Inorganica Chimica Acta, *121* (1986) 161–166

Vibrational Spectra and Structure of $M(CO_2)$ and $M_2(CO_2)$ Molecules

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(Received April 28, 1986)

Abstract

Atomic Na, K and Cs were codeposited with CO_2 in excess of matrix gas at the temperature of 12 K. The IR spectra revealed the presence of ionic aggregates corresponding to the molecules $M(CO)_2$ and $M_2(CO_2)$ (M = Na, K, Cs). Both molecular species have C_{2v} symmetry; $M(CO_2)$ species have a planar ring structure while $M_2(CO_2)$ have a W-shape structure. $M_2(CO_2)$ molecules with C_s symmetry were also identified. The geometrical parameters of all the molecules were determined by $^{12}C/^{13}C$ and $^{16}O/^{18}O$ isotopic shifts. Raman spectra were also recorded and the results are reported in this study. The effect of photolysis on the structure of these molecules was examined. It was determined that photolysis promotes the formation of $Na(CO_2)$ and transforms the $M_2(CO_2)$ molecules with C_{2v} symmetry into C_s symmetry isomers.

Introduction

The interaction of alkali metal atoms with CO_2 has been the subject of IR [1–3], ESR [3, 4] and theoretical [5] studies. It has been established that the CO_2^- anion derives from CO_2 activated by alkali metals in inert gas matrices. The process occurs through electron transfer from the metal to the molecule. $Li(CO_2)$ molecule was identified and structurally characterized in a matrix isolation IR study [2]. It was determined that this molecule exists in two isomeric forms of C_{2v} and C_s symmetry; the C_s isomer is photolytically converted into the more stable C_{2v} configuration. The theoretical calculations [5] performed on $Li(CO_2)$ were confirmed by the experimental results [2].

The aim of this work is to extend the knowledge of the structure of $M(CO_2)$ type molecules by means of matrix isolation IR and Raman spectroscopy coupled with ^{13}C and ^{18}O isotopic substitution. It is also interesting to establish how the cation interacts with CO_2^- in the $M(CO_2)$ molecules. Jacox *et al.* [1] proposed the possibility of an asymmetric interaction, but this contrasts with the theoretical previsions [5] and some experimental results [2, 6] where symmetric interaction was proposed.

Experimental

Details of the experimental apparatus and procedure are reported elsewhere [2]. The alkali metals were vaporized by heating the metal loaded in a platinum crucible placed in a heat resistant tantalum sheet. Sodium, potassium and cesium were vaporized at 570, 520 and 315 K respectively. The metal vapour was codeposited with CO_2 in excess of matrix gas on a copper block cooled at 12 K. The IR reflection spectra were measured by means of a Perkin Elmer 580-B spectrophotometer. The Raman spectra were recorded using an Ar Laser Cary Raman spectrometer. The IR frequencies reported in the study have an accuracy of ± 0.5 cm^{-1} while the Raman shifts are accurate within ± 1 cm^{-1}.

Results and Discussion

In previous studies it was pointed out that atomic lithium [2] as well as sodium potassium and cesium [1] causes the formation of the radical anion CO_2^- when the metal is codeposited with CO_2 in inert gas matrices maintained at cryogenic temperatures. It was also observed that the complexity of the spectrum depends on the M/CO_2 ratio. In particular, the formation of molecular aggregates where CO_2^{2-} coordinates more than one alkali metal was mentioned [1, 2]. In our experiments, the metals were codeposited with CO_2 in the approximate M/CO_2 ratios of 1:1 and 2:1 at the matrix temperature of 12 K. The effect of the deposition temperature on the formation of different molecules was also checked at 25 K. Matrix annealings were also carried out raising the matrix temperature from 12 K to 30 K and then bringing the temperature back down to the initial value. These

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experiments suggested that the $M(CO_2)$ species are predominant when the M/CO_2 ratio is *ca.* 1:1, while $M_2(CO_2)$ systems predominate when the ratio is *ca.* 2:1 and when diffusion of the species trapped in the matrix is allowed. Matrix annealing experiments showed a considerable presence of carbonates $M_2(CO_3)$ [7] and of more complex molecules where CO_2 coordinates more than two alkali metals. The alkali metals have different affinity towards CO_2; cesium was found to be more reactive than potassium and sodium. In particular, it was noted that the formation of $Na(CO_2)$ is influenced by photolysis. In fact, when sodium was deposited with CO_2 on a matrix irradiated with a Hg lamp, metal reactivity towards CO_2 was enhanced. Photolysis also has a catalytic effect on potassium and cesium. At last, the IR spectra suggested the presence of two geometrical isomers for the $M_2(CO_2)$ molecules. The isomers have C_{2v} and C_s structures; the former is photolytically converted into the latter one by means of IR source exposure.

Conclusions concerning the molecular structure and the geometry of the molecules identified in the matrix isolation study were achieved from ^{13}C and ^{18}O isotopic shift measurements and normal coordinate calculations. Table I summarizes the IR and Raman bands observed from the codeposition experiments.

TABLE I. IR Bands[a] Observed in the $M + CO_2$ (M = Na, K, Cs) Codeposition Experiments[b]

$Na + CO_2$ (Ar)	$K + CO_2$ (N_2)	$Cs + CO_2$	
		(Ar)	(N_2)
1601.5 (A)	1610.0 (A)	1595.5 (A)	1608.3 (A)
	1342.4 (B)	1353.1 (A)	1345.5 (A)
	1328.5 (C)*	1341.5 (A)	1328.7 (B)
	1183.7 (B)	1335.0 (C)*	1319.8 (C)*
	1052.4 (C)*	1173.7 (B)	1186.7 (B)
	738.7 (B)	1018.0 (C)*	1050.0 (C)*
		744.5 (B)	745.5 (B)

[a] Frequencies are in cm^{-1}. [b] A and B stand for C_{2v} $M(CO_2)$ and $M_2(CO_2)$ molecules, C for C_s $M_2(CO_2)$ molecules, * indicates the bands which increase intensity after photolysis.

1. The $M(CO_2)$ Molecules

The IR spectra show an intense absorption at *ca.* 1600 cm^{-1} and a weak band at *ca.* 1350 cm^{-1}. The latter band appears as a medium intensity Raman absorption. The measured frequencies slightly differ when changing the metal atom coordinating the CO_2^- group. This fact indicates that the influence of the metal on the vibrational levels of the radical anion is small. Since sodium, potassium and cesium produce the same results, the discussion is restricted to the cesium system. Figure 1a shows the IR spectrum relative to the codeposition of cesium and CO_2 in a N_2 matrix. When ^{12}C and ^{16}O were substituted with ^{13}C and ^{18}O respectively, the bands at *ca.* 1600 cm^{-1} shift down to lower frequencies (see Fig. 1b). The ^{13} ^{13}C and ^{18}O shifts are *ca.* 40 and 30 cm^{-1} for the CO_2^- mode occurring at *ca.* 1600 cm^{-1}. The isotopic shift down to lower frequencies (see Fig. 1b). The ^{13}C and ^{18}O shifts are *ca.* 40 and 30 cm^{-1} for the CO_2^- mode occurring at *ca.* 1600 cm^{-1}. The isotopic $C^{18}O_2$ present in a gaseous mixture in the ratio 1:2:1 consists of triplets with the intensity pattern 1:2:1 (see Fig. 1c). This result implies the presence of CO_2^- of C_{2v} symmetry with the two oxygen atoms symmetrically interacting with the alkali metal. On the basis of the C_{2v} planar ring model and following the procedure adopted in the IR study of $Li(CO_2)$ [2], the molecular geometry, force constants and isotopic vibrational frequencies of the radical anion CO_2^- were determined. The O–C–O bond angle was calculated through the triatomic molecule approximation [8] using the B_2 frequencies of the isotopic couples $^{13}C^{16}O_2^-/^{12}C^{16}O_2^-$ and $^{12}C^{16}O_2^-/^{12}C^{18}O_2^-$. The bond angle was corrected for anharmonicity according to Green's method [9]. The use of the experimental frequencies of all the isotopic species allowed the computer optimization of the force constants and molecular geometry of the anion by means of normal coordinate calculations. The agreement between the calculated and measured frequencies of

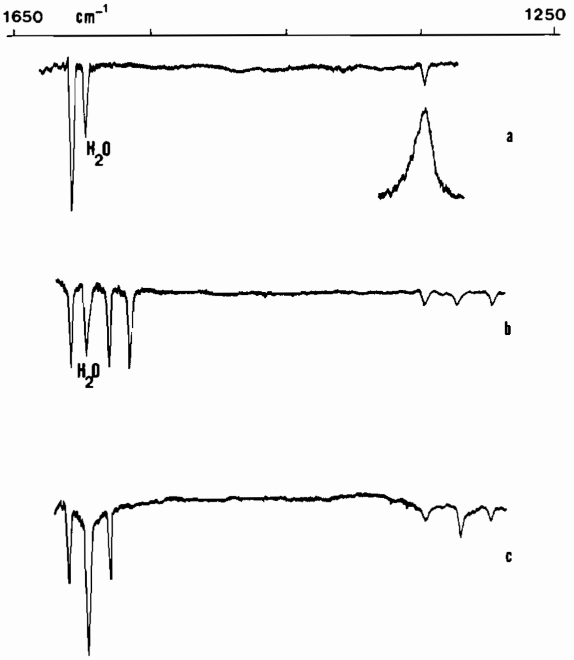

Fig. 1. (a) IR and Raman spectra of $Cs(CO_2)$, (b) IR spectrum of $Cs(CO_2)$, $Cs(^{13}CO_2)$, $Cs(C^{18}O_2)$, (c) IR spectrum of 50% ^{18}O-enriched $Cs(CO_2)$.

TABLE II. Summary of the Vibrational Studies on Matrix-isolated M(CO$_2$) Molecules of C_{2v} Symmetry[a]

Vibrational mode	Observed frequencies in the M + CO$_2$ codeposition experiments		
	Na(CO$_2$) (Ar)	K(CO$_2$) (N$_2$)	Cs(CO$_2$) (N$_2$)
B$_2$	1601.5	1610.0	1608.3
A$_1$	(1367)[b]	(1364)[b]	1345.5 1346[b]

Vibrational mode	Na(^{13}CO$_2$)		K(^{13}CO$_2$)		Cs(^{13}CO$_2$)	
	Exp. (Ar)	Calc.	Exp. (N$_2$)	Calc.	Exp. (N$_2$)	Calc.
B$_2$	1561.0	1559.0	1568.0	1567.2	1567.0	1565.1
A$_1$		1346.8		1343.6	1324.5	1329.1
A$_1$		745.0		744.9		759.1

Vibrational mode	Na(C^{18}O$_2$)		K(C^{18}O$_2$)		Cs(C^{18}O$_2$)	
	Exp. (Ar)	Calc.	Exp. (N$_2$)	Calc.	Exp. (N$_2$)	Calc.
B$_2$	1574.2	1573.1	1582.5	1581.4	1580.5	1580.2
A$_1$		1320.8		1317.7	1298.0	1297.9
A$_1$		725.9		725.8		741.4

Vibrational mode	Observed and calculated frequencies of ^{18}O-enriched M(CO$_2$) (C_{2v}) molecules					
	Na(CO$_2$)		K(CO$_2$)		Cs(CO$_2$)	
	Exp. (Ar)	Calc.	Exp. (N$_2$)	Calc.	Exp. (N$_2$)	Calc.
B$_2$ (C^{16}O$_2$)$^-$	1601.5	1601.5	1610.0	1610.0	1608.3	1608.3
A′ (C^{16}O^{18}O)$^-$	1589.8	1588.7	1598.2	1597.0	1596.4	1595.4
B$_2$ (C^{18}O$_2$)$^-$	1574.2	1573.1	1582.5	1581.4	1580.5	1580.2
A$_1$ (C^{16}O$_2$)$^-$		1367.3		1364.1	1345.5	1345.5
A′ (C^{16}O^{18}O)$^-$	1343.5	1342.6	1340.5	1339.5	1320.8	1320.4
A$_1$ (C^{18}O$_2$)$^-$		1320.8		1317.7	1298.0	1297.9
A$_1$ (C^{16}O$_2$)$^-$		755.2		755.2		770.3
A′ (C^{16}O^{18}O)$^-$		740.8		740.8		756.1
A$_1$ (C^{18}O$_2$)$^-$		725.9		725.8		741.4

Molecular geometry and force constants of CO$_2^-$ calculated for the M(CO$_2$) molecules

	Na(CO$_2$)	K(CO$_2$)	Cs(CO$_2$)
R(C–O) (nm)	0.1255[c]	0.1250	0.1250
Angle (O–C–O)	128°[c]	131°[d]	127°[d]
F(CO) (N/m)	9.863×10^2	9.876×10^2	9.866×10^2
F(CO/CO) (N/m)	2.188×10^2	2.120×10^2	2.267×10^2
F(OCO) (Nm)	1.77×10^{-18}	1.77×10^{-18}	1.77×10^{-18}
F(CO/OCO) (N)	0.7×10^{-8}	0.7×10^{-8}	0.7×10^{-8}

[a] Frequencies are in cm^{-1}. [b] Raman shift (cm^{-1}). [c] From ref. 5. [d] Value calculated using the triatomic molecule approximation and corrected for anharmonicity (see text).

the M(CO$_2$) molecules is good. The summary of the measurements and normal coordinate calculations is given in Table II.

2. *The M$_2$(CO$_2$) Molecules*

These species are predominant when the M/CO$_2$ ratio is kept equal to 2:1. M$_2$(CO$_2$) molecules were detected for cesium and potassium only. Fig. 2a shows the IR bands observed from the codeposition experiments of cesium with CO$_2$ in the 2:1 molecular ratio. The IR spectrum consists of two distinct groups of bands: **A** (1328.7, 1186.7 and 745.5 cm^{-1}) and **B** (1319.8 and 1050.0 cm^{-1}). Isotopic substitution with ^{13}C and ^{18}O isotopes indicates that these bands

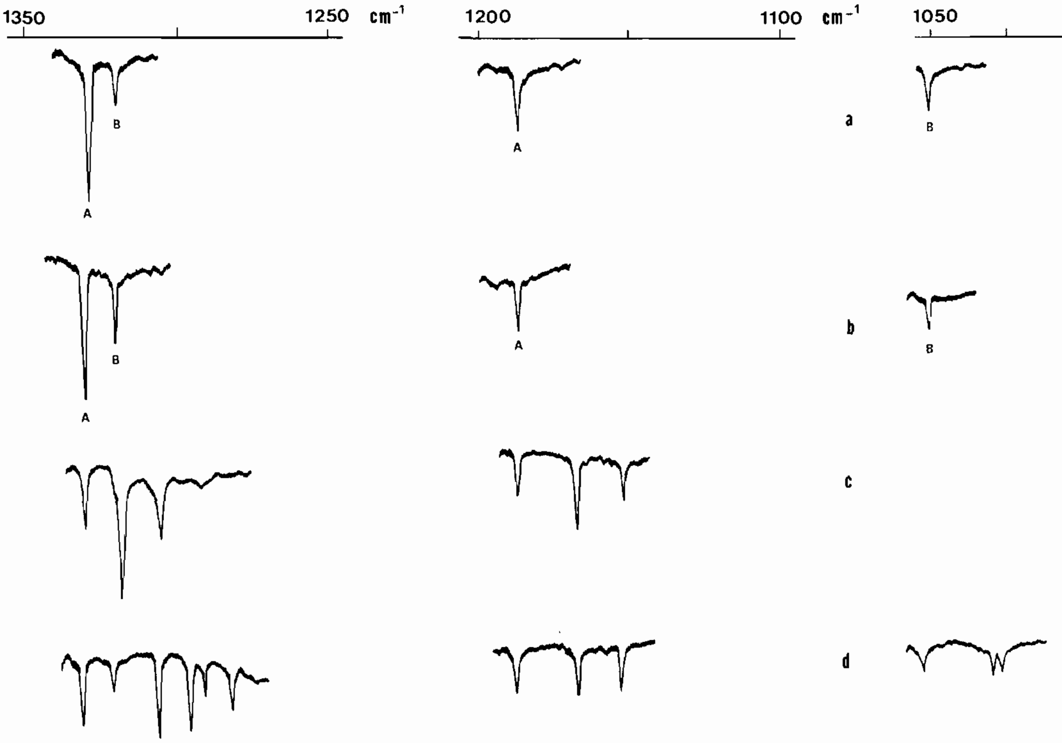

Fig. 2. (a) IR spectrum obtained from codeposition of cesium metal and CO_2 in the ratio 2:1, (b) spectrum (a) measured after matrix photolysis, (c) IR spectrum obtained from codeposition of cesium metal and 1:2:1 gaseous mixture $C^{16}O_2$, $C^{16}O^{18}O$ and $C^{18}O_2$ (Cs/CO_2 ratio 2:1), (d) IR spectrum obtained from codeposition of cesium metal and $^{13}CO_2$ and $C^{18}O_2$ (Cs/CO_2 ratio 2:1).

belong to the C_{2v} and C_s symmetry geometrical isomers. It was also observed that the exposure of the matrix to the Nerst glower IR source partially converts the C_{2v} isomer **A** into the other **B**. This fact is represented in Fig. 2b where the weak bands of **B** gain intensity with respect to the more intense absorptions of the isomer **A**. It can be concluded that the two isomers have different stability and that the C_s symmetry molecules might be more stable than the C_{2v} ones. The effect of the matrix material on the stability of the two isomers was checked using argon as matrix gas but it was concluded that the matrix has no influence. Table III and Table IV report the bands assigned to the C_{2v} and C_s symmetry isomers of type $M_2(CO_2)$.

The molecular structure of the isomers was established by means of ^{13}C and ^{18}O frequency shifts. The results of these measures indicate that the isomers have different structural parameters. In fact, the IR frequencies of $C^{16}O_2^{2-}$, $^{13}C^{16}O_2^{2-}$, and $C^{18}O_2^{2-}$ of $Cs_2(CO_2)$ and $K_2(CO_2)$ were calculated in satisfactorily agreement with the experimental values when a symmetric bent CO_2^{2-} group was assumed for the C_{2v} symmetry isomer **A** and an asymmetric bent configuration with inequal C—O bonds was assumed for the C_s symmetry isomer **B**. It is interesting to see that the vibrational frequencies of the $^{16}O/^{18}O$ isotopomers of the C_{2v} isomers agree with the expected values provided by normal coordinate calculations (see Table III) and it is remarkable the fact that the bands of the mixed oxygen isotopic species appear in the IR spectrum of Fig. 2c in the 1:2:1 intensity pattern typical of a CO_2^{2-} dianion with equivalent C—O bonds.

As far as the C_s isomers, normal coordinate calculations provide an asymmetric structure with distinct C—O bond lengths, $R_1 = 0.126$ nm and $R_2 = 0.138$ nm and consequently with distinct C—O stretching force constants (see Table IV). Also in this case, the calculated isotopic frequencies of $^{13}CO_2^{2-}$ and $C^{18}O_2^{2-}$ are in reasonable agreement with the experimental results. The IR bands observed for $Cs_2(C^{18}O_2)$ and $Cs_2(^{13}CO_2)$ of C_{2v} and C_s symmetry are shown in Fig. 2d.

Conclusion

The spectroscopic investigation indicates that the $M(CO_2)$ molecules are ionic aggregates of C_{2v} symmetry. No C_s symmetry isomers of these molecules, was observed, notwithstanding that for $Li(CO_2)$ both C_{2v} and C_s isomers were identified [2]. Theoretical calculations [5] predict the existence of the C_s isomer for $Na(CO_2)$ but its relative stability is much lower than the C_{2v} isomer. Furthermore, the two isomers

TABLE III. Summary of the Vibrational Studies on Matrix-isolated $M_2(CO_2)$ Molecules of C_{2v} Symmetry[a]

Vibrational mode	Observed frequencies in the M + CO_2 codeposition experiments	
	$K_2(CO_2)$ (N_2)	$Cs_2(CO_2)$ (N_2)
B_2	1342.4	1328.7
A_1	1183.7 (1184)[b]	1186.7 (1187)[b]
A_1	738.7	745.5

Vibrational mode	$K_2(^{13}CO_2)$		$Cs_2(^{13}CO_2)$	
	Exp. (N_2)	Calc.	Exp. (N_2)	Calc.
B_2	1307.0	1306.9	1294.5	1293.8
A_1	1164.2	1164.2	1166.0	1165.5
A_1	731.4	729.8	737.5	737.3

Vibrational mode	$K_2(C^{18}O_2)$		$Cs_2(C^{18}O_2)$	
	Exp. (N_2)	Calc.	Exp. (N_2)	Calc.
B_2	1318.5	1318.3	1305.0	1304.3
A_1	1148.0	1146.4	1152.0	1151.7
A_1	706.6	708.1	711.0	712.9

Vibrational mode	Observed and calculated frequencies of ^{18}O-enriched $M_2(CO_2)$ (C_{2v}) molecules			
	$K_2(CO_2)$		$Cs_2(CO_2)$	
	Exp. (N_2)	Calc.	Exp. (N_2)	Calc.
B_2 $(C^{16}O_2)^{2-}$	1342.4	1342.4	1328.7	1328.7
A' $(C^{16}O^{18}O)^{2-}$	1331.7	1331.7	1318.0	1318.0
B_2 $(C^{18}O_2)^{2-}$	1318.3	1318.5	1305.0	1304.3
A_1 $(C^{16}O_2)^{2-}$	1183.7	1183.7	1186.7	1186.7
A' $(C^{16}O^{18}O)^{2-}$	1164.5	1163.6	1167.5	1167.6
A_1 $(C^{18}O_2)^{2-}$	1148.0	1146.4	1152.0	1151.7
A_1 $(C^{16}O_2)^{2-}$	738.7	738.7	745.5	745.5
A' $(C^{16}O^{18}O)^{2-}$	723.1	723.6	737.0	737.5
A_1 $(C^{18}O_2)^{2-}$	706.6	708.1	711.0	712.9

Molecular geometry and force constants of $CO_2{}^{2-}$ group calculated for the $M_2(CO_2)$ isomers of C_{2v} symmetry

	$K_2(CO_2)$	$Cs_2(CO_2)$
R(C–O) (nm)	0.127	0.127
Angle (O–C–O)	126°[c]	123°[c]
F(CO) (N/m)	7.181×10^{2}	7.018×10^{2}
F(CO/CO) (N/m)	1.730×10^{2}	1.578×10^{2}
F(OCO) (Nm)	1.743×10^{-18}	1.851×10^{-18}
F(CO/OCO) (N)	0.686×10^{-8}	0.7×10^{-8}

[a] Frequencies are in cm^{-1}. [b] Raman shift (cm^{-1}). [c] Value calculated using the triatomic approximation and corrected for anharmonicity (see text).

differ for a stabilization energy of 0.20 eV [5] and this difference is higher than the value of 0.02 eV calculated for the C_{2v} and C_s isomers of Li(CO_2) [5]. It is evident that a low temperature matrix favours the formation and the stabilization of the most stable C_{2v} isomer. From this study it was established that the $CO_2{}^-$ anion is a bent group with equivalent C–O bonds. Any possible asymmetric interaction of the alkali metal with the radical also excludes the M(CO_2) molecules because the bands of the mixed oxygen

TABLE IV. Summary of the IR Studies on $M_2(CO_2)$ (C_s) Matrix-isolated Molecules[a]

Vibrational mode	Observed frequencies in the M + CO_2 codeposition experiments	
	$K_2(CO_2)$ (N_2)	$Cs_2(CO_2)$ (N_2)
A'	1328.5	1319.8
A'	1052.4	1050.0

Vibrational mode	$K_2(^{13}CO_2)$		$Cs_2(^{13}CO_2)$	
	Exp. (N_2)	Calc.[b]	Exp. (N_2)	Calc.[b]
A'	1295.7	1296.8	1280.8	1288.4
A'	1026.8	1030.4	1026.8	1028.4
		737.9		737.9

Vibrational mode	$K_2(C^{18}O_2)$		$Cs_2(C^{18}O_2)$	
	Exp. (N_2)	Calc.	Exp. (N_2)	Calc.
A'	1299.5	1299.8	1290.2	1291.5
A'	1029.8	1025.5	1028.3	1023.5
		711.4		711.3

Molecular geometry and force constants of CO_2^{2-} calculated for the $M_2(CO_2)$ isomers of C_s symmetry

	$K_2(CO_2)$	$Cs_2(CO_2)$
R_1(C–O) (nm)	0.126	0.126
R_2(C–O) (nm)	0.138	0.138
Angle (O–C–O)	116°	116°
F_1(CO) (N/m)	7.483×10^2	7.392×10^2
F_2(CO) (N/m)	5.239×10^2	5.221×10^2
F(CO/CO) (N/m)	1.10×10^2	1.10×10^2
F(OCO) (Nm)	2.19×10^{-18}	2.19×10^{-18}
F(CO/OCO) (N)	0.95×10^{-8}	0.95×10^{-8}

[a] Frequencies are in cm^{-1}. [b] Values obtained from the refinement of the molecular geometry parameters and of the force constants.

isotopomers show no frequency splitting. Probably the doubling of the bands of the mixed isotopic species observed by Jacox *et al.* [1] was due to a matrix effect. The same effect was observed for $K(Sb^{16}O^{18}O)$ in a previous study [6] and any inequivalence was excluded.

Concerning the structure of the C_{2v} symmetry isomers $M_2(CO_2)$, the IR data indicate that the CO_2^{2-} anion has equal C–O bonds symmetrically interacting with the two metals. For these molecules both structure **I** and **II** shown in Fig. 3 are consistent with isotopic labelling and normal coordinate calculations. Probably structure **I** is favoured with respect to structure **II** because in the former the metal bridges both the oxygen and the carbon atoms and in this configuration the dianion still acts as a bidentate ligand. The structure of the C_s isomers was rationalized in terms of inequal C–O bonds. Regarding the position of the two metal atoms, one would expect a structure close to the W-shape model proposed for the C_{2v} isomers. If so, the metals asymmetrically bridge the oxygen and carbon atoms.

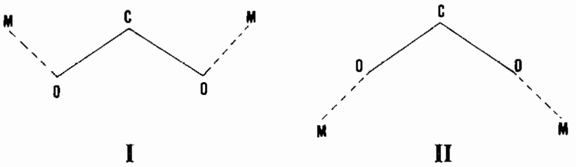

Fig. 3. Structure **I**, W-shape model proposed for C_{2v} $M_2(CO_2)$ molecules; structure **II**, alternative V-shape model for C_{2v} $M_2(CO_2)$ molecules.

Finally, $K(CO_3)$ [10], $K_2(CO_3)$ and $Cs_2(CO_3)$ [7] bands were observed in the course of this study. The carbonates are present in annealed matrices. Prolonged matrix annealing favours the formation of more complex aggregates $M_x(CO_2)$ where x is probably equal to three.

Acknowledgements

The authors gratefully acknowledge Professor G. Balducci for useful discussions and Dr L. Vitalini Sacconi for his kind assistance.

References

1 M. E. Jacox and D. E. Milligan, *Chem. Phys. Lett., 28,* 163 (1974).

2 R. Teghil, B. Janis and L. Bencivenni, *Inorg. Chim. Acta, 88,* 115 (1984).

3 K. O. Hartman and I. C. Hisatsune, *J. Chem. Phys., 44,* 1913 (1966).

4 J. E. Bennett, B. Mile and A. Thomas, *Trans. Faraday Soc., 61,* 2357 (1965).

5 Y. Yoshioka and K. D. Jordan, *Chem. Phys. Lett., 84,* 370 (1981).

6 L. Bencivenni and K. A. Gingerich, *J. Mol. Struct., 99,* 23 (1983).

7 J. S. Ogden and S. J. Williams, *J. Chem. Soc., Dalton Trans., 2,* 456 (1981).

8 G. Herzberg, 'Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra of Polyatomic Molecules', Van Nostrand, New York, 1945.

9 D. Green and K. M. Ervin, *J. Mol. Spectrosc., 88,* 51 (1981).

10 M. E. Jacox and D. E. Milligan, *J. Mol. Spectrosc., 52,* 363 (1974).