anhydrous, with reported purities >98%, and the matrix gases (Ar and N_2) were from B.O.C. (99.99%). Oxygen-18 enriched samples of $K_2[CO_3]$ were obtained from Prochem with an enrichment of 74.2 atom % ^{18}O, and were either vaporised directly, or converted to a lower degree of enrichment by fusing with an appropriate proportion of $K_2[C^{16}O_3]$: the resulting product was found to be statistically randomised. All samples were subsequently vaporised from a platinum boat contained inside a cylindrical alumina holder fitted with an external tantalum sleeve which could be heated inductively.[7] The temperatures required for vaporisation were monitored using an optical pyrometer, and were typically *ca.* 1 100 K ($Cs_2[CO_3]$), *ca.* 1 150 K ($Rb_2[CO_3]$), and *ca.* 1 200 K ($K_2[CO_3]$) and matrix ratios were estimated to be >1 000 : 1. Deposition times were typically *ca.* 1 h, and during this period, the CsI deposition surface was maintained at *ca.* 12 K, although in subsequent diffusion experiments the matrix deposits were warmed to 30—35 K. All spectra were recorded using a PE 225 spectrophotometer (200—5 000 cm^{-1}) and the frequencies reported have an estimated accuracy of ±0.5 cm^{-1}.

RESULTS AND DISCUSSION

Infrared Spectra of $Cs_2[C^{16}O_3]$, $Rb_2[C^{16}O_3]$, *and* $K_2[C^{16}O_3]$.—When samples of $Cs_2[C^{16}O_3]$ were heated to *ca.* 1 100 K and the vapours condensed in a nitrogen matrix at *ca.* 12 K, the resulting i.r. spectrum (500—1 500 cm^{-1}) showed two intense bands at 1 461.5 and 1 318.9 cm^{-1}, a prominent band at *ca.* 662 cm^{-1} due to matrix isolated CO_2, and four weaker features at 1 314.2 (sh), 1 018.0, 870.8, and 684.7 cm^{-1}. A typical spectrum of this region is shown in Figure 1. Diffusion experiments on this system produced little change in the CO_2 peak, but gentle warming to 20 K was sufficient to cause a rapid disappearance of the shoulder at 1 314.2 cm^{-1}, and more extensive diffusion at around 30 K resulted in a gradual decrease in intensity of the five remaining features, and the growth of new bands at 1 465, 1 455.5, and 1 310.5 cm^{-1}. These latter features could also be obtained *before* controlled diffusion in experiments where the matrix gas deposition rate was deliberately reduced, or where carbonate vaporisation occurred too rapidly, and they are tentatively assigned to ' polymer species '. Their ' monomer ' precursors at 1 461.5, 1 318.9, 1 018.0, 870.8, and 684.7 cm^{-1} always maintained the same relative intensities throughout a wide range of experimental conditions, and they are assigned to a single species.

Various additional features were also observed in these experiments. The most prominent of these was the bending mode of H_2O (at 1 599 cm^{-1}), and a weaker low frequency band was also observed at *ca.* 455 cm^{-1}, the origin of which was not determined. However, the intensity of this additional band showed no correlation with the ' monomer ' bands listed above. Argon matrix spectra obtained from this system were generally of poorer quality, but again showed five related ' monomer ' bands at corresponding frequencies 1 477.4, 1 317.1, 1 018.9, 866.3, and 691.5 cm^{-1}. No Cs–O modes were observed.

When $Rb_2[CO_3]$ was vaporised under similar conditions, the nitrogen matrix i.r. spectrum of the deposit showed five bands with similar growth and decay characteristics to those reported above. Samples of $K_2[CO_3]$ also produced a set of bands very similar to those observed from $Cs_2[CO_3]$. Table 1 summarises the frequencies of these bands in nitrogen matrices, and although there is a small but significant cation dependence, the close comparison between them suggests that similar molecular species have been isolated. This observation, taken in conjunction with the vibrational frequencies previously reported for the CO_3 group in carbonate melts,[3] indicates that the bands observed here are due to matrix-isolated $Cs_2[CO_3]$, $Rb_2[CO_3]$, and $K_2[CO_3]$. Support for this assignment comes from the fact that these five bands show a very similar intensity and frequency pattern to the NO_3 modes recently identified [6] in matrix isolated $K[NO_3]$, where two strong bands are observed at 1 460.5 and 1 293.1 cm^{-1}, and weaker features at 1 031.1, 827.5, and 721.0 cm^{-1}.

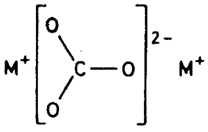
TABLE 1

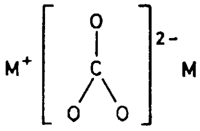
Vibrational fundamentals (cm^{-1}) observed for alkali-metal carbonates

Raman [a]			Infrared [b]			Assignment	
$Li_2[CO_3]$	$Na_2[CO_3]$	$K_2[CO_3]$	$K_2[CO_3]$	$Rb_2[CO_3]$	$Cs_2[CO_3]$	C_{2v}	D_{3h}
1 496	1 440	1 407	1 471.6	1 467.1	1 461.5	B_2	E'
1 422	1 400	1 380	1 317.4	1 320.9	1 318.9	A_1	
1 074	1 050	1 040	1 010.1	1 016.2	1 018.0	A_1	A_1'
872	880		869.8	870.6	870.8	B_1	A_2''
704	695	687	696.7	690.8	684.7	B_2	E'

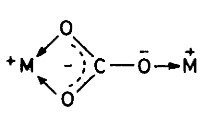
[a] Chloride melts; values from ref. 3. [b] This work; nitrogen matrices, frequency accuracy ±0.5 cm^{-1}.

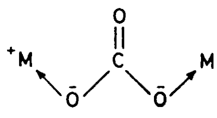
Structure Evaluation: Use of ^{18}O *Isotope Patterns.*—One of the problems encountered in the studies on matrix-isolated $K[NO_3]$ was how to distinguish between monodentate and bidentate co-ordination,[6] and a similar problem exists over the possible shapes of monomeric alkali-metal carbonates. Using a simple electrostatic model for triple ion formation, it is evident that two structures in particular are likely to be favoured depending upon the orientation of the carbonate ion within a linear M–C–M framework (see below). In terms of





cation–anion co-ordination, these might alternatively be depicted as (I) and (II). It is clearly of interest to establish whether either of these structures is adopted by matrix-isolated $M_2[CO_3]$ species.


(I)


(II)

In our earlier paper on $K[NO_3]$,[6] it was shown that a mixture of ^{18}O-enriched $M[XO_3]$ species would generate distinctive i.r. isotope frequency and intensity patterns in the X–O stretching region which could be used to differentiate between monodentate and bidentate co-ordination. Using this approach, bidentate binding was established in $K[NO_3]$, and subsequently also in $Na[PO_3]$.[7] A similar procedure may be applied to $M_2[CO_3]$ species, and in particular to structures (I) and (II) above, where the D_{3h} symmetry of free CO_3^{2-} is reduced to C_{2v} by the presence of the two cations. This co-ordination results in two types of C–O bond, giving rise to two principal C–O stretching constants, which may be defined as K_1 for the unique C–O bond lying on the C_2 axis, and K_2 for each of the other bonds. In model (II), consideration of C–O bond orders would indicate $K_1 > K_2$, whilst for model (I), $K_2 > K_1$.

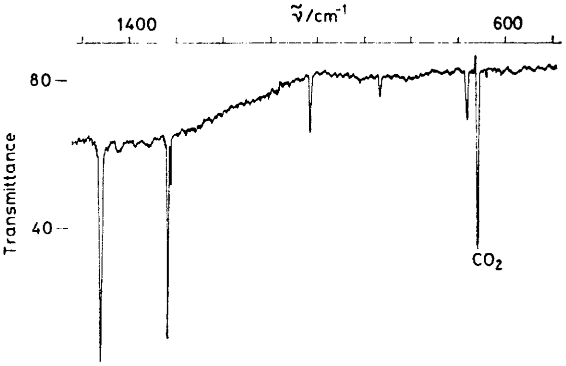


FIGURE 1 Nitrogen matrix i.r. spectrum obtained from the vaporisation of $Cs_2[CO_3]$

A series of calculations was therefore carried out on the stretching modes of the carbonate ion using a general-purpose interaction constant K_{rr} and a range of values of K_1 and K_2, subject to the constraint $K_1 + 2K_2 = 3K_r$, where K_r and K_{rr} are the principal and interaction stretching constants evaluated from the 'free' CO_3^{2-} ion. For the purposes of these calculations, typical stretching frequencies for the D_{3h} ion were taken as 1 460 (E') and 1 080 (A_1'),[8] yielding values of K_r and K_{rr} of 8.13 and 1.43 mdyn Å^{-1} * respectively. As in the case of our nitrate calculations, each set of force constants K_1, K_2, and K_{rr} was used to generate a line diagram showing the spectrum predicted for an isotopically scrambled mixture of ^{18}O-enriched carbonates, and attention was focused on the patterns associated with the intense i.r. bands in the region 1 300—1 650

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* Throughout this paper: 1 dyn = 10^{-5} N.

cm^{-1} arising from the E'(C–O) stretching mode. Figure 2(*a*)—(*f*) shows the results of six of these calculations assuming 75 atom % ^{18}O enrichment.

Calculation (*a*) is typical of solutions in which $K_1 > K_2$ and predicts that structure (II) should lead to an isotope pattern very similar to that previously predicted (and found) for bidentate binding in $K[NO_3]$.[6] Calculation (*b*) shows the characteristic four-line pattern from the E' mode in D_{3h} CO_3^{2-} ($K_1 = K_2$), whilst calculations (*c*)—(*f*) show the four types of pattern which can arise when $K_2 > K_1$. In these latter calculations, the highest frequency group of bands is predicted to be a 1 : 6 : 9 triplet for 75% ^{18}O enrichment for each solution of the force field, and although the lower group is predicted to comprise six bands with relative intensities 1 : 3 : 6 : 9 : 18 : 27, the relative *positions* of these depend on the extent to which K_2 exceeds K_1. For relatively large values of $K_2 - K_1$, this sextet approaches a simple triplet with intensity ratios (1 + 3) : (6 + 18) : (9 + 27) as indicated in (*f*), but lower values of $K_2 - K_1$ are predicted to give the rather asymmetric patterns indicated by (*c*)—(*e*). These model calculations therefore suggest that the two possible structures (I) and (II) proposed here for alkali-metal carbonates might readily be distinguished from ^{18}O experiments.

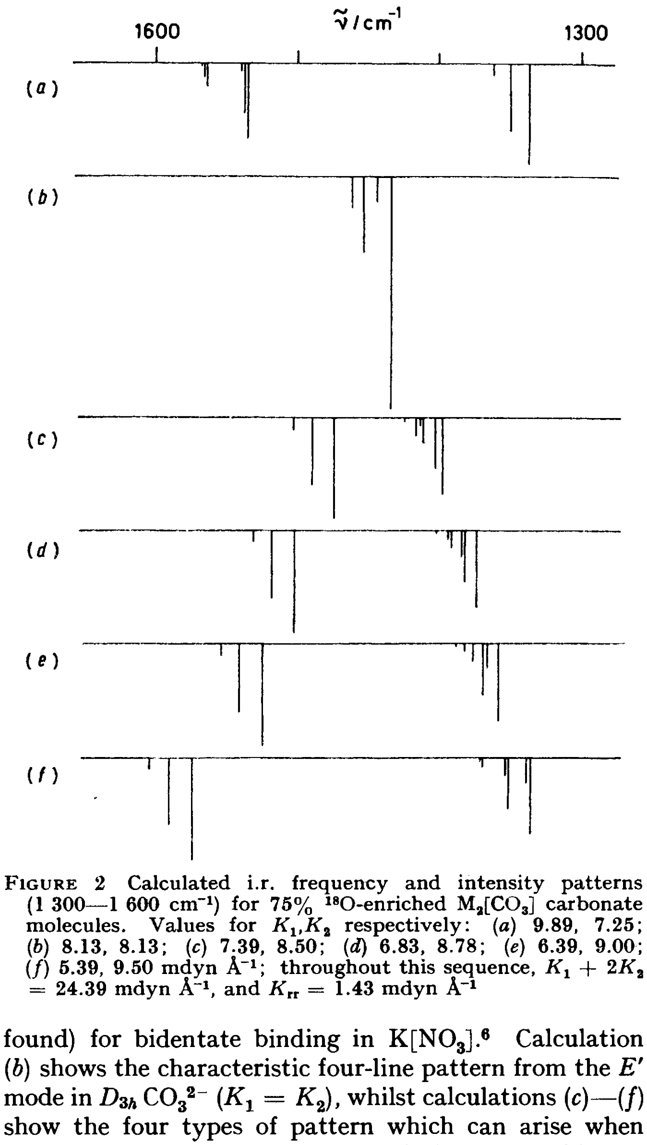
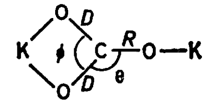


FIGURE 2 Calculated i.r. frequency and intensity patterns (1 300—1 600 cm^{-1}) for 75% ^{18}O-enriched $M_2[CO_3]$ carbonate molecules. Values for K_1,K_2 respectively: (*a*) 9.89, 7.25; (*b*) 8.13, 8.13; (*c*) 7.39, 8.50; (*d*) 6.83, 8.78; (*e*) 6.39, 9.00; (*f*) 5.39, 9.50 mdyn $Å^{-1}$; throughout this sequence, $K_1 + 2K_2 = 24.39$ mdyn $Å^{-1}$, and $K_{rr} = 1.43$ mdyn $Å^{-1}$

^{18}O *Enrichment Studies on* $K_2[CO_3]$.—The nitrogen matrix i.r. spectrum obtained from $K_2[C^{16}O_3]$ shows five bands assigned to molecular $K_2[CO_3]$ (Table 1) and also several unrelated weaker features which will be discussed later. Figure 3(*a*) shows a typical low-resolution i.r. spectrum obtained in the region 1 280—1 500 cm^{-1} and Figure 3(*b*) shows the corresponding spectral region in an experiment using 74.2 atom % ^{18}O-enriched material. Even under low resolution, it is evident that the higher frequency band now appears as a triplet, and that structure (I) is therefore favoured over structure (II). Figure 3(*c*) shows the bands in 3(*b*) under higher resolution, whilst Figure 3(*d*) shows the same spectral region in an experiment employing 35.5% ^{18}O enrichment. These isotope features were typically *ca.* 1 cm^{-1} wide, and a complete frequency list is included in Table 2.

TABLE 2

Vibrational frequencies (cm^{-1}) of isotopically labelled $K_2[CO_3]$ species isolated in nitrogen matrices



Observed [a]	Calc. (I) [b]	Calc. (II) [b]	Assignment [c]	
1 471.6	1 471.6	1 471.6	$K^{16}O^{16}OC^{16}OK$	B_2
	1 471.4	1 471.2	$K^{16}O^{16}OC^{18}OK$	
1 461.6	1 460.6	1 461.2	$K^{16}O^{18}OC^{16}OK$	
	1 460.4	1 460.7	$K^{16}O^{18}OC^{18}OK$	
1 450.7	1 447.9	1 449.3	$K^{18}O^{18}OC^{16}OK$	
	1 447.7	1 448.8	$K^{18}O^{18}OC^{18}OK$	
1 317.4	1 317.4	1 317.4	$K^{16}O^{16}OC^{16}OK$	A_1
1 311.9	1 311.1	1 310.8	$K^{16}O^{16}OC^{18}OK$	
1 308.9	1 310.1	1 309.7	$K^{16}O^{18}OC^{16}OK$	
1 305.5	1 304.3	1 303.5	$K^{16}O^{18}OC^{18}OK$	
1 302.7	1 303.1	1 302.3	$K^{18}O^{18}OC^{16}OK$	
1 295.1	1 296.5	1 295.3	$K^{18}O^{18}OC^{18}OK$	
1 010.1	1 010.1	1 010.1	$K^{16}O^{16}OC^{16}OK$	A_1
696.7	696.7	696.7	$K^{16}O^{16}OC^{16}OK$	B_2
869.8		869.8	$K^{16}O^{16}OC^{16}OK$	B_1
866.4		866.7	$K^{16}O^{16}OC^{18}OK$	
		866.5	$K^{16}O^{18}OC^{16}OK$	
863.4		863.4	$K^{16}O^{18}OC^{18}OK$	
		863.2	$K^{18}O^{18}OC^{16}OK$	
860.1		860.1	$K^{18}O^{18}OC^{18}OK$	

[a] Frequency accuracy ±0.5 cm^{-1}. [b] Parameters used for Calc. (I), Calc. (II) respectively: F_R 6.49, 7.03; F_D 8.19, 7.92; F_{RD} 1.18, 1.19; F_{DD} 0.91, 0.85 (all mdyn $Å^{-1}$). $F_\theta(= F_\phi)$ 1.61, 1.61 mdyn Å rad^{-2}; $F_{R\theta}$ 1.0, 1.37 mdyn rad^{-1}; $F_{D\theta}$ 1.0, 0.81 mdyn rad^{-1}; F(out-of-plane) 4.28 mdyn $Å^{-1}$ [for Calc. (II)]. [c] Assuming the structure shown at head of table: bond lengths $R = 1.35$ Å, $D = 1.25$ Å; $\theta = 120°$, $\phi = 120°$ [Calc. (I)], or $\theta = 122°$, $\phi = 116°$ [Calc. (II)].

With structure (I) favoured over structure (II), it is now possible to identify the symmetries of the C–O stretching modes in $K_2[CO_3]$ as 1 471.6 (B_2), 1 317.4 (A_1), and 1 010.1 (A_1) cm^{-1}, and to make parallel assignments for $Rb_2[CO_3]$ and $Cs_2[CO_3]$ (Table 1). The two other fundamentals assigned to these matrix-isolated carbonates are the B_1 and B_2 bending modes at *ca.* 870 and 690 cm^{-1}, and although it was not possible to obtain ^{18}O isotope data for the band at 696.7 cm^{-1} in $K_2[CO_3]$, we were able to observe fine structure on the fundamental at 869.8 cm^{-1}. This consisted of three additional bands at 866.4, 863.4, and 860.1 cm^{-1}.

Isotope Frequency Assignments and Force-constant Calculations.—Partial ^{18}O enrichment in structure (I) leads to six different isotopomers $M^{16}O^{16}OC^{16}OM$, $M^{16}O^{16}OC^{18}OM$, $M^{16}O^{18}OC^{16}OM$, $M^{18}O^{18}OC^{16}OM$, $M^{16}O^{18}OC^{18}OM$, and $M^{18}O^{18}OC^{18}OM$. In a sample of $K_2[CO_3]$ containing 74.2 atom % ^{18}O, these species will be present in the approximate proportions 1 : 3 : 6 : 9 : 18 : 27, whilst 35.5% ^{18}O enrichment will correspondingly produce a ratio of *ca.* 13 : 7 : 14 : 4 : 8 : 1. The high-resolution spectra shown in Figure 3(*c*) and (*d*) show sextet patterns associated with the fundamental at 1 317.4 cm^{-1} which correspond very closely to these intensity ratios, and this provides both a basis for band assignment (Table 2) and also an indication that force-constant parameters similar to those used to generate the line diagram in Figure 2(*d*) will be a useful starting point for the vibrational analysis. As in our previous force-constant analyses for $K[NO_3]$ and $Na[PO_3]$, the in-plane and out-of-plane modes may be considered separately, and a fit was initially sought for all the observed isotopic frequencies for the in-plane modes using the fundamentals of $K_2[C^{16}O_3]$ at 1 471.6, 1 317.4, 1 010.1, and 696.7 cm^{-1} as constraints. Four sets of calculations were carried out altogether. In the first of these, the bond angles at carbon were each assumed to have values of 120°, and the positions of the in-plane modes then optimised with respect to the observed frequencies. The results of this calculation are tabulated under 'Calc. (I)' in Table 2. Although the overall agreement is satisfactory, the root mean square (r.m.s.) deviation using this geometry and eight potential constants was 1.4 cm^{-1}, and thus larger than both the observed band widths (*ca.* 1.0 cm^{-1}) and the uncertainty in absolute frequency (*ca.* 0.5 cm^{-1}). In an attempt to improve this, three further calculations were carried out in which the O–C–O angle ϕ (see Table 2) was progressively reduced to 114°. The set of frequencies under 'Calc. (II)' in this table was obtained when $\phi = 116°$ and these now show a r.m.s. deviation from the observed bands of *ca.* 0.95 cm^{-1}. This is a small but significant improvement, and the force constants obtained for this geometry were used to generate the line diagrams accompanying Figure 3(*c*) and (*d*). It will be noted that using this more complete force field each component of the upper (B_2) triplet is now predicted to appear as a closely spaced (*ca.* 0.5 cm^{-1}) doublet in contrast to the patterns obtained in Figure 2(*c*)—(*f*). This is basically because the inclusion of bending modes now provides a mechanism for an isotope-dependent stretch–bend interaction, resulting in a small splitting between the B_2 stretching modes in pairs of molecules such as $K^{16}O^{16}OC^{16}OK$ and $K^{16}O^{16}OC^{18}OK$.

One final assumption made in this model deserves further comment. In order to carry out the force-constant calculations summarised in Table 2, the secular equations require realistic values for the C–O

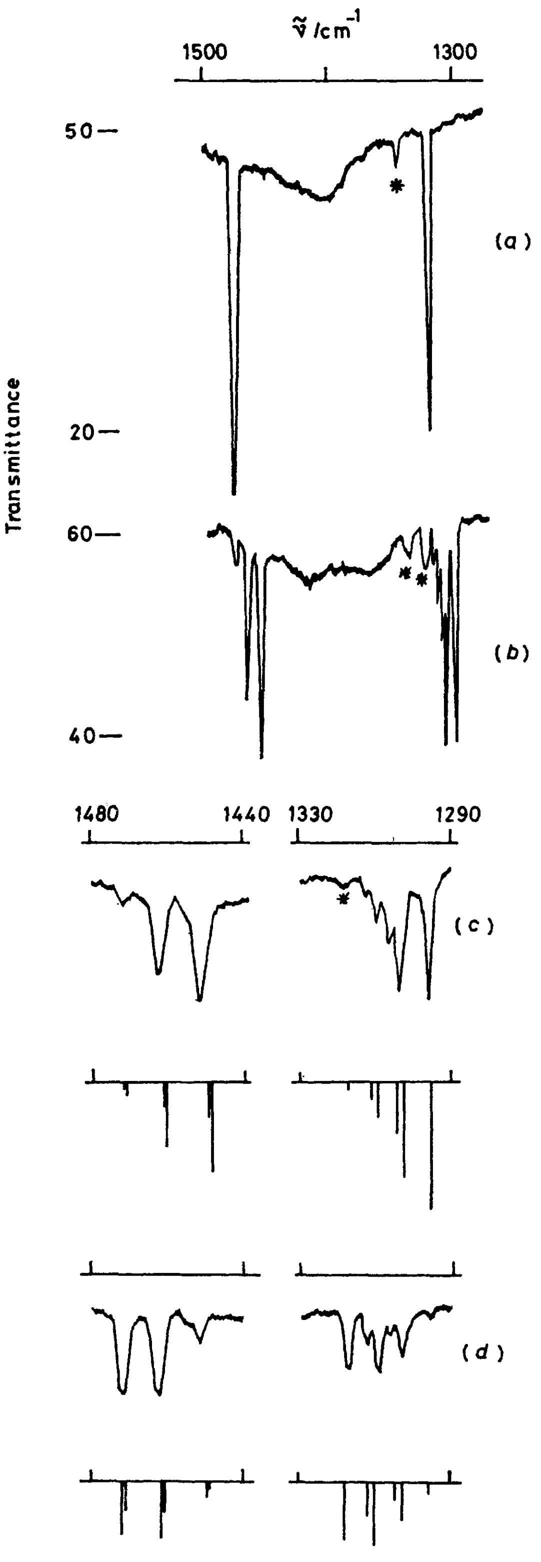


FIGURE 3 (*a*) Nitrogen matrix i.r. spectrum (1 280—1 500 cm^{-1}) obtained from $K_2[C^{16}O_3]$. (*b*) Nitrogen matrix i.r. spectrum obtained from 74.2% ^{18}O-enriched $K_2[CO_3]$ under similar conditions. (*c*) High-resolution spectra of multiplets present in (*b*); calculated isotope patterns are shown below. (*d*) As (*c*), but using a 35.5% O^{18}-enriched sample. The bands denoted by asterisks (*) do not arise from $K_2[CO_3]$ molecules bond lengths. The distances chosen here (1.25 Å and 1.35 Å) were selected on the basis of literature values [9] for CO_3^{2-}, $C_2O_4^{2-}$, and HCO_2^- and we believe them to be reasonable estimates. As is shown below, the *ratio* of these lengths is a significant parameter in computing the isotope patterns associated with the B_1 out-of-plane mode, and small uncertainties in these values will lead to detectable differences. However, it may be shown that such uncertainties have a negligible effect on the isotope frequency fit for the *stretching* modes, and that the somewhat arbitrary choice of C–O bond lengths does not affect the calculation of these in-plane isotope patterns.

Out-of-plane CO_3 *Mode.*—The band at 869.8 cm^{-1} observed for matrix-isolated $K_2[CO_3]$ is assigned to the B_1 out-of-plane vibration of the CO_3 group (Table 1). This assignment was made initially by comparison with the corresponding A_2'' mode in ' free ' CO_3^{2-} (*ca.* 860 cm^{-1}) [8] and by reference to carbonate melts,[3] where the same mode has been observed in the range 860—880 cm^{-1}. Confirmation for this assignment is provided by the ^{18}O enrichment experiments.

If one considers the out-of-plane mode of a planar molecule AXYZ in which atom A is centrally bound to X, Y, and Z by bonds of length l_1, l_2, and l_3 respectively, it may be shown * that the frequency of this mode is given by equation (1) where θ_1, θ_2, and θ_3 are the angles

$$4\pi^2\nu^2 = \frac{F}{R^2}\left[\frac{R^2}{M_A} + \frac{\sin^2\theta_1}{l_1^2M_X} + \frac{\sin^2\theta_2}{l_2^2M_Y} + \frac{\sin^2\theta_3}{l_3^2M_Z}\right] \quad (1)$$

YAZ, XAZ, and XAY; $R = [(\sin\theta_1)/l_1 + (\sin\theta_2)/l_2 + (\sin\theta_3)/l_3]$, and F is the force constant for an out-of-plane potential function $2V = F(\Delta S)^2$ in which ΔS represents a small displacement of atom A out of the XYZ plane.

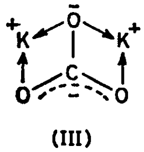
For the D_{3h} carbonate ion, equation (1) simplifies considerably, and ^{18}O enrichment produces a total of four distinct isotopomers, each with a different out-of-plane vibration frequency. In particular, if one assumes $\nu(A_2'')$ $[C^{16}O_3]^{2-}$ at 869.8 cm^{-1}, the three additional bands are then expected at 866.6 $[C^{16}O_2{}^{18}O]^{2-}$, 863.3 $[C^{16}O^{18}O_2]^{2-}$, and 860.1 cm^{-1} $[C^{18}O_3]^{2-}$. However, the isotope patterns observed for matrix-isolated $K_2[CO_3]$ in the C–O stretching region indicate a basic C_{2v} symmetry, and although this results in some simplification of equation (1) (*e.g.* $l_1 = l_2 \neq l_3$, $\theta_1 = \theta_2 \neq \theta_3$), the inequalities which remain give rise to six isotopically distinct species, and a prediction of six bands in this region on partial ^{18}O enrichment. Our experiments on ^{18}O-enriched $K_2[CO_3]$ yielded only four bands at 869.8, 866.4, 863.4, and 860.1 cm^{-1} and several calculations were carried out to clarify the position.

Using equation (1), the angles θ_1, θ_2, and θ_3 were given the values 122, 122, and 116° respectively, consistent with best analysis of the stretching modes, and the bond lengths $l_1(= l_2)$ and l_3 were independently varied from $l_1 = 1.6$ Å, $l_3 = 1.0$ Å, to $l_1 = 1.0$ Å, $l_3 = 1.6$ Å. These calculations generated six-line patterns for mixtures of isotopomers, but the frequency separations between the modes of $K^{16}O^{18}OC^{16}OK$ and $K^{16}O^{16}OC^{18}OK$, and between $K^{16}O^{18}OC^{18}OK$ and $K^{18}O^{18}OC^{16}OK$ were found to be particularly dependent on the ratio $l_1 : l_3$. Thus for $l_1(= l_2) = 1.25$ Å, and $l_3 = 1.35$ Å, the six bands are predicted at 869.8, 866.7, 866.5, 863.4, 863.2, and 860.1 cm^{-1} where the out-of-plane constant $F = 4.28$ has been chosen to reproduce the 869.8 cm^{-1} band. However, for $l_1 = l_2 = 1.0$ Å, and $l_3 = 1.6$ Å, the positions are now predicted to be 869.8, 868.0, 865.7, 864.9, 861.6, and 859.8 cm^{-1}. In this second solution, there is an almost uniform separation of *ca.* 1.2 cm^{-1} between adjacent bands, whilst in the former, two of the spacings in particular are predicted to be only 0.2 cm^{-1}.

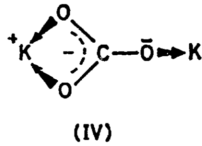
The experimental line widths observed in this work were typically *ca.* 1 cm^{-1}, and whilst one might expect to observe a six-line pattern for widely differing values of l_1 and l_3, one would not anticipate resolving the smallest splittings predicted in a molecule with similar C–O bond lengths. Instead, one might anticipate an effective four-line pattern, with band centres at 869.8, *ca.* 866.6, *ca.* 863.3, and 860.1 cm^{-1}. This calculated spectrum is in very good agreement with the four bands observed (Table 2), and in addition to confirming the assignment of this mode as an out-of-plane CO_3 vibration, the frequency fit indicates that coupling with out-of-plane cation motion is negligible.

The Shape of $K_2[CO_3]$.—The basic conclusions which may be drawn from these results are that in molecular $K_2[CO_3]$ one C–O bond is weaker than the other two, and that the two stronger bonds appear to be equivalent. Subsequent spectral interpretation leading to structure (I) as a probable shape is then based on two additional assumptions. The first of these is that the equilibrium configuration is planar and contains the linear K–C–K unit anticipated by considering the ions as point charges. The second assumes that we are able to detect any *inequivalence* in the C–O bonds from our isotope patterns. If these assumptions do not hold, then a large number of shapes become possible.

Thus, if we allow non-linear K–C–K units, we can retain the equivalence of two strong C–O bonds in the bis-bidentate structure (III), and in non-planar varieties of (I), such as (IV). Neither of these can be rejected solely on the basis of the observed isotope patterns. Lower symmetry structures derived from (I) in which all C–O bond equivalence is destroyed, as in (V), could also give rise to the observed spectra if this departure from C_{2v} symmetry produces only a very minor difference in the C–O bonds labelled D in Table 2. In particular, if the two resultant values of F_D arising from this asymmetry were to differ by less than about 1%, we would



(III)



(IV)

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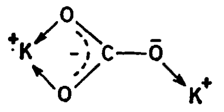
* Equation derived using Wilson G.F. matrix approach.

not expect to detect the difference spectroscopically, by resolving, for example, the vibrations of $K^{16}O^{18}OC^{16}OK$ and $K^{18}O^{16}OC^{16}OK$.

At the present time, the experimental technique which seems most appropriate for distinguishing between these various geometries is perhaps electron diffraction on a cooled molecular beam, but it would also be interesting to carry out calculations on these vapour phase carbonates similar to those recently reported for molecular Li[NO$_3$].[10] Here, the lowest energy configuration proved to be the C_{2v} bidentate structure.



(V)

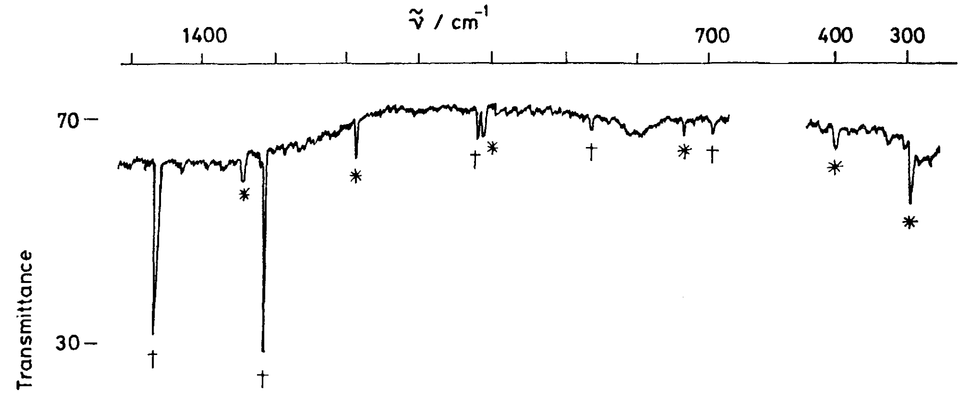


FIGURE 4 Nitrogen matrix i.r. spectrum obtained from the vaporisation of K$_2$[CO$_3$]. The band due to CO$_2$ (at *ca.* 662 cm^{-1}) has been omitted, and those labelled (*) do not correlate with those assigned to molecular K$_2$[CO$_3$] (†)

Additional Bands observed in K$_2$[CO$_3$] *Vaporisation.*— By comparison with the Cs$_2$[CO$_3$] system, our matrix studies on K$_2$[CO$_3$] frequently produced spectra which contained several weak features in addition to the bands assigned to molecular K$_2$[CO$_3$] and CO$_2$. Figure 4 shows a typical nitrogen matrix spectrum obtained from K$_2$[CO$_3$] vaporisation. In this spectrum, these bands (denoted *) lie at 1 340, 1 180, 1 006, 720, 398, and 293 cm^{-1}. Although none of these bands was found to be correlated with the K$_2$[CO$_3$] fundamentals, the three bands at 1 340, 1 180, and 720 cm^{-1} were found to maintain the same relative intensities throughout a range of experimental conditions, and further work is in progress in an attempt to identify this species. The band at 1 006 cm^{-1} has a counterpart at 993 cm^{-1} in argon matrices, and is assigned to KO$_4$. This molecule has been studied extensively by Andrews,[11] as a product of K atom + O$_2$ co-condensation reactions. He reports an argon matrix frequency of 993.3 cm^{-1}, and the presence of KO$_4$ in our experiments indicates that a limited amount of decomposition to elemental potassium occurs during sample vaporisation. The remaining bands at 398 and 293 cm^{-1} lie in the K–O stretching region, and are close to those previously assigned to KO (384 cm^{-1}) [12] and KO$_2$ (307 cm^{-1} in Ar).[11] However, they were not observed with sufficient intensity to carry out a definitive isotope study. No evidence was found from our results for matrix isolated K$_2$O, which is reported [12] to have a prominent i.r. band at 502 cm^{-1}.

CONCLUSIONS

The principal conclusions which emerge from this work are that the vapours over heated Cs$_2$[CO$_3$], Rb$_2$[CO$_3$], and K$_2$[CO$_3$] contain significant amounts of undissociated molecular carbonates, and that these species may readily be isolated in low-temperature matrices. The K$_2$[CO$_3$] system was studied in detail using ^{18}O enrichment, and the resulting spectrum is interpreted in terms of a C_{2v} structure for molecular K$_2$[CO$_3$] in which the CO$_3$ group co-ordinates in a bidentate fashion to one of the potassium atoms, and in a monodentate fashion to the other. This structure is supported by a force-constant analysis on the vibrations of the CO$_3$ unit which satisfactorily reproduces the frequencies observed for six isotopic varieties of K$_2$[CO$_3$]. It is not, however, the only structure consistent with the spectroscopic data. In addition, all three carbonate systems showed some evidence of thermal decomposition, as indicated by the observation of bands due to matrix-isolated CO$_2$, and in the studies on K$_2$[CO$_3$] there is additional evidence for atomic potassium and molecular oxygen in the high-temperature vapour, but no indication of K$_2$O. These observations therefore support the previous mass spectrometric data by Simmons *et al.*[4] as regards the probable *identity* of the vapour species in the K$_2$[CO$_3$] system. However we would doubt whether the proportion of K$_2$[CO$_3$] in the vapour phase is as low as their estimate of *ca.* 1%. It is well known that fragmentation is a serious problem in high-temperature mass spectrometric studies in ionic systems, and will necessarily lead to anomalous ion intensities unless refinements such as angular-distribution mass spectrometry are available.[13] Unfortunately, we cannot provide an alternative estimate of the relative proportions of K$_2$[CO$_3$] and CO$_2$ in our matrix spectra, as the i.r. extinction coefficients for our carbonate bands are not known, but on the basis of qualitative comparisons with related systems (*e.g.* K[NO_3], Na[PO_3]) we feel that the molecular alkali-metal carbonate species characterised in this work represent a significant proportion of the vapour, and may therefore play an important role in vapour transport.

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