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Matrix-Isolation IR Studies on Alkali Metal M(XO_2) Species. Bonding and Structure of Li(CO_2), M(ClO_2) and M(BO_2) Molecules

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Li(CO_2) was produced by vaporizing Li_2CO_3. Li(CO_2) has a planar ring structure of C_{2v} symmetry with an OCO bond angle of ca. *124°. C_{2v} and C_s Li(CO_2) isomers were identified when atomic Li was allowed to react with CO_2 in Ar matrix at* ca. *12 K. The C_s isomer photolytically rearranges to the C_{2v} structure after prolonged exposure of the matrix to the Nernst glower IR source.*

Alkali metal chlorites and metaborates were studied in inert matrixes. The IR spectra of ^{18}O-enriched Cs(ClO_2) and of M(BO_2) molecules indicate that M(ClO_2) molecules are gaseous ion couples of C_{2v} symmetry while metaborates have C_s symmetry with linear BO_2^- group and M–O–B bond angles higher than 100°. This study reports for the first time an ^{18}O study for the observed interionic stretching frequencies.

Introduction

There is a considerable interest in the characterization of new molecular species found in high temperature vapours, particularly in the area of inorganic ion pairs such as alkali metal perrhenates [1, 2], arsenites and antimonites [3], sulphates [4, 5] and tungstates [5] because ternary oxyanion salts are important in high temperature vapour transport and corrosion phenomena. Further, such systems are of remarkable interest in theoretical chemistry for a better understanding of the concept of polytopic bonding [6].

Notwithstanding the amount of data collected for several systems, much work is still needed in the field of matrix-isolation IR spectroscopy of stable high temperature molecules and we are currently investigating species of type M(XO_2) for which mass-spectrometric and structural data are lacking or incomplete.

This paper reports the results of IR studies on Li(CO_2), alkali chlorites and metaborates, M(ClO_2) and M(BO_2) molecules. The study of Li(CO_2) and M(ClO_2) vapour species was undertaken to complete our earlier investigations on M(XO_2) molecules [3, 7, 8], and in order to obtain the molecular geometry parameters of the CO_2^- and ClO_2^- anions. Furthermore, it is considered important to extend previous IR studies on M(CO_2) complexes [9, 10] produced by allowing an alkali metal atom to react with CO_2 in a low-temperature Ar matrix.

Recent spin-restricted Hartree-Fock calculations [11] carried out on Li(CO_2) and Na(CO_2) complexes show that M(CO_2) complexes may exist as C_{2v} and C_s symmetry geometric isomers. **Ab initio** calculations predict the C_{2v} isomers to be more stable than the C_s ones and that interconversion energy from the C_s to the C_{2v} configuration is of 161.3 cm^{-1} and of 1612.8 cm^{-1} for Li(CO_2) and Na(CO_2) respectively. The available IR data [9, 10] suggest the presence of M(CO_2) complexes (M = Na, K and Cs) of C_s symmetry and this seems to be in contrast with the conclusions of the theoretical findings. In this work we report the existence of molecular Li(CO_2) obtained from the vaporization of Li_2CO_3 and from high temperature transport of lithium metal in CO_2-doped Ar atmosphere, or from the reaction of atomic lithium and CO_2 in an Ar matrix at *ca.* 12 K. In particular the production of Li(CO_2) from the vaporization of Li_2CO_3 completes an earlier matrix-isolation IR study on alkali metal carbonates which were found to exist in the vapour phase as $M_2(CO_3)$ species [12].

Regarding the M(BO_2) molecules (M = Li → Cs), we report the IR spectra of ^{18}O-enriched metaborates with the main aim of estimating the M–O–B bond angles.

Experimental

The matrix-isolation apparatus basically consists of a resistively heated evaporator for the production of high temperature vapours and of a cryostat (Displex CSA-202) for the matrix gas and effusing vapour deposition onto a polished copper surface maintained

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at *ca.* 12 K. The molecular source is a platinum liner placed inside an alumina holder surrounded by a tungsten coil. Li_2CO_3 was vaporized at *ca.* 1150 K from such an assembly. Alkali metal metaborates were vaporized over the temperature range 1170–1350 K from an alumina double oven, the top of which was kept at *ca.* 200 K warmer than the base of the evaporator. Alkali metal chlorites were heated at *ca.* 450 K in a quartz oven and the vapours were superheated at *ca.* 525 K. Experiments concerning Li/CO_2 reactions were carried out by heating lithium metal in a stainless steel oven at *ca.* 625 K.

Temperature above 1100 K was monitored by an optical pyrometer, and by an iron-constantan thermocouple for the measurements at lower temperatures. IR reflection spectra were recorded using Beckman IR-4260 and Perkin-Elmer 180 spectrometers. The spectrometers were calibrated against atmospheric H_2O vapour, CO_2 gas and the NH_3 bands. IR bands were measured using a spectral resolution of 0.5 cm^{-1} and a recording speed of 0.8 cm^{-1}/min. Frequencies above 400 cm^{-1} and below 400 cm^{-1} are reported accurate to within ±0.5 cm^{-1} and ±1 cm^{-1} respectively.

Argon and krypton (Matheson, 99.9995%) were used as matrix gases. Samples used in this study were commercially available, and isotopically enriched compounds were supplied by S.I.C.

The Characterization of $Li(CO_2)$

Figure 1 shows the IR matrix spectrum obtained from the vaporization of Li_2CO_3 heated at *ca.* 1100 K in a platinum cell. The bands observed in Ar matrix at 1570.0, 1330.1, 799.0 and 533.5 cm^{-1} were found to be the reproducible absorptions in all the adopted experimental conditions, including extensive diffusion at *ca.* 30 K and vapour depositions on less dilute matrixes. The latter experiments were for distinguishing monomer species from polymers. Evidently the bands at 1570.0, 1330.1, 799.0 and 533.5 cm^{-1} are vibrations of a new matrix-isolated species. These bands are not in the range of the modes expected for molecular $Li_2(CO_3)$ [13] and this fact indicates that contrary to the other alkali metal carbonates [12], the vaporization of Li_2CO_3 is accompanied by thermal decomposition which does not produce gaseous $Li_2(CO_3)$ species.

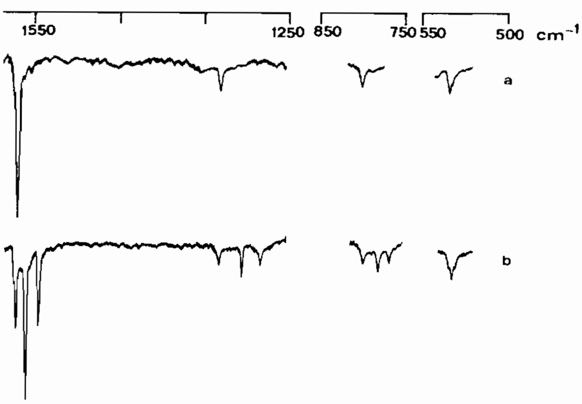


Fig. 1. (a) IR spectrum of $Li(CO_2)$ isolated in Ar matrix (12 K) and (b) of 50% ^{18}O-enriched $Li(CO_2)$.

Isotopic label experiments led to conclude that the molecule under examination is $Li(CO_2)$. $^{12}C/^{13}C$, $^{16}O/^{18}O$ and $^7Li/^6Li$ isotopic substitution experiments indicated that the bands at 1570.0, 1330.1 and 799.0 cm^{-1} are the vibrations of the CO_2^- group while the band at 533.5 cm^{-1} is one of the $Li-(CO_2)$ interionic modes. The summary of isotopic label experiments is given in Table I. Of particular interest is the IR spectrum shown in Fig. 1(b) corresponding to the pattern of a 50% ^{18}O-enriched $Li(CO_2)$ molecule. It is evident that the vibrations of the CO_2^- ion are present as 1:2:1 triplets at 1570.0–1557.5–1542.5 cm^{-1}, 1330.1–1304.0–1282.5 cm^{-1} and 799.0–782.7–766.2 cm^{-1}. This reflects the fact that the $Li(CO_2)$ species has two equivalent oxygen atoms.

The availability of isotopic frequencies made possible the vibrational assignment of the modes of $Li(CO_2)$ and it was also a valuable source of data for geometrical and force constant estimates. The use of the Teller-Redlich product rule [14] suggested that the bands at 1330.1, 799.0 and 533.5 cm^{-1} are A_1 symmetry modes of C_{2v} $Li(CO_2)$. In turn, the frequency 1570.0 cm^{-1} is the B_2 asymmetric stretching of the CO_2^- frame. The calculated and experimental Teller-Redlich ratios for the A_1 symmetry frequencies are reported in Table II. The conclusion of a C_{2v} symmetry structure is further consistent with normal coordinate calculations carried out using the force constants and the geometrical parameters reported in Table I.

The number of experimental frequencies of the various $Li(CO_2)$ isotopic species is large enough to derive an accurate force field consisting of eight selected force constants. Regarding the molecular geometry of $Li(CO_2)$, the OCO apex angle was determined by using the triatomic molecule approximation and the B_2 frequencies of the isotopic couples $^{12}C^{16}O_2^-/^{13}C^{16}O_2^-$ and $^{12}C^{16}O_2^-/^{12}C^{18}O_2^-$, and from this procedure an average value of 123.6° was obtained. The remaining geometrical parameters were firstly estimated and then optimized through cycles of normal coordinate calculations, repeated until the calculated isotopic frequencies were found to fit satisfactorily with the experimental ones. The agreement between the expected and measured isotopic frequencies of C_{2v} $Li(CO_2)$ is excellent, especially as anharmonicity corrections were not considered.

The study of $Li(CO_2)$ offers for the first time the opportunity of testing how much the vibrations of a coordinated oxyanion are coupled with the motions

TABLE I. Summary of the Matrix-Isolation IR Measurements (Ar, 12 K) on Li(CO$_2$) (C_{2v} symmetry).

A. Observed IR frequencies (cm^{-1}) of Li(CO$_2$) and its ^{13}C, ^{6}Li and ^{18}O labelled isotopomers

Li(CO$_2$)	Li(^{13}CO$_2$)	^{6}Li(CO$_2$)	Li(C^{18}O$_2$)	Assignment (C_{2v})	
1570.0	1529.5	1570.5	1542.5	B_2	ν(CO)
1330.1	1302.4	1328.5	1282.5	A_1	ν(CO)
799.0	789.4	799.0	766.2	A_1	δ(CO$_2$)
533.5	533.1	570.7	530.8	A_1	ν(Li–CO$_2$)

B. Measured ^{12}C/^{13}C, ^{7}Li/^{6}Li and ^{16}O/^{18}O frequency shifts[a] (cm^{-1})

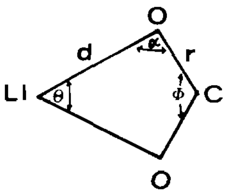
Vibration		^{12}C/^{13}C	^{7}Li/^{6}Li	^{16}O/^{18}O
B_2	ν(CO)	40.5	0.5	27.5
A_1	ν(CO)	27.7	1.6	47.6
A_1	δ(CO$_2$)	9.6	0.0	32.8
A_1	ν(Li–CO$_2$)	0.4	37.2	2.7

C. Observed and calculated IR frequencies (cm^{-1}) of 50% ^{18}O-enriched Li(CO$_2$)

Isotopomer	Obsd.	Calcd.[b]	Symmetry Species
Li(C^{16}O$_2$), C_{2v}	1570.0	1570.5	B_2
	1330.1	1330.0	A_1
	799.0	799.0	A_1
	533.5	533.5	A_1
Li(C^{16}O^{18}O), C_s	1557.5	1557.7	A'
	1304.0	1304.2	A'
	782.7	782.7	A'
	531.8	532.0	A'
Li(C^{18}O$_2$), C_{2v}	1542.5	1542.0	B_2
	1282.5	1283.8	A_1
	766.2	765.9	A_1
	530.8	530.7	A_1

[a] Measured shifts are calculated with respect to Li(CO$_2$).

[b] Structure and internal coordinate definition



r = 1.25 Å, d = 1.93 Å, ϕ = 123.6°, θ = 70°

Force constants used for normal coordinate calculations: f_r = 9.070, f_{rr} = 1.551, f_d = 0.450, f_{dd} = 0.050 (mdyn/Å); f_ϕ = 1.770, f_θ = 0.707, f_α = 0.338 (mdyn·Å), $f_{r\phi}$ = 0.729 (mdyn).

of the metal. It was evident from previous studies [*e.g.*, 15] that interionic mode coupling is small for gaseous ion pairs and that the vibrations of the anion are practically autonomous from those involving the metal cation. This observation was confirmed by measurements of the shifts of the CO$_2^-$ frequencies due to ^{6}Li substitution on molecular Li(CO$_2$) (see Table I). In fact, the CO$_2^-$ frequencies are unshifted on passing from Li(CO$_2$) to ^{6}Li(CO$_2$). Normal coordinate calculations predicted the asymmetric B_2 Li–CO$_2$ interionic frequency at 400 cm^{-1}; however no band was observed around that frequency.

Finally, our conclusion regarding the shape and the geometry of C_{2v} Li(CO$_2$) is in agreement with the

TABLE II. Experimental and Calculated Teller-Redlich Product Rule for the Ratios of A_1 Symmetry Frequencies of $Li(CO_2)$ (C_{2v} isotopomers).

Isotopic Couples	Exptl.	Calcd.
$Li(CO_2)/Li(^{13}CO_2)$	0.9682	0.9701
$Li(CO_2)/^6Li(CO_2)$	0.9352	0.9350
$Li(CO_2)/Li(C^{18}O_2)$	0.9204	0.9231

results of S.C.F. Hartree-Fock computations [11] indicating the existence of stable $Li(CO_2)$ species. In particular, the spectroscopic value for the OCO bond angle (123.6°) supports the predicted one (124.5°) [11]. It is interesting to note that the value of 123.6° increases to 125.8° if anharmonic corrections are considered [14].

Ab initio calculations predict the possibility of C_{2v} and C_s symmetry isomers for $Li(CO_2)$ with stabilization energy of 0.85 and 0.83 eV respectively. From our experiments we conclude that C_{2v} $Li(CO_2)$ is the species produced from the vaporization of Li_2CO_3. Probably the C_s symmetry isomer if present in the vapor phase, might not be stabilized in an Ar matrix at *ca.* 12 K.

As far as we are aware, $M^+{-}CO_2^-$ complexes (M = Na, K, Cs) were identified in Ar matrix at 14 K as result of CO_2 activation by alkali metals [10]. The IR spectra of the reaction products suggested the presence of C_s $M^+{-}CO_2^-$ ion couples. This result is however only in partial agreement with the computations performed by Yoshioka and Jordan [11]. In fact, S.C.F. Hartree-Fock calculations would not exclude C_{2v} $M^+{-}CO_2^-$ complexes. As a first attempt of solving such discrepancy it was decided to extend Jacox and Milligan's study [10] to the Li/CO_2 system, in order to explore the possibility of identifying both the C_{2v} and C_s isomer of $Li(CO_2)$.

When a gaseous mixture of Ar and CO_2 was passed through lithium metal heated at *ca.* 620 K and the gaseous beam was condensed at *ca.* 12 K, the IR spectrum showed several absorptions. Among them bands at 1570.0, 1330.1, 799.0 and 533.5 cm^{-1} are the absorptions of C_{2v} $Li(CO_2)$, while the frequencies at 1751.0, 1221.5, 739.5 and 599.5 cm^{-1} (see Fig. 2(a)) are bands of a different species which was found to exhibit $^{12}C/^{13}C$, $^{16}O/^{18}O$ and $^7Li/^6Li$ isotopic shifts. The summary of these experiments is given in Table III. Further, when lithium was allowed to react with a mixture of $C^{16}O_2/C^{16}O^{18}O/C^{18}O_2$, the bands at 1751.0, 1221.5 and 739.5 cm^{-1} produced a series of quartets with typical intensity ratios of 1:1:1:1 (see Fig. 2(b)). This fact suggested the presence of a species with two non-equivalent oxygen atoms. Evidently this species is the C_s symmetry isomer. The measured frequencies of C_s $Li(CO_2)$ and its isotopomers were successfully calculated on the basis of the force constants listed in Table III and of the geometrical parameters derived for the C_s isomer by Yoshioka and Jordan [11].

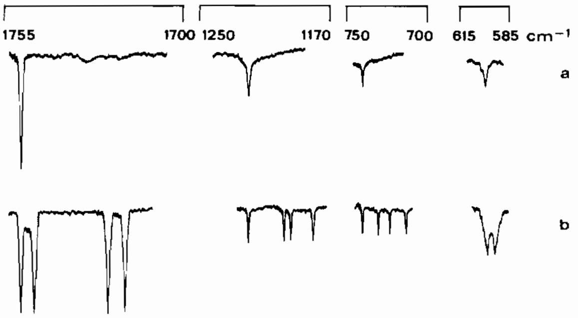


Fig. 2. (a) Portion of the IR spectrum (Ar, 12 K) showing the bands of C_s $Li(CO_2)$ observed from transport of atomic Li vapour with Ar (CO_2) (estimated vapour composition of Li: CO_2 = 1:1 at 625 K). (b) Portion of the IR spectrum showing the effect of 50% ^{18}O-substitution on the bands of C_s $Li(CO_2)$.

The two geometrical isomers were also obtained by trapping lithium vapours onto an Ar matrix doped with CO_2. In these conditions additional absorptions were observed, along with the features of C_{2v} and C_s $Li(CO_2)$. The new bands were observed at 1969.2, 1662.5, 1448, 1316, 1160, 984, 806 and 498 cm^{-1}. These bands of variable intensity are likely to be due to polymers of the type $Li_x(CO_2)_y$, and their appearance in the spectra was checked to be also dependent on the Li *vs.* CO_2 ratio. Usually this ratio was conveniently fixed at *ca.* 1 but in some of the experiments was deliberately increased or decreased. Evidently a series of reaction takes place in the Ar matrix, and $Li(CO_2)$ molecules can easily react with Li atoms and/or CO_2 to produce possible species of type $Li_2(CO_2)$, $Li_2(CO_2)_2$ and even more complex aggregates.

A further remarkable result of condensation experiments of atomic lithium vapours in $Ar(CO_2)$ atmospheres is that prolonged exposure of the matrix to the Nernst glower IR source causes photolytical rearrangement of C_s $Li(CO_2)$ to the C_{2v} isomer. This suggests that the C_s isomer is an intermediate product of the reaction between Li(g) and CO_2, and it is likely to be metastable species.

Alkali Metal Chlorites

The matrix-isolation spectra obtained from the vaporization of alkali metal chlorites heated between 460 K and 440 K produces a series of bands in the range of the ν_1, ν_2 and ν_3 models of the ClO_2^- anion [16], typically at 790, 400 and 840 cm^{-1}. These bands were found to be cation dependent and show the characteristic Cl isotope effect consisting of

TABLE III. Summary of the Vibrational Study on C_s Li(CO$_2$) Isolated in Ar Matrix (12 K).

A. Observed IR frequencies (cm^{-1}) of C_s Li(CO$_2$) and its $^{12}C/^{13}C$, $^7Li/^6Li$ and $^{16}O/^{18}O$ labelled isotopomers

Li(CO$_2$)	Li(^{13}CO$_2$)	^{6}Li(CO$_2$)	Li(C^{18}O$_2$)	Assignment (C_s)	
1751.0	1707.1	1751.4	1718.0	A′	ν(C=O)
1221.5	1204.1	1222.0	1180.0	A′	ν(C–O)
739.5	730.0	745.5	713.1	A′	δ (OCO)
599.5	596.7	633.5	593.5	A′	ν(Li–O)

B. Measured $^{12}C/^{13}C$, $^7Li/^6Li$ and $^{16}O/^{18}O$ frequency shifts[a] (cm^{-1})

		$^{12}C/^{13}C$	$^7Li/^6Li$	$^{16}O/^{18}O$
A′	ν(C=O)	43.9	0.4	33.0
A′	ν(C–O)	17.4	0.5	41.5
A′	δ (OCO)	9.5	6.0	26.4
A′	ν(Li–O)	2.8	34.0	6.0

C. Observed and calculated IR frequencies (cm^{-1}) of 50% ^{18}O-enriched C_s Li(CO$_2$)

Isotopomers	Obsd.	Calcd.[b]	Symmetry species
Li(C^{16}O$_2$) C_s	1751.0	1751.4	A′
	1221.5	1219.5	A′
	739.5	739.5	A′
	599.5	599.1	A′
Li(^{16}OC^{18}O) C_s	1723.0	1724.2	A′
	1198.7	1202.0	A′
	730.5	730.8	A′
	597.0	597.5	A′
Li(^{18}OC^{16}O) C_s	1746.0	1745.9	A′
	1193.1	1193.5	A′
	722.7	723.0	A′
	593.8	594.0	A′
Li(C^{18}O$_2$) C_s	1718.0	1717.7	A′
	1180.0	1177.7	A′
	713.1	713.9	A′
	593.5	592.6	A′

[a] Measured shifts are calculated with respect to Li(CO$_2$). [b] Calculated from the following force constants: $f_R = 12.022$, $f_r = 9.318$, $f_d = 1.459$, $f_{Rr} = 2.087$, $f_{rd} = 1.367$, $f_{Rd} = 1.286$ (mdyn/Å); $f_\phi = 1.120$; $f_\theta = 0.290$; $f_{\phi\alpha} = -0.158$ (mdyn·Å); $f_{r\phi} = 0.888$, $f_{d\phi} = 0.040$ (mdyn). Structural parameters taken from Ref. [11]. (R, r, d, ϕ, θ and α are the C=O, C–O, Li–O, O–C–O, C–O–Li and O–Li–O bond distances and angles respectively).

doublets, the components of which are in the intensity ratio of 1:3. Table IV summarizes the bands which according to ^{18}O-substitution experiments were assigned to C_{2v} M(ClO$_2$) vapour species. Other bands occurring with variable intensity were identified as ClO$_2$ (1104.7, 947.9 and 451.1 cm^{-1}) [16], and polymeric species the presence of which was practically eliminated by superheating the effusing vapours at *ca.* 525 K.

The presence of ClO$_2$, even if in small concentration, indicates that alkali chlorites undergo partial thermal decomposition. In our experimental conditions it was observed that tendency towards decomposition decreases on passing from LiClO$_2$ to CsClO$_2$. For this reason, ^{18}O-substitution experiments were carried out on Cs^{35}ClO$_2$. Figure 3 shows the IR spectra of Cs(ClO$_2$) (Cl natural abundance) and of ^{18}O-enriched Cs(^{35}ClO$_2$) (50% ^{18}O) in the regions of the ν_1, ν_2 and ν_3 modes of the ClO$_2^-$ anion. It is evident that the three vibrations of the chlorite group (823.5, 789.9 and 418.2 cm^{-1}) in the molecular species Cs(ClO$_2$) are present as 1:2:1 triplets,

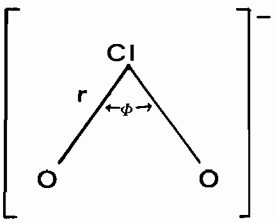
TABLE IV. Summary of the Matrix IR Studies on C_{2v} Alkali Metal Chlorites (Ar, 12 K)[a].

$Li(ClO_2)$	$Na(ClO_2)$	$K(ClO_2)$	$Rb(ClO_2)$	$Cs(ClO_2)$	Assignment
819.5	831.0	824.5	824.6	823.5	B_2 ν ^{35}ClO
811.4	823.0	815.8	816.7	815.3	^{37}ClO
786.6	795.1	789.1	790.6	789.9	A_1 ν ^{35}ClO
779.5	789.9	783.1	783.9	783.7	^{37}ClO
–	401[b]	440[b]	426.8	418.2	A_1 δ ^{35}ClO
408.5					A_1 ν $^{7}Li–ClO_2$
428.7					$^{6}Li–ClO_2$

Observed and theoretical IR frequencies[a] of ^{18}O-enriched Cs ($^{35}ClO_2$)

Observed	Calculated[c]	Assignment
823.5	823.5	(B_2) $^{35}Cl^{16}O_2^-$, C_{2v}
814.5	814.6	(A') $^{35}Cl^{16}O^{18}O^-$, C_s
793.9	794.3	(B_2) $^{35}Cl^{18}O_2^-$, C_{2v}
789.9	789.9	(A_1) $^{35}Cl^{16}O_2^-$, C_{2v}
768.5	768.2	(A') $^{35}Cl^{16}O^{18}O^-$, C_s
757.5	757.8	(A_1) $^{35}Cl^{18}O_2^-$, C_{2v}
418.2	418.2	(A_1) $^{35}Cl^{16}O_2^-$, C_{2v}
408.7	408.6	(A') $^{35}Cl^{16}O^{18}O^-$, C_s
390[b]	398.9	(A_1) $^{35}Cl^{18}O_2^-$, C_{2v}

[a] Frequencies are in cm^{-1}. [b] Frequency accurate within ±1 cm^{-1}. [c] Internal coordinate definition, structural parameters and force constants:



$r(ClO) = 1.57$ Å, $\phi = 108°$, $f_r = 4.205$, $f_{rr} = 0.207$ (mdyn/Å),
$f_\phi = 1.42$ (mdyn·Å), $f_{r\phi} = 0.105$ (mdyn).

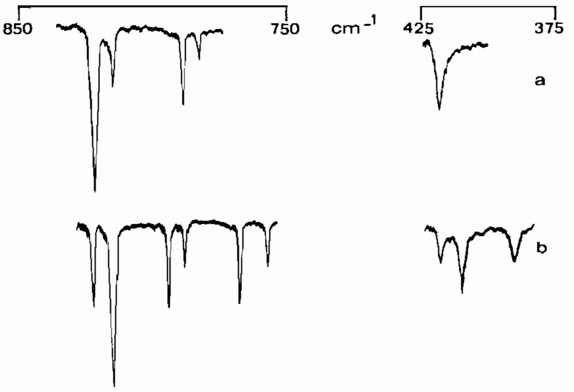


Fig. 3. (a) IR spectrum of $Cs(ClO_2)$ isolated in Ar matrix (12 K) (spectrum observed from superheater condition). (b) Observed IR pattern of ^{18}O-enriched $Cs(^{35}ClO_2)$ (50% ^{18}O-atom).

indicative of a ClO_2^- anion with two equivalent oxygen atoms. Evidently the ClO_2^- anion is acting as a bidentate ligand. The IR spectrum of Fig. 3(b) was satisfactorily interpreted assuming for $Cs(ClO_2)$ a planar ring structure of C_{2v} symmetry.

Normal coordinate calculations were of aid for assigning the measured ^{18}O isotope shifts of the C_{2v} and C_s isotopomers of ^{18}O-enriched $Cs(ClO_2)$. The observed frequencies of $Cs(Cl^{16}O_2)$ were fitted using as force constants $f_r = 4.205$, $f_{rr} = 0.207$ (mdyn/Å), $f_\phi = 1.42$ (mdyn·Å) and $f_{r\phi} = 0.105$ (mdyn), a Cl–O bond distance of 1.57 Å and the O–Cl–O bond angle equal to 108°. The last value was estimated from the $^{35}Cl/^{37}Cl$ isotopic shift of the B_2 mode of ClO_2^-, assuming the triatomic molecule approximation [14]. The observed and predicted frequencies of the three $^{16}O/^{18}O$ isotopomers of C_{2v} $Cs(ClO_2)$ are reported for a comparison in Table IV. The agreement between

TABLE V. Observed IR Frequencies (cm^{-1}) of Matrix Isolated (Ar, 12 K) Alkali Metal Metaborates[a].

$Li(BO_2)$	$Na(BO_2)$	$K(BO_2)$	$Rb(BO_2)$	$Cs(BO_2)$	Assignment (C_s)
1975.8	1960.0	1951.8	1951.2	1945.6	A′ ν $^{11}B{=}O$
2046.7	2032.0	2023.0	2021[b]	2017.5	$^{10}B{=}O$
1094.2	1087.0	1081.5	1080.4	1076.9	A′ ν $^{11}B{-}O$
1106.6	1096.4	1089.0	1087[b]	1083[b]	$^{10}B{-}O$
577.5	577[b]	581.0	582[b]	581[b]	A″ γ $^{11}BO_2$
592[b]	596[b]	602.5	603[b]	602[b]	$^{10}BO_2$
568.6	572.9	576.5	577.0	576.5	A′ δ $^{11}BO_2$
589[b]	594[b]	597[b]	597.5	596[b]	$^{10}BO_2$
470[c]	363[c]	265[c]	226[c]	207[c]	A′ $\nu(MO)$; $\nu(^7LiO)$
496[c]					A′ ν (^6LiO)

[a] $M(BO_2)$ molecules. ^{11}B and ^{10}B naturally occurring isotopes (^{11}B = 81.2% and ^{10}B = 18.8%). For $Li(BO_2)$, ^7Li = 92.9% and ^6Li = 7.4% isotopic abundances. [b] Frequency accurate within ±1 cm^{-1}. [c] Krypton matrix measurements (matrix temperature *ca.* 12 K and frequencies accurate within ±1 cm^{-1}).

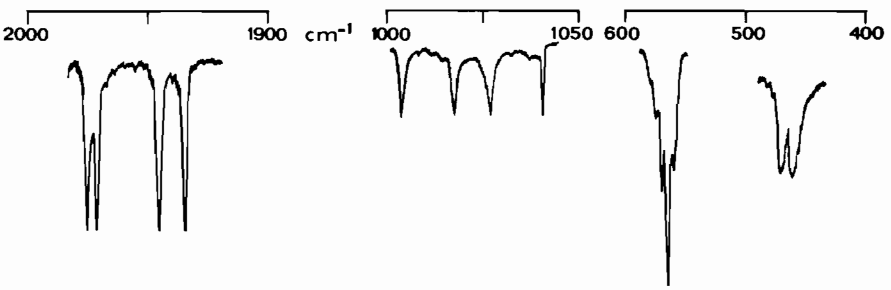


Fig. 4. IR spectrum of ^{18}O-enriched $^7Li(^{11}BO_2)$ (Ar, 12 K). (Ar matrix from 2000 cm^{-1} to 500 cm^{-1} and Kr below 500 cm^{-1}).

expected and experimental frequencies confirms the correctness of the adopted C_{2v} symmetry model for $Cs(ClO_2)$.

(III) Alkali Metal Metaborates

With respect to the earlier matrix IR spectroscopy work on metaborates [17], the present study accomplished some conclusions regarding the shape of gaseous $M(BO_2)$ species with particular reference to the M–O–B bond angle estimates. Our IR measurements (see Table V) on matrix-isolated $M(BO_2)$ molecules agree within experimental error with the results of ref. [17]. In order to reach definitive information on the structure of these molecules, ^{18}O-substitution experiments were carried out on ^{18}O-enriched $M(^{11}BO_2)$ molecules (M = Li, Na, K, Rb, Cs). As expected for C_s symmetry species [17], the fact that the two oxygen atoms of the BO_2^- group are not equivalent is inferred by the series of quartets in correspondence of the isotopic modes of the $(^{11}B^{16}O_2)^-/(^{11}B^{16}O^{18}O^*)^-/(^{11}B^{18}O^{16}O^*)^-/(B^{18}O_2)^-$ groups (O* stands for terminal O atom). Further, the observed M–O stretching modes appear as 1:1 intensity ratio doublets related to the $M{-}^{16}O$ and $M{-}^{18}O$ vibrations.

Figure 4 shows the IR spectrum of 50% ^{18}O-enriched $^7Li^{11}BO_2$. This molecule was purposely chosen for the discussion of the ^{18}O-isotope pattern of a C_s symmetry $M(BO_2)$ molecule; the observed frequencies of ^{18}O-enriched ^{11}B-metaborates are reported in Table VI. From Fig. 4 it is clear that the BO_2^- group stretching frequencies, 1975.8 and 1094.2, and the ^7Li–O frequency at 470.5 cm^{-1} are present as quartets (1975.8–1972.2–1946.6–1938.8 cm^{-1} and 1094.2–1072.9–1056.6–1032.0 cm^{-1}) and doublets (469–462 cm^{-1}) respectively. Each line of the latter doublet is expected to appear as a doublet as a consequence of ^{18}O-labelling but the separation between the split components is calculated to be so small that there is no chance of successful resolution. The ^{18}O-isotope pattern of the in-plane (568.9 cm^{-1}) and out-of-plane (577.5 cm^{-1}) BO_2^- deformations produces a somewhat complex cluster of lines, because these vibrations have close-lying frequencies and band overlap frequently occurs.

TABLE VI. Observed and Calculated Isotopic Frequencies of ^{18}O-enriched $M(^{11}BO_2)$ Molecules (Ar, 12 K).

$^{7}Li(^{11}BO_2)$		$Na(^{11}BO_2)$		$K(^{11}BO_2)$		$Rb(^{11}BO_2)$		$Cs(^{11}BO_2)$		Assignment
Obsd.	Calcd.^{a}	Obsd.	Calcd.^{a}	Obsd.	Calcd.^{a}	Obsd.	Calcd.^{a}	Obsd.	Calcd.^{a}	
1975.8	1975.8	1960.0	1960.1	1951.8	1951.8	1951.2	1951.2	1945.6	1945.6	$M(^{11}B^{16}O_2)$
1972.2	1971.8	1957.7	1957.2	1948.0	1949.0	1947.7	1948.4	1942.5	1943.1	$M(^{11}B^{18}O^{16}O)$
1946.6	1945.4	1929.5	1930.2	1920.0	1921.9	1921.8	1921.0	1916.0	1915.3	$M(^{11}B^{16}O^{18}O)$
1938.8	1941.9	1924.0	1926.8	1916.0	1918.6	1915.1	1917.8	1910.0	1912.3	$M(^{11}B^{18}O_2)$
1094.2	1094.2	1087.0	1087.0	1081.5	1081.5	1080.4	1080.4	1076.6	1076.9	$M(^{11}B^{16}O_2)$
1072.9	1071.8	1063.3	1064.7	1058.0	1059.3	1056.0	1058.4	1054.0	1055.6	$M(^{11}B^{16}O^{18}O)$
1056.6	1057.1	1051.9	1049.8	1046.0	1044.6	1045.0	1043.3	1041.0	1039.6	$M(^{11}B^{18}O^{16}O)$
1032.0	1034.6	1025.0	1027.6	1020.0	1022.4	1019.5	1021.4	1017.5	1018.2	$M(^{11}B^{18}O_2)$
577.5	577.5	577^{b}	577.0	581^{b}	581.0	582^{b}	582.0	581^{b}	581.0	$M(^{11}B^{16}O_2)$
573.5	573.9	572.5	572.8	577^{b}	577.2	576.5	576.9	577^{b}	577.9	$M(^{11}B^{18}O^{16}O)$
	572.9		572.7		576.5		576.9		577.8	$M(^{11}B^{16}O^{18}O)$
568.9	569.2		572.1		576.5		576.9	576^{b}	576.4	$M(^{11}B^{18}O_2)$
	568.6	568.5	569.0	573^{b}	572.7	573^{b}	572.9	573^{b}	573.7	$M(^{11}B^{16}O_2)$
564.5	564.8		568.4		572.7		572.7	571^{b}	572.3	$M(^{11}B^{16}O^{18}O)$
	564.1		568.2		572.0		572.7		572.3	$M(^{11}B^{18}O^{16}O)$
559^{b}	560.3	565^{b}	564.6	567^{b}	568.2	568^{b}	568.6	567^{b}	568.1	$M(^{11}B^{18}O_2)$
470^{c}	470.5	363^{c}	363.5	265^{c}	264.9	226^{c}	225.4	207^{c}	206.6	$M(^{11}B^{16}O_2)$
	470.4		363.5		264.8		225.2		205.7	$M(^{11}B^{16}O^{18}O)$
462^{c}	462.6	352^{c}	351.9	253^{c}	254.4	214^{c}	215.2	199^{c}	197.9	$M(^{11}B^{18}O^{16}O)$
	462.5		351.8		254.3		214.9		197.0	$M(^{11}B^{18}O_2)$

[a] Structural parameters and force constants used for normal coordinate calculations are reported in Table VII. [b] Frequencies accurate within ±1 cm^{-1}. [c] Kr matrix measurements at 12 K. Frequencies accurate within ±1 cm^{-1}.

TABLE VII. Molecular Constants[a] Estimated for the M(BO_2) Molecules.

	Li(BO_2)	Na(BO_2)	K(BO_2)	Rb(BO_2)	Cs(BO_2)
R(B=O) (Å)	1.2	1.2	1.2	1.2(5)	1.3
r(B–O) (Å)	1.3	1.3	1.3	1.2(5);	1.2
d(M–O) (Å)	1.8	2.14	2.4	2.6	2.7
(M–O–B) (deg.)	100°	106°	100°	113°	127°
f_R[b]	14.096	13.943	13.857	13.873	13.864
f_r[b]	7.800	7.654	7.583	7.538	7.406
f_{rR}[b]	1.955	1.955	1.956	1.957	1.957
f_d[b]	0.639	0.758	0.476	0.437	0.462
f_{dr}[b]	0.015	0.015	0.015	0.015	0.015
f_θ[c]	0.597	0.616	0.634	0.627	0.626
f_γ[c]	0.653	0.624	0.644	0.638	0.636
$f_{R\theta}$[d]	0.03	0.03	0.03	0.03	0.03
$f_{r\theta}$[d]	0.02	0.02	0.02	0.02	0.02

[a] R, r and d stand for the B=O, B–O and M–O stretching internal coordinates, θ and γ are the BO_2^- group in-plane and out-of-plane deformation internal coordinates. [b] (mdyn/Å). [c] (mdyn·Å). [d] (mdyn).

The plethora of frequency offered the opportunity of computing the force constants and in particular the availability of the M–^{16}O and M–^{18}O stretching frequencies made possible to estimate the values of the M–O–B bond angles. For this purpose, several cycles of normal coordinate calculations were performed assuming different sets of bond distances and angles; trial and error F, G matrix calculations [18] were repeated until calculated and observed frequencies were satisfactorily fitted. It must be mentioned that the experimental and calculated isotopic stretching frequencies differ up to *ca.* 3 cm^{-1} and this evidently reflects the fact that the stretching vibrations of the metaborates are not harmonic. Normal coordinate calculations showed that the choice of the interatomic bond lengths is not—within reasonable limits—crucial, while a difference higher than ±5° with respect to the more likely value of the M–O–B bond angle produces a less satisfactory agreement between experimental and theoretical frequencies of the ^{18}O isotopomers.

The estimated structural parameters and the force constants of alkali metaborates are summarized in Table VII. Spectroscopic estimates of the M–O–B bond angles compare well with the electron diffraction results on gaseous Rb(BO_2) [19] and Cs(BO_2) [19, 20].

Conclusion

The conclusions accomplished from this study can be summarized as follows:

a) C_{2v} Li(CO_2) is present in the vapours above heated Li_2CO_3, the vaporization of which occurs with decomposition.

b) The C_{2v} and C_s isomers of Li(CO_2) are present when CO_2 reacts with lithium vapours. It would be interesting to establish whether the two isomers are formed in the gas phase by collision of Li(g) with CO_2 or in the solid phase by activation of CO_2 by Li metal. Whatever the reaction mechanism the C_s isomer is an intermediate product photolytically convertible into the most stable configuration.

c) ^{18}O-substitution experiments on Cs(ClO_2) establish a planar ring structure of C_{2v} symmetry for the M(ClO_2) molecules. This study completes our former matrix-isolation investigations on coordinated ClO_4^- and ClO_3^- oxyanions [21, 22].

d) The M–O–B bond angles estimated for the M(BO_2) species appear to be reliable values in agreement with earlier electron-diffraction studies on Rb(BO_2) [19] and Cs(BO_2) [19, 20]. A reasonable uncertainty to be associated with our bond angle estimates is probably no larger than 5°.

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