Matrix-Isolation Studies on M$^+$(AsO$_3^-$) and M$^+$(ClO$_3^-$) Ion Couples

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Stable vapours of type M$^+$(AsO$_2^-$) were studied by means of i.r. matrix-isolation spectroscopy [1] as a part of our research program of high temperature molecules such as alkali metal sulfates and tungstates [2, 3], perrhenates [4] and M$^+$(XO$_2^-$) species (X = B, C, N and Cl) [5]. This paper is a further development of our studies on gaseous metal coordinated oxyanions since M$^+$(AsO$_3^-$) ion pairs (M = K, Rb, Cs) were identified and structurally characterized in the course of matrix-isolation experiments on alkali arsenates.

As far as we are aware, neither mass-spectrometric nor electron-diffraction reports are available for arsenic ternary oxides, therefore information on the vaporization and structure of these inorganic molecules can be provided by spectroscopic investigations. In this paper we also summarize our results on Li$^+$(ClO$_3^-$), Na$^+$(ClO$_3^-$) and Rb$^+$(ClO$_3^-$) chlorates in order to complete preliminary work on these species [6].

The i.r. matrix spectra of K$^+$(AsO$_3^-$), Rb$^+$(AsO$_3^-$) and Cs$^+$(AsO$_3^-$) were studied in N$_2$ matrixes. The spectra consist of prominent bands of the respective arsenites [1] and of new bands which according to ^{18}O-studies were assigned to the vibrations of the AsO$_3^-$ anion coordinated in a bidentate fashion. The coordination of the AsO$_3^-$ group with different cations is evident from the cation dependence of its vibrations. The vibrational coupling between the low-frequency modes of the cation is however very weak, as expected for interionic vibrations [5, 7]. This fact reflects the autonomous character of the anion in ionic pairs with polytopic bonds [8]. The i.r. bands assigned to M$^+$(AsO$_3^-$) alkali meta-arsenates are reported in Table I. The assignment of the observed bands of the C$_{2v}$ M$^+$(AsO$_3^-$) species is consistent with the analysis of the i.r. spectrum of (^{18}O) Cs$^+$(AsO$_3^-$) (see Fig. 1(b)), the isotopic frequencies of which are listed in Table I. The interpretation of this experiment was based on the satisfactory conclusions of normal coordinate calculations by means of which isotopic modes and i.r. band intensities of the C$_{2v}$ and C$_s$ isotopomers of ^{18}O-substituted Cs$^+$(AsO$_3^-$) were predicted. The input data for these calculations are listed in Table I and the expected frequency-line diagram is shown in Fig. 2(c). The

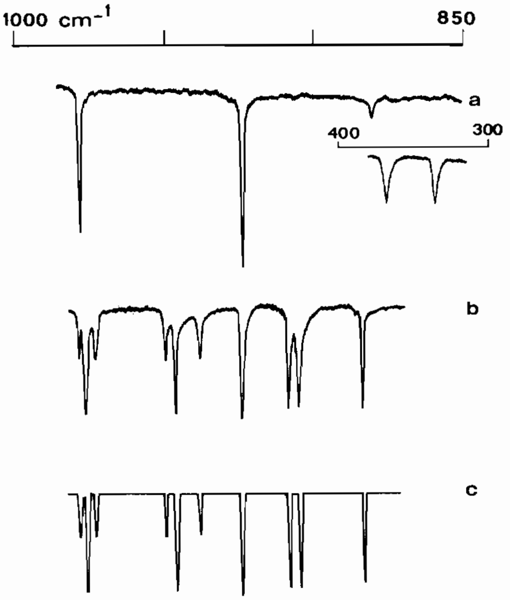

Fig. 1. (a) I.r. matrix spectrum (N$_2$, 12 K) of Cs$^+$(AsO$_3^-$). (b) of ^{18}O-enriched Cs$^+$(AsO$_3^-$), (c) calculated spectrum for a 50% ^{18}O-enrichment (bands of Cs$^+$(AsO$_2^-$) left out in all the spectra).

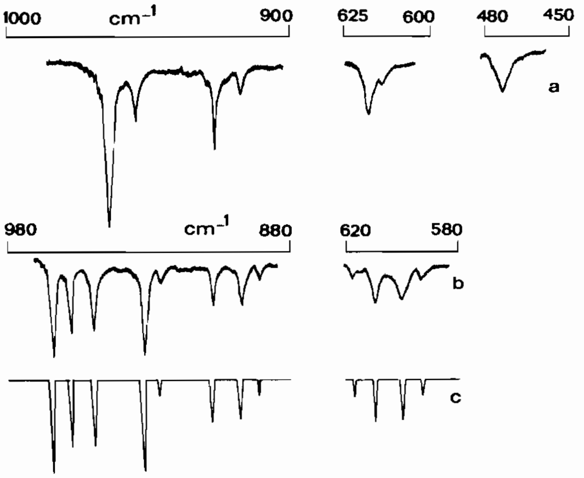

Fig. 2. (a) I.r. spectrum (Ar, 6 K) of Li$^+$(ClO$_3^-$), (b) of ^{18}O-enriched Li$^+$(^{35}ClO$_3^-$), (c) calculated spectrum for a 50% ^{18}O-enrichment.

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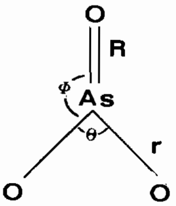
TABLE I. Observed (N_2, 12 K) I.r. Frequencies (cm^{-1}) of Matrix-isolated $M^+(AsO_3^-)$ Species and Band Assignment.

$K^+(AsO_3^-)$	$Rb^+(AsO_3^-)$	$Cs^+(AsO_3^-)$	Assignment	(C_{2v})
980.7	980.2	978.2	$\nu(As{=}O)$	A_1
922.2	922.9	923.6	$\nu(As{=}O)$	B_2
878.0	880.0	879.9	$\nu(As{-}O)$	A_1
377.5 [a]	377 [a]	368 [a]	$\delta(AsO_3^-)$	B_2
355	335	334	$\gamma(AsO_3^-)$	B_1

Isotopic Frequencies of ^{18}O-enriched $Cs^+(AsO_3^-)$

Observed	Calculated[b]		Assignment		
	I[c]	II[c]			
978.2	978.2	978.2	$(As^{16}O_3^-)$	A_1	C_{2v}
975.5	975.8	975.3	$(As^{16}O_2{}^{18}O^-)$	A'	C_s
972.2	972.6	971.6	$(As^{16}O^{18}O_2^-)$	A_1	C_{2v}
949.5	949.1	951.6	$(As^{16}O_2{}^{18}O^-)$	A_1	C_{2v}
945.5	945.0	946.9	$(As^{16}O^{18}O_2^-)$	A'	C_s
937.7	936.5	937.6	$(As^{18}O_3^-)$	A_1	C_{2v}
923.6	923.6	923.6	$(As^{16}O_3^-)$	B_2	C_{2v}
	923.5	923.5	$(As^{16}O_2{}^{18}O^-)$	B_2	C_{2v}
908.5	910.3	910.5	$(As^{16}O_2{}^{18}O^-)$	A"	C_s
905.0	905.5	905.4	$(As^{16}O^{18}O_2^-)$	A"	C_s
883.3	882.7	884.1	$(As^{16}O^{18}O_2^-)$	B_2	C_{2v}
	882.7	884.1	$(As^{18}O_3^-)$	B_2	C_{2v}
879.9	879.9	879.9	$(As^{16}O_3^-)$	A_1	C_{2v}

[a] Accuracy of ±1 cm^{-1}. [b] Structure and intermal coordinate definition:



R = 1.75 Å, r = 1.79 Å; θ = 111°, ϕ = 124.5°

[c] Force constants*: (I) $f_R = 7.192$, $f_{Rr} = 0.300$, $f_r = 6.510$, $f_{rr} = 0.280$; (II) $f_r = 7.105$, $f_{Rr} = 0.296$, $f_r = 6.478$, $f_{rr} = 0.343$, $f_\varphi = f_\theta = 1.062$, $f_{R\varphi} = 0.106$, $f_{r\theta} = 0.085$, $f_{R\theta} = 0.071$, $f_{r\varphi} = 0.080$; $f'_{r\varphi} = 0.010$, $f_\gamma = 1.916$ (γ = o.p.).

*Stretching and stretching–stretching force constants are in mdyn Å^{-1}, bending and stretching–bending force constants are in mdyn Å rad^{-2} and mdyn rad^{-1} respectively.

two force constant sets used in normal coordinate calculations produce equally accurate isotopic modes and the small differences between calculated and observed frequencies reflect the fact that As–O vibrations are not harmonic.

The O–As–O ring angle was 111°, this compares well with the 107° of $Cs^+(PO_3^-)$ [9] and the 115° of $Rb^+(NO_3^-)$ [10]. The lowering of the ring bond angle with respect to the expected one (120°) for planar XO_3^- oxyanions is an evident consequence of the coordination of the anion with an alkali cation. Another effect is the difference between the X–O bond force constants, F_R and Fr with $F_R >$ Fr.

The spectra of matrix-isolated $Cs^+(ClO_3^-)$ and $K^+(ClO_3^-)$ were recently investigated [6], and from ^{18}O-substitution experiments on $Cs^+(^{35}ClO_3^-)$ we reached the conclusion that the ClO_3^- group is a tridentate ligand. Table II summarizes the results on alkali chlorates including new data for Li, Na and Rb matrix-isolated chlorates. Our series of results indicates that all $M^+(ClO_3^-)$ molecules are ionic vapour couples of C_{3v} symmetry. In this system, the three oxygen atoms are equivalent and the coordina-

TABLE II. Observed (Ar, 6 K) I.r. Frequencies (cm^{-1}) of Matrix-isolated $M^+(ClO_3^-)$ Species and Band Assignment.

$Li^+(ClO_3^-)$	$Na^+(ClO_3^-)$	$K^+(ClO_3^-)$[a]	$Rb^+(ClO_3^-)$	$Cs^+(ClO_3^-)$[a]	Assignment (C_{3v})	
972.2	971.0	969.5	967.0	963.0	$\nu_3(E)$	$(^{35}Cl{-}O)$
961.0	960.9	957.5	957.5	953.6		$(^{37}Cl{-}O)$
904.0	915.5	926.9	927.0	925.6	$\nu_1(A_1)$	$(^{35}Cl{-}O)$
896.3	908[b]		919.5	917.1		$(^{37}Cl{-}O)$
630.5	623[b]	627.9	623.5	618.2	$\nu_2(A_1)$	$(^{35}Cl{-}O)$
625.7	618[b]	623[b]	619.0	614.0		$(^{37}Cl{-}O)$
481.2	480[b]	481.5	478.0	474.0	$\nu_4(E)$	$(^{35}Cl{-}O)$

Isotopic Frequencies of ^{18}O-enriched $Li^+(^{35}ClO_3^-)$

Observed	Calculated[c]	Assignment[d]		
972.2	972.2	$(Cl^{16}O_3^-)$	E	C_{3v}
	971.9	$(Cl^{16}O_2{}^{18}O^-)$	A″	C_s
955.8	955.9		A′	
964.4	964.5	$(Cl^{16}O^{18}O_2^-)$	A′	C_s
940.5	941.7		A″	
	941.2	$(Cl^{18}O_3^-)$	E	C_{3v}
904.0	904.0	$(Cl^{16}O_3^-)$	A_1	C_{3v}
886.9	887.8	$(Cl^{16}O_2{}^{18}O^-)$	A′	C_s
875.0	876.3	$(Cl^{16}O^{18}O_2^-)$	A′	C_s
869.1	869.4	$(Cl^{18}O_3^-)$	A_1	C_{3v}
630.5	630.5	$(Cl^{18}O_3^-)$	A_1	C_{3v}
622.1	622.5	$(Cl^{16}O_2{}^{18}O^-)$	A′	C_s
615[b]	614.0	$(Cl^{16}O^{18}O_2^-)$	A′	C_s
604[b]	603.4	$(Cl^{18}O_3^-)$	A_1	C_{3v}

[a] Ref. [6]. [b] Accuracy of ±1 cm^{-1}. [c] Calculated from: $R(Cl{-}O) = 1.5$ Å; $\sphericalangle O{-}Cl{-}O = 109°$, $f_r = 5.524$ and $f_{rr} = 0.245$ (mdyn $Å^{-1}$), $f_\theta = 2.524$ and $f_{\theta\theta} = 0.93$ (mdyn Å rad^{-2}). [d] Cl stands for ^{35}Cl isotope.

tion with the alkali metal is of the tridentate type. The absence of any observed degeneracy lifting for the ν_3 and ν_4 modes indicates that the ClO_3^- group retains C_{3v} symmetry. This is evident from our spectra (*e.g.* see Fig. 2(a)) and from the spectrum of ^{18}O-enriched $Li^+(^{35}ClO_3^-)$ shown in Fig. 2(b). This spectrum compares well with that of $Cs^+(^{35}ClO_3^-)$ [6] for the presence of the typical 1:3:3:1 and 5:3:3:5 intensity patterns expected for the non-degenerate (ν_1, ν_2) and degenerate (ν_3, ν_4) modes respectively. Both calculated i.r. isotopic frequencies and band intensities of $C_{3v}Li^+(^{35}ClO_3^-)$ agree with the experimental results (see Table II and Fig. 2(c)).

Our conclusions are different from those reported by Smyrl [11] who interpreted the spectra of alkali chlorates assuming C_s symmetry. Evidently the interpretation of Smyrl's spectra was complicated by the presence of several bands arising from either vapour phase polymers or matrix aggregates. Our studies, as suggested by previous experience [6], were carried out using extensive super-heating vaporization conditions and lower deposition temperatures (6 K) in order to eliminate the interference of bands of any polymeric species and to distinguish those of monomer chlorate from alien species. Smyrl's assignment should be therefore conformed with ours. Further, in the light of the correct assignment it is possible to explain the unsatisfactory normal coordinate calculations performed by Smyrl, especially for the claimed split components of the ν_4 mode [11].

Experimental

Features of the matrix-isolation apparatus are reported in previous papers [2, 6]. Samples were supplied by Alfa Ventron and matrix gases (99.9995%) by Matheson. Alkali meta-arsenates $MAsO_3$ were obtained by heating the corresponding MH_2AsO_4 arsenates *in vacuo* at *ca.* 920 K. Meta-arsenates were vaporized from a platinum cell over the temperature range 1150–1200 K. ^{18}O-enriched $CsAsO_3$ was prepared by ^{18}O exchange between CsH_2AsO_4 and $H_2{}^{18}O$ (S.I.C., 99% ^{18}O). Isotopically pure sample of $Li^{35}Cl^{16}O_3$ was purchased by S.I.C. and ^{18}O-enrichment of this sample was carried out using $H_2{}^{18}O$. Alkali chlorates were vaporized from a quartz double oven at *ca.* 750 K and the vapour was superheated at *ca.* 1000 K. Typical temperatures of matrix gas deposition were *ca.* 12 K; conclusive experiments on chlorates were performed at *ca.* 6 K. I.R. reflection spectra were measured with a Perkin-Elmer 580-B spectrometer. Frequencies are accurate to within ±0.5 cm^{-1}.

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References

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

2 R. M. Atkins and K. A. Gingerich, *Chem. Phys. Lett., 53,* 347 (1978).

3 R. M. Atkins and K. A. Gingerich, *High Temp. Sci., 14,* 103 (1981).

4 L. Bencivenni, H. M. Nagarathna and K. A. Gingerich, *Chem. Phys. Lett., 99,* 258 (1983).

5 L. Bencivenni, R. Teghil and K. A. Gingerich, work to be submitted for publication.

6 L. Bencivenni, H. M. Nagarathna, K. A. Gingerich and R. Teghil, submitted to *J. Chem. Phys.* (1983).

7 A. A. Belyaeva, M. I. Dvorkin and L. D. Shcherba, *Russ. J. Phys. Chem., 21,* 738 (1980).

8 N. G. Rambidi, *J. Mol. Struct., 28,* 77 (1975).

9 K. P. Petrov, A. I. Kolesnikov, V. V. Ugarov and N. G. Rambidi, *Zh. Strukt. Khim., 21,* 198 (1980).

10 K. P. Petrov, A. I. Kolesnikov, V. V. Ugarov and N. G. Rambidi, *Zh. Strukt. Khim., 22,* 196 (1981).

11 N. Smyrl and J. P. Devlin, *J. Chem. Phys., 60,* 2540 (1974).