Matrix Isolation Studies on Alkali Metal Arsenates: The Characterisation of Molecular $CsAsO_3$ †

J. Steven Ogden,* Timothy J. Sibley, and Stephen J. Williams
Department of Chemistry, The University, Southampton SO9 5NH

The matrix i.r. spectra obtained from the vaporisation of samples of potassium, rubidium, and caesium arsenate show characteristic bands due to the species $MAsO_2$ and new features which are assigned to molecular arsenates $MAsO_3$. For $CsAsO_3$, fundamentals are assigned at 978.2, 923.4, 880.0, 368, and 335 cm^{-1}, and ^{18}O enrichment experiments indicate a C_{2v} bidentate structure.

The characterisation of high-temperature chemical species by matrix isolation i.r. spectroscopy is now well established, and we are currently using these techniques to explore a wide range of inorganic systems. In particular, we have confirmed the mass spectrometric observation that *molecular* KNO_3 and $NaPO_3$ are important species produced in the vaporisation of the parent solids, and have established their shapes by the use of ^{18}O enrichment.[1,2]

In contrast to these nitrate and phosphate systems, however, there appears to be no experimental data on the vaporisation of alkali metal arsenates, although we have recently shown that molecular arsenites ($MAsO_2$) can be identified as vaporisation products from solids such as $NaAsO_2$ or from Cs_2CO_3–As_2O_3 mixtures.[3] This paper describes our recent work on the vaporisation of alkali metal arsenates.

Experimental

The samples of KH_2AsO_4 used in this work were obtained from BDH (>98% purity) whilst RbH_2AsO_4 and CsH_2AsO_4 were prepared from the partial neutralisation of H_3AsO_4 solution by the appropriate carbonate using the procedure described by Shklowskaya and Romanova.[4] Oxygen-18 enriched CsH_2AsO_4 was obtained from $CsH_2As^{16}O_4$ by oxygen atom exchange with $H_2{}^{18}O$ in a sealed tube, and all MH_2AsO_4 (M = K, Rb, or Cs) samples were converted into the corresponding ' meta-arsenates ' ($MAsO_3$) by heating *in vacuo* to *ca.* 900 K for *ca.* 60 min prior to deposition.[5]

The general features of our matrix isolation apparatus have been described elsewhere.[6] For this work, samples were vaporised from a small platinum boat contained inside an alumina holder fitted with an inductively heated tantalum sleeve. Sample temperatures during deposition were monitored using an optical pyrometer, and matrix-gas flows were regulated with a fine-control needle valve. The matrix gases used in these experiments were high purity nitrogen and argon (B.O.C. 99.999%) but nitrogen was found to give superior spectra, and the results discussed here refer to nitrogen matrices.

Deposition times were typically 30—60 min, and during this period, the central CsI window in the cryostat was maintained at *ca.* 12 K. The matrix ratio was estimated to be >1 000 : 1. Controlled-diffusion studies were carried out up to *ca.* 35 K, and all spectra were recorded at *ca.* 12 K using a Perkin-Elmer 225 i.r. spectrometer (5 000—200 cm^{-1}) calibrated using standard procedures.

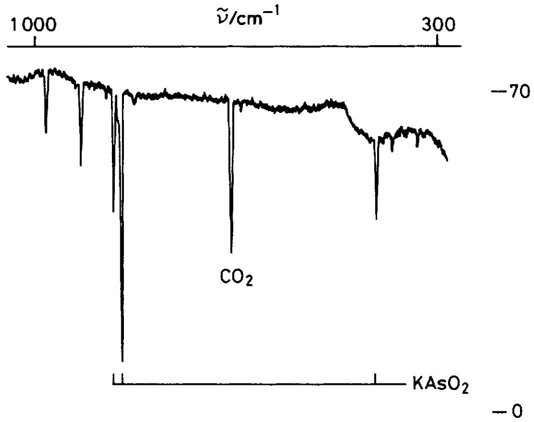

Figure 1. Nitrogen-matrix i.r. spectrum obtained from the vaporisation of $KAsO_3$

Results and Discussion

Figure 1 shows a typical nitrogen-matrix i.r. spectrum (1 000—300 cm^{-1}) obtained from a sample of potassium arsenate heated to *ca.* 1 200 K. In addition to the sharp peak at 662 cm^{-1} which is due to CO_2, this spectrum shows prominent bands at 865.4, 852.6, and 409.2 cm^{-1} which are due to matrix-isolated $KAsO_2$,[3] and two relatively intense features at 981.0 and 922.0 cm^{-1} which have not been reported previously. Traces of As_4O_6 are also present in this spectrum (*ca.* 829 cm^{-1}) and three other weak features are found at 878, 378, and 335 cm^{-1}. Corresponding experiments on rubidium and caesium arsenate reveal a similar pattern of bands, and in particular indicate a smaller proportion of $MAsO_2$ and As_4O_6 species in the matrix.

Table 1 summarises the bands assigned to $MAsO_2$ and the five new features observed in these experiments, and it is evident that they show a small cation dependence. Three of these new features lie in the As–O stretching region (1 000—700 cm^{-1}) and by analogy with our earlier studies on nitrate and phosphate systems [1,2] are provisionally assigned to molecular arsenates $MAsO_3$ with a C_{2v} bidentate structure. These three bands, together with the weak low-frequency features at *ca.* 370 and *ca.* 335 cm^{-1}, showed the same relative intensities throughout a range of experimental conditions (*e.g.* variation of spray-on rate, diffusion studies) and their assignment to a species $MAsO_3$ is supported by ^{18}O enrichment studies.

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† *Non-S.I. unit employed*: 1 dyn = 10^{-5} N.

Table 1. Infrared absorptions (cm^{-1}) * observed in nitrogen-matrix studies on alkali metal arsenates

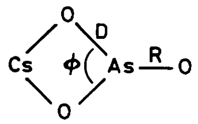
System			Assignment		
$KAsO_3$	$RbAsO_3$	$CsAsO_3$	(M = K, Rb, or Cs)		
981.0	979.0	978.2	ν(AsO)	$MAsO_3$	(A_1)
922.0	923.3	923.4	ν(AsO)	$MAsO_3$	(B_2)
878.0	880.0	880.0	ν(AsO)	$MAsO_3$	(A_1)
865.4	865.0	863.0	ν(AsO)	$MAsO_2$	(A_1)
852.6	853.5	851.5	ν(AsO)	$MAsO_2$	(B_2)
409.2	398.5	393.0	δ(AsO_2)	$MAsO_2$	(A_1)
378	376	368	δ(AsO_3)	$MAsO_3$	(B_2)
335	334	335	δ(AsO_3)	$MAsO_3$	(B_1)

* Frequency accuracy ±0.5 cm^{-1} for stretching modes, ±1 cm^{-1} for bending modes.

Table 2. Observed and calculated frequencies (cm^{-1}) for isotopically enriched $CsAsO_3$ molecules isolated in nitrogen matrices

Observed [a]	Calculated [b]	Assignment	
978.2	978.2	$Cs^{16}O^{16}OAs^{16}O$	A_1
975.7	975.8	$Cs^{16}O^{18}OAs^{16}O$	A'
972.5	972.7	$Cs^{18}O^{18}OAs^{16}O$	A_1
949.3	949.1	$Cs^{16}O^{16}OAs^{18}O$	A_1
945.5	945.0	$Cs^{16}O^{18}OAs^{18}O$	A'
937.5	936.6	$Cs^{18}O^{18}OAs^{18}O$	A_1
923.4	923.4	$Cs^{16}O^{16}OAs^{16}O$	B_2
	923.4	$Cs^{16}O^{16}OAs^{18}O$	B_2
908.2	910.4	$Cs^{16}O^{18}OAs^{16}O$	A''
904.8	905.5	$Cs^{16}O^{18}OAs^{18}O$	A''
883.0	882.7	$Cs^{18}O^{18}OAs^{16}O$	B_2
	882 7	$Cs^{18}O^{18}OAs^{18}O$	B_2
880.0	880.0	$Cs^{16}O^{16}OAs^{16}O$	A_1

[a] Frequency accuracy ±0.5 cm^{-1}. [b] Parameters used in C_{2v} bidentate structure are as follows:



$F_R = 7.192$, $F_D = 6.511$, $F_{RD} = 0.299$, $F_{DD} = 0.280$ mdyn Å^{-1}; $\varphi = 111°$.

^{18}O *Enrichment in* $CsAsO_3$.—Figure 2(*a*) shows part of the nitrogen-matrix i.r. spectrum (810—990 cm^{-1}) obtained from the vaporisation of caesium [$^{16}O_3$]arsenate. The two lower-frequency peaks are due to $CsAs^{16}O_2$, whilst those at 978.2 and 923.4 cm^{-1} are assigned to $CsAs^{16}O_3$. The third As–O mode expected for this species (880 cm^{-1}, Table 1) is too weak to be observed in this spectrum.

Figure 2(*b*) shows the effect of *ca.* 50% ^{18}O enrichment on this system. $CsAsO_2$ produces a total of six lines, all of which have been satisfactorily interpreted in terms of a C_{2v} structure,[3] whilst to higher frequency, the effect of isotope enrichment has been to produce at least ten peaks. A pattern of this complexity can only arise from a species containing at least three oxygen atoms, and an interpretation was therefore sought based on the C_{2v} bidentate model for $CsAsO_3$. As in our earlier studies on nitrate isotope patterns,[1] our initial choice of force field retained two principal As–O stretching constants, and a general-purpose stretch interaction constant, whilst neglecting all coupling with bending modes. With these restrictions, together with the assumption that the OAsO bond angles were each 120°, model calculations gave a predicted isotope pattern in this region of ten lines which could usefully be regarded as two high-frequency triplets and a lower-frequency quartet. The frequency fit, however, was well outside experimental error, and a much better agreement with the experimental spectrum was obtained by decreasing the OAsO angle in the ring to 111° and allowing two independent interaction constants.

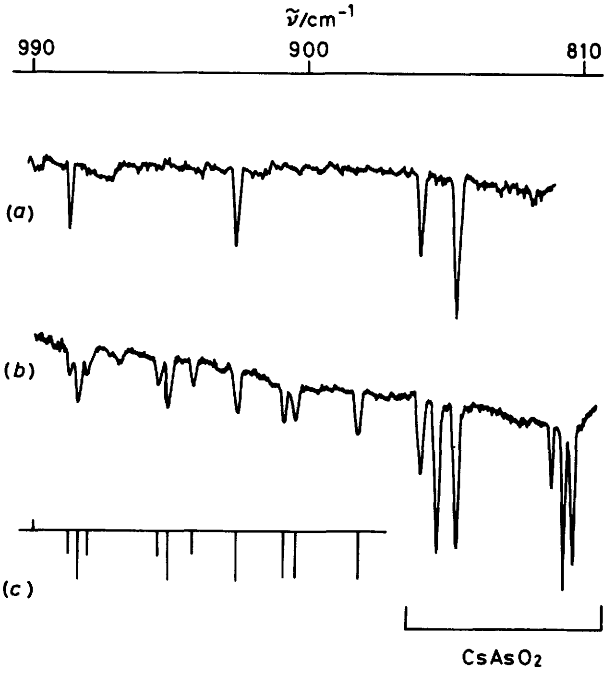


Figure 2. (*a*) Nitrogen-matrix i.r. spectrum (810—990 cm^{-1}) obtained from the vaporisation of $CsAsO_3$. (*b*) Nitrogen-matrix i.r. spectrum obtained from $CsAsO_3$ with *ca.* 50% ^{18}O enrichment. (*c*) Calculated spectrum for $CsAsO_3$ isotopomers, assuming C_{2v} bidentate structure

Figure 2(*c*) shows the line diagram which summarises this second set of calculations, whilst the numerical results and parameters used are given in Table 2. The agreement is satisfactory, and confirms the identity of the trapped species as a molecular arsenate. The principal force constants derived from this analysis (*ca.* 7.2 and 6.5 mdyn Å^{-1}) are similar to those found in other As^V complexes in which multiple bonding between As and O has been invoked.[7] In molecular $CsAsO_2$, the principal stretching constant for the As–O bond was found to be 5.74 mdyn Å^{-1}. Isotope patterns could not be observed for the three weak fundamentals at 880, 368, and 335 cm^{-1}. However, our analysis of the observed isotope pattern is consistent with an A_1 stretching mode at *ca.* 880 cm^{-1} and by comparison with the value found for the AsO_2 bending mode in $CsAsO_2$ (Table 1) the two lower-frequency bands are in the region expected for the bending modes of an AsO_3 unit. Our choice of the lower-frequency feature (335 cm^{-1}) as the (B_1) out-of-plane mode is made by comparison with the earlier phosphate studies.[2]

Conclusions

This series of experiments provides the first evidence for the existence of molecular alkali metal arsenates $MAsO_3$ in high-temperature vapours, and demonstrates that in low-temperature matrices they adopt a C_{2v} bidentate structure. These species are therefore isostructural with the corresponding nitrate and phosphate molecules, and the force-constant parameters derived from the vibrational analysis indicate significant π bonding in the As–O framework. The value of 111° for the OAsO angle in the ring, which also emerges from the analysis for $CsAsO_3$, is estimated to carry an attendant error of *ca.* ±5° in view of the approximations inherent in the use of the simplified force field.[3]

In addition, these experiments show that significant amounts of the corresponding arsenites $MAsO_2$ are also trapped in the matrix, thus indicating that the vaporisation of the parent solids is accompanied by partial thermal decomposition.

Acknowledgements

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