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Infrared and Raman Study of Matrix Isolated M(SO_2) Molecules. The Structure of the Molecular Ion SO_2^-

L. BENCIVENNI, F. RAMONDO, R. TEGHIL

Dipartimento di Chimica, Università degli Studi di Roma, I-00185 Rome, Italy

and M. PELINO

Dipartimento di Chimica, Ingegneria Chimica e Materiali, Università di L'Aquila, I-67100, Italy

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Abstract

The IR and Raman spectra of Cs(SO_2), K(SO_2) and Na(SO_2) molecules were studied by $^{32}S/^{34}S$ and $^{16}O/^{18}O$ isotopic substitution technique. These molecules have a planar ring configuration of C_{2v} symmetry with the O–S–O angle equal to 109° ± 5° and the S–O bond length of 0.149 ± 0.001 nm. The alkali metal atom interacts symmetrically with the oxygen atoms of the SO_2^- group. The doubling observed for the vibrations of Cs($S^{16}O^{18}O$) was attributed to a matrix effect.

Introduction

The interaction of alkali metal atoms with molecules such as CO_2, ClO_2 and O_2 was the subject of studies turned to characterize the molecular anions CO_2^- [1], ClO_2^- [2] and O_2^- [3] by means of vibrational spectroscopy. These anions are produced in low temperature matrices through a process involving electron transfer from a metal, usually an alkali atom, to the neutral molecule. The geometry of the CO_2^- anion formed in inert matrices from the reaction of lithium [1] and alkali metal atoms [4, 5] has been the subject of IR studies. The anion was identified by means of matrix isolation spectroscopy and the geometry of this group in the M(CO_2) molecules was established using ^{13}C and ^{18}O isotopic enrichment method. For these molecules, as well as for the M(AsO_2) and M(SbO_2) [6] and M(PO_2) [7, 8] systems, the rhombic ring structure of C_{2v} symmetry was proposed as the most stable configuration. As part of our systematic investigation of the structure of stable oxyanions coordinated by alkali metals, we report in the present study the IR and Raman investigation of the SO_2^- molecular ion produced in argon matrix by interaction with some alkali metals.

Experimental

The details of the experimental apparatus, sample deposition device and cryogenic equipment have already been covered elsewhere [1]. The beam of alkali metals was produced by vaporizing cesium at 320 K, potassium at 500 K and sodium at 550 K. The metal vapour was codeposited with argon gas onto a copper block kept at the temperature of 12 K. The usual M:SO_2:Ar molar ratio was approximately equal to 1:1:2000. In the experiment performed with ^{34}S and ^{18}O isotopes, gaseous mixtures of 45% ^{34}S-enriched SO_2 and 50% ^{18}O-enriched SO_2 were employed. The IR and Raman spectra were measured using a Perkin Elmer 580-B and an Ar laser Cary Raman spectrophotometer respectively. IR frequencies reported in this study are accurate within 0.5 cm^{-1}. The accuracy of the Raman shifts is of ±1 cm^{-1}.

Results and Discussion

The condensation of atomic cesium vapours with molecular SO_2 diluted in a large excess of argon (Cs:SO_2:Ar 1:1:2000) on the surface of a reflecting copper block maintained at the temperature of 12 K yielded the IR spectrum shown in Fig. 1a. The spectrum consists of the well known absorptions of matrix-isolated SO_2 [9, 10] and of three reproducible peaks at 1041.9, 985.1 and 495.5 cm^{-1}. The Raman spectrum obtained for the same codeposition experiment shows a band at 985 cm^{-1}. This band correlates well with the IR counter part at 985.1 cm^{-1}. The condensation of potassium and sodium with SO_2 in argon matrices at 12 K (M:SO_2:Ar 1:1:2000) produces analogous results. The summary of the new observed main bands is given in Table I.

In order to assign the measured frequencies to the vibrations of a molecular species, codeposition experiments were carried out employing $^{34}SO_2$ and $S^{18}O_2$.

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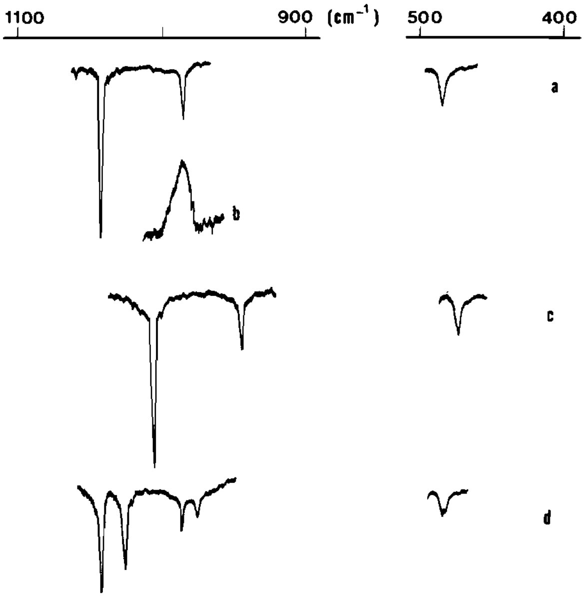

Fig. 1. (a) IR spectrum of Cs(SO_2), (b) Raman spectrum of Cs(SO_2), (c) IR spectrum of Cs($S^{18}O_2$) and (d) IR spectrum of 45% ^{34}S-enriched Cs(SO_2).

TABLE I. IR and Raman* Frequencies (cm^{-1}) Observed from the Codeposition Experiments of Na, K and Cs with: (a) SO_2, (b) 55% SO_2 + 45% $^{34}SO_2$ and (c) 50% SO_2 + 50% $S^{18}O_2$. Argon Matrix Measurements at 12 K

Na	K	Cs
(a) + SO_2		
1041.2; 1042*	1041.4; 1042*	1041.9; 1043*
984.8	984.7	985.1
495.0	495.0	495.5
(b) + $SO_2/^{34}SO_2$		
1041.2	1041.4	1041.9
1028.7	1029.0	1029.6
984.8	984.7	985.1
976.1	976.0	976.5
495.0	495.0	495.5
492.0	492.1	492.6
(c) + $SO_2/S^{18}O_2$		
1041.2	1041.4	1041.9
1005.8	1005.9	1006.6
984.8	984.7	985.1
945.0	945.3	945.3
495.0	495.0	495.5
472.5	472.3	473.0

In Table I, the IR absorptions relative to these experiments are reported. In Fig. 1b and 1c the spectra obtained after codeposition of cesium with $^{34}SO_2$ and $S^{18}O_2$ respectively, are shown. They consist of bands due to the interaction of $SO_2/^{34}SO_2$ and $SO_2/S^{18}O_2$ with the alkali metal atom. The spectra also show the $^{32}S/^{34}S$ and $^{16}O/^{18}O$ isotope frequency shifts. These observations lead to assigning the bands occurring at *ca.* 1042, 985 and 495 cm^{-1} as the $\nu_3(B_2)$, $\nu_1(A_1)$ and $\nu_2(A_1)$ modes of the bent anion SO_2^- interacting with the alkali metal cation. The apex angle of SO_2^-, 2θ, was evaluated on the grounds of the triatomic molecule approximation [11] employing the ν_3 frequencies of the isotopic couples $^{32}S^{16}O_2^-/^{34}S^{16}O_2^-$ and $^{32}S^{16}O_2^-/^{32}S^{18}O_2^-$. The values of 110.4° and 108.1° were obtained for the O–S–O bond angle in the Cs(SO_2) molecule. The average of the two values, 109.2°, was taken as the selected bond angle of the SO_2^- anion. The molecular geometry and the best set of force constants were determined on the basis of normal coordinate calculations employing the experimental frequencies of C_{2v} symmetry SO_2^-, $^{34}SO_2^-$ and $S^{18}O_2^-$. The vibrational force field of the anion was described using f_r, f_θ, f_{rr} and $f_{r\theta}$ as force constants. The results of normal coordinate calculations are reported in Table II. In this Table, under the heading 'calc.I' the frequencies obtained using 0.149 nm as S–O bond length and 109.2° as O–S–O bond angle are listed. In the same Table under the heading 'calc.II' and 'calc.III' the frequencies calculated using the values 104° and 114° respectively as SO_2^- bond angle are reported. The latter calculations were performed with the aim of testing the influence of the bond angle on the values of the experimental isotopic frequencies. For this purpose the bond angle was varied within ±5° with respect to the average value (109.2°). The best agreement between the experimental and calculated isotopic frequencies was obtained employing $2\theta = 109.2°$. Table II also reports the expected and the experimental Redlich–Teller ratio values [11] for the B_2 and A_1 modes of SO_2^-.

Figure 2a shows the IR spectrum observed when atomic cesium was codeposited with a gaseous mixture containing SO_2, $S^{16}O^{18}O$ and $S^{18}O_2$ in the relative ratio of 1:2:1. The bands previously assigned to the vibrations of SO_2^- in molecular Cs(SO_2), namely 1041.9, 985.1 and 495.5 cm^{-1}, are present in this spectrum together with the bands of $S^{18}O_2^-$ (1006.6, 945.3 and 473.0 cm^{-1}) and with the bands due to the mixed isotopomer $S^{16}O^{18}O^-$ (1028.2–1030.6, 958.7–960.7 and 484.0 cm^{-1}). The measured IR frequencies of ^{18}O-enriched SO_2^- isotopomer of the molecular species Cs(SO_2) are reported in Table III. ^{18}O-enrichment produces three isotopic species with statistical weight of 1:2:1 for a C_{2v} symmetry molecule. The doubling of the two stretching modes of the mixed isotopomer could suggest an inequivalence of the S–O bonds, that is a distortion from C_{2v} symmetry (see Fig. 3a). The possible occurrence of the distortion was tested by means of normal coordinate calculations on the bent ion SO_2^- with different S–O bonds, r_1 and r_2. This type of model (see Fig. 3b) requires a more complex

TABLE II. Calculated Frequencies[a] (cm^{-1}) of SO_2^-, $S^{18}O_2^-$ and $^{34}SO_2^-$ using 2θ Values of 109.2° (selected bond angle), 104° and 114°. Molecular Geometry Parameters and Force Constants of SO_2^-

Vibrational mode		Exp.[b]	Calc.(I)	c	Calc.(II)	c	Calc.(III)	c
B_2	$S^{16}O_2^-$	1041.9	1041.9	0.0	1041.8	0.1	1041.9	0.0
	$S^{18}O_2^-$	1006.6	1006.4	0.2	1005.5	1.1	1007.3	0.6
	$^{34}SO_2^-$	1029.6	1029.6	0.0	1030.0	0.4	1029.1	0.5
A_1	$S^{16}O_2^-$	985.1	985.1	0.0	985.2	0.1	985.5	0.4
	$S^{18}O_2^-$	945.3	945.1	0.2	947.3	2.0	944.9	0.4
	$^{34}SO_2^-$	976.5	976.5	0.0	975.9	0.6	977.7	1.2
A_1	$S^{16}O_2^-$	495.5	495.5	0.0	495.5	0.0	495.6	0.1
	$S^{18}O_2^-$	473.0	472.9	0.1	472.1	0.7	473.6	0.5
	$^{34}SO_2^-$	492.6	492.5	0.1	492.8	0.2	492.1	0.5
Molecular geometry and force constants								
r(S–O) (nm)			0.149		0.149		0.149	
2θ			109.2°		104°		114°	
F_r (N/m)			6.429×10^2		6.400×10^2		6.469×10^2	
F_{rr} (N/m)			0.280×10^2		0.088×10^2		0.461×10^2	
$F_{r\theta}$ (N)			0.102×10^{-8}		0.102×10^{-8}		0.102×10^{-8}	
F_θ (Nm)			1.755×10^{-18}		1.814×10^{-18}		1.702×10^{-18}	

Teller–Redlich frequency ratios and isotopic shifts

Isotopic couple	Mode	Teller–Redlich ratio		Isotopic shifts (cm^{-1})					
		Exp.	Calc.	Exp.			Calc.		
				ν_1	ν_2	ν_3	ν_1	ν_2	ν_3
$^{32}S^{18}O_2^-/^{32}S^{16}O_2^-$	B_2	0.9334	0.9334			35.3			35.5
	A_1	0.8391	0.8395	39.8	22.5		40.0	22.6	
$^{34}S^{16}O_2^-/^{32}S^{16}O_2^-$	B_2	0.9765	0.9765			12.3			12.3
	A_1	0.9711	0.9706	8.6	2.9		8.6	3.0	

[a] Normal coordinate calculations performed on the SO_2^- modes of $Cs(SO_2)$. [b] Frequencies of $Cs(SO_2)$ (see Tables I and II).
[c] $\Delta\bar{\nu} = |\bar{\nu}_{calc.} - \bar{\nu}_{exp.}|$ (cm^{-1}).

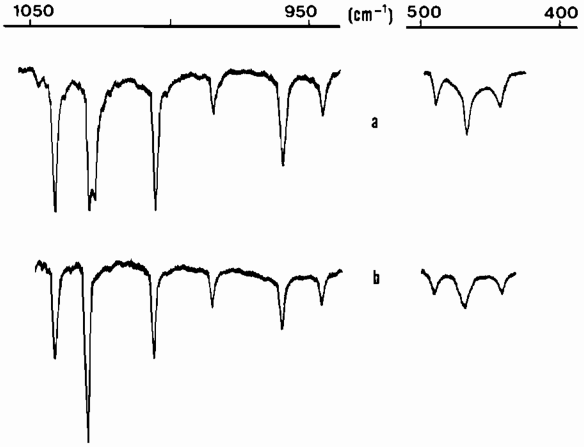

Fig. 2. (a) IR spectrum of 50% ^{18}O-enriched $Cs(SO_2)$, (b) IR spectrum of 50% ^{18}O-enriched $K(SO_2)$.

force field, because two stretching force constants, and two stretching–bending interaction force constants must be employed in the calculations. The results of this series of normal coordinate calculations are summarized in Table IV as models (A), (B) and (C). It is evident that, although the asymmetric bent ion models of Fig. 3b are described by different force constants, the calculated isotopic frequencies occur at practically identical values. In particular, the calculations predict that the modes of the mixed isotopomer have almost zero frequency splitting. The amount of the calculated splittings is in fact *ca.* 0.2 cm^{-1} while the stretching vibrations of the isotopic species $S^{16}O^{18}O^-$ show a splitting of *ca.* 2 cm^{-1}. The doubling of the stretching modes of the mixed isotopomer might be due, alternatively, to the matrix perturbation caused by trapping in a low symmetry site. The matrix perturbation can be simulated either assuming for SO_2^- an asymmetric planar configuration with equal S–O bonds (see Figs 3c) or an asymmetric non planar configuration (see Fig. 3d). Both the models need the use of two stretching and two stretching–bending interaction force constants. The results of these calculations are reported in Table IV under the heading model D. In this case, one predicts a fre-

TABLE III. Observed IR Frequencies (Ar matrix) of ^{18}O-enriched $Cs(SO_2)$ and $K(SO_2)$ and Calculated Isotopic Frequencies

Vibrational mode	$Cs(SO_2)$		$K(SO_2)$	
	Exp. (cm^{-1})	Calc. (cm^{-1})[a]	Exp. (cm^{-1})	Calc. (cm^{-1})[b]
$S^{16}O_2^-$ (B_2)	1041.9	1041.9	1041.4	1041.4
$S^{16}O^{18}O^-$ (A′)	1028.2 1030.6	1029.4	1029.3	1029.2
$S^{18}O_2^-$ (B_2)	1006.6	1006.4	1006.3	1006.1
$S^{16}O_2^-$ (A_1)	985.1	985.1	984.7	984.7
$S^{16}O^{18}O^-$ (A′)	958.7 960.7	959.5	959.9	959.7
$S^{18}O_2^-$ (A_1)	945.3	945.1	945.7	945.5
$S^{16}O_2^-$ (A_1)	495.5	495.5	495.0	495.0
$S^{16}O^{18}O^-$ (A′)	484.0	484.3	483.5	483.8
$S^{18}O_2^-$ (A_1)	473.0	472.9	472.5	472.4

[a] Calculated using the data of calc.(I) of Table II. [b] Calculated from: $r(S-O) = 0.149$ nm; $\measuredangle(O-S-O) = 109°$; $F_r = 6.424 \times 10^2$ (N/m), $F_{rr} = 0.281 \times 10^2$ (N/m), $F_\theta = 1.751 \times 10^{-18}$ (Nm) and $F_{r\theta} = 0.102 \times 10^{-18}$ (Nm).

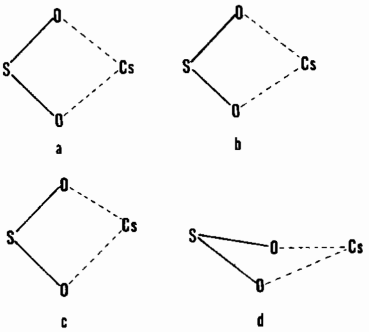

Fig. 3. (a) Planar ring equilibrium configuration of C_{2v} symmetry of SO_2^- in molecular $Cs(SO_2)$, (b) asymmetric planar configuration of SO_2^- corresponding to models (A), (B) and (C), (c) planar asymmetric configuration and (d) non planar asymmetric configuration of SO_2^- in molecular $Cs(SO_2)$ corresponding to model (D).

quency splitting of *ca.* 0.5 cm^{-1}. Such a splitting was obtained considering a difference of 0.2% between the main stretching force constants. Evidently, increasing the difference between the values of the stretching force constants, a larger splitting would have been calculated. From these considerations one might conclude that the measured frequency splitting of *ca.* 2 cm^{-1} is not caused by the inequivalence of the S–O bonds and that SO_2^- has C_{2v} symmetry in $Cs(SO_2)$.

TABLE IV. Calculated Frequencies (cm^{-1}) of SO_2^- [a] Assuming Asymmetric Bent Configurations (models A, B, C) and a Perturbed Anion Configuration (model D)

Molecular parameters	A	B	C	D
r_1 (S–O) (nm)	0.148	0.147	0.145	0.149
r_2 (S–O) (nm)	0.150	0.151	0.153	0.149
2θ (degree)	109°	109°	109°	109°
F_{r_1} (N/m)	6.429×10^2	6.429×10^2	6.439×10^2	6.436×10^2
F_{r_2} (N/m)	6.426×10^2	6.426×10^2	6.416×10^2	6.426×10^2
$F_{r_1r_2}$ (N/m)	0.273×10^2	0.273×10^2	0.273×10^2	0.276×10^2
$F_{r_1\theta}$ (N)	0.102×10^{-8}	0.102×10^{-8}	0.103×10^{-8}	0.102×10^{-8}
$F_{r_2\theta}$ (N)	0.101×10^{-8}	0.101×10^{-8}	0.100×10^{-8}	0.101×10^{-8}
F_θ (Nm)	1.756×10^{-18}	1.756×10^{-18}	1.754×10^{-18}	1.750×10^{-18}
Vibrational mode	Calculated frequencies			
B_2 $S^{16}O_2^-$	1041.9	1041.9	1041.9	1041.9
$S^{16}O^{18}O^-$	1029.6	1029.6	1029.7	1029.4
$S^{18}O^{16}O^-$	1029.6	1029.6	1029.5	1029.9
$S^{18}O_2^-$	1006.5	1006.5	1006.5	1006.5
A_1 $S^{16}O_2^-$	985.1	985.1	985.1	985.1
$S^{16}O^{18}O^-$	960.2	960.2	960.0	960.4
$S^{18}O^{16}O^-$	960.1	960.0	960.3	959.8
$S^{18}O_2^-$	945.9	945.9	946.0	945.9
A_1 $S^{16}O_2^-$	495.5	495.5	495.5	495.5
$S^{16}O^{18}O^-$	484.4	484.4	484.7	484.3
$S^{18}O^{16}O^-$	484.2	484.0	483.9	484.3
$S^{18}O_2^-$	472.8	472.8	472.8	472.9

[a] Frequencies are those of $Cs(SO_2)$.

The experimental confirmation of this conclusion was given by the studies on $K(SO_2)$ with ^{18}O-enrichment. The spectrum shown in Fig. 2b revealed that the bands of the mixed isotopomer do not present any band doubling. The bands observed in this experiment are reported in Table III, along with the calculated isotopic frequencies.

The doubling of the stretching frequencies observed for $Cs(S^{16}O^{18}O)$ is very likely due to a matrix effect [6, 12] induced on SO_2^- by a slight asymmetric interaction of cesium. This type of interaction might occur either in the plane or out of the plane of the SO_2^- group as shown in Fig. 3c and 3d. Obviously, the symmetric planar model of C_{2v} symmetry represented in Fig. 3a corresponds to the most stable equilibrium configuration.

Conclusion

The experimental data are consistent with the assignment of the IR absorptions at *ca.* 1042, 985 and 485 cm^{-1} to the three fundamental modes of the radical ion SO_2^- of C_{2v} symmetry. The ion is stabilized in an inert matrix as a charge-transfer $M(SO_2)$ species. These species are particularly stable in a low temperature matrix and the stability is not influenced by the matrix temperature. This conclusion arises from the observation that minor changes occur in the IR absorptions when the codeposition experiments are carried out at a temperature of *ca.* 20 K or when the matrix temperature is raised from 12 K to *ca.* 35 K. At the latter temperature, the bands become broad with a half-width of *ca.* 10 cm^{-1}, thus indicating the occurrence of molecular diffusion. An additional point is the negligible perturbation on the vibrational levels and molecular geometry of SO_2^- caused by the coordination of the anion with the different metal cations. In fact, different metals cause slight frequency shifts (see Table I) and this fact indicates a high electrostatic contribution to the $M^+ \cdots SO_2^-$ bond.

Another interesting point to be dealt with is the presence in the IR spectra of peaks at 1081.8 and 1089.7 cm^{-1}. This doublet appears in all the codeposition experiments of cesium, potassium and sodium as a variable intensity band. It disappears when the matrix is gently warmed up to *ca.* 30 K and then cooled down to 12 K with the only exception being the cesium system. The components of the doublet are shifted down by *ca.* 12 cm^{-1} (1067.8–1075.1 cm^{-1}) and by *ca.* 35 cm^{-1} (1045.9–1052.8 cm^{-1}) in the case of the ^{34}S and ^{18}O isotopic species, respectively. These shifts compare well with those measured for the ν_3 mode of the molecular ion SO_2^- in the $M(SO_2)$ species (see Table I). The doublet is likely to be the ν_3 vibration of 'free' SO_2^-, that is, the radical anion completely surrounded by argon. Probably 'free' SO_2^- is stabilized in argon matrix in the presence of cesium atoms which undergo limited diffusion through the inert medium. The fact that the doublet is relatively prominent in a highly diluted amount of SO_2 in an argon matrix is further evidence of the correct assignment of these bands. At least, the doublet components at 1081.8 and 1089.7 cm^{-1} might be due to 'free' SO_2^- trapped in two different argon matrix sites [9, 10].

The last conclusion concerns the molecular geometry estimates. The data reported in this study indicate that the bond angle of molecular SO_2^- is close to 109°. The uncertainty associated with this value is likely to be ±5° because the anharmonicity effect was neglected. Further source of uncertainty arises from the use of the triatomic molecule approximation [11]. A more accurate bond angle value would have been determined on the ground of a more complete vibrational force field including the interionic frequencies. However, notwithstanding these approximations our geometry estimates can be considered as reliable ones [13, 14]. Finally, it seems interesting to compare the molecular geometry of the molecular anion SO_2^- with that of SO_2 [9]. Our data indicates that the bond angle of SO_2^- is *ca.* 10° lower than in the case of SO_2. In addition, the calculated apex angle of 'free' SO_2^-, determined from the isotopic frequencies using the triatomic molecule method [11], and equal to 119.5° is very close to the bond angle of SO_2 which is 119°37′ [9]. The data lead to the conclusion that electron transfer from the alkali metal to the neutral molecule reduces the value of the O–S–O angle and makes the S–O bonds weaker than those of SO_2 in the $M(SO_2)$ species. In fact, the S–O stretching force constant f_r of SO_2 is *ca.* 10×10^2 N/m [9] while it is *ca.* 6.4×10^2 N/m in the case of SO_2^-.

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