Matrix-isolation Studies on the Vaporisation of Arsenic(V) Oxide: The Characterisation of Molecular Species As_4O_n (n = 7—10) by Infrared Spectroscopy

Alan K. Brisdon, Robin A. Gomme, and J. Steven Ogden *
Department of Chemistry, The University, Southampton SO9 5NH

The vapour species produced on heating arsenic(V) oxide *in vacuo* have been isolated in low-temperature matrices, and examined by i.r. spectroscopy. Detailed studies reveal the existence of As_4O_6 and four higher oxides As_4O_7, As_4O_8, As_4O_9, and As_4O_{10} which are characterised for the first time as stable molecular entities. Band assignments are proposed for several of the more intense absorptions, and the effects of ^{18}O enrichment in the terminal As=O stretching region are interpreted on the basis of a restricted force-field analysis.

There have been many studies on molecular As_4O_6 in the gas phase, and in particular, a combination of structural[1] and vibrational[2-5] techniques has led to the characterisation of this species as a T_d cage structure. Numerous studies have also been carried out on arsenic(III) oxide in the solid state, several detailed structural and vibrational analyses being reported.[2,3,6]

However, very little is known about possible higher oxides of arsenic (*e.g.* As_4O_7) which would be the logical counterparts to P_4O_{7-10}.[7] Indeed, the only evidence for such species comes from mass spectrometric studies on the vaporisation of solid arsenic(V) oxide. Two independent groups have reported ion peaks corresponding to $As_4O_n^+$ (n = 6—10) for this system,[8,9] and made various estimates concerning the relative proportions of species present in the vapour. However, these studies also found significant ion intensities from lower mass fragments and from O_2^+.

In this paper, we report a matrix-isolation i.r. study on the vaporisation of arsenic(III) and arsenic(V) oxides. The primary aim was to establish both the identity and symmetry of the molecular species present in the vapour above heated arsenic(V) oxide, and to understand the principal features of their i.r. spectra in terms of an appropriate vibrational analysis.

Experimental

In these experiments, samples of solid arsenic(V) oxide (BDH, 97%) were vaporised from platinum boats at *ca.* 1 000 K using induction heating, and samples of arsenic(III) oxide (H & W, 99.8%) were vaporised from Pyrex holders heated to *ca.* 550 K. The matrix gases used were high-purity nitrogen and argon (BOC, 99.99%) and deposition times were typically *ca.* 30 min during which period the central CsI window in our system† was maintained at *ca.* 12 K. Infrared spectra were subsequently recorded on PE225 and 983G instruments.

In addition to the straightforward vaporisation of arsenic-(V) and -(III) oxides, experiments were also performed in which *mixtures* of these two oxides were vaporised, and studies were also carried out on mixtures of arsenic(V) oxide and tantalum powder. These experiments were generally successful in changing the relative proportions of vapour species trapped in the matrix.

Studies were also carried out on ^{18}O-enriched samples of the pentoxide. These were conveniently prepared by dissolving $As_2{}^{16}O_5$ in [^{18}O]water and then allowing several days for equilibration, after which time the residual water was removed under vacuum.

Results and Discussion

^{16}O *Species*.—These systems were studied using both argon and nitrogen as matrix gases, but nitrogen matrices consistently yielded superior spectra, and the majority of results therefore refer to species isolated in nitrogen.

Figure 1(*a*) shows a typical nitrogen-matrix i.r. spectrum obtained from the vaporisation of arsenic(III) oxide. Four bands are observed at *ca.* 829, 498, 378, and 255 cm^{-1} and these are assigned ‡ as the four T_2 modes of molecular As_4O_6.

Figure 1(*b*) shows a typical spectrum (1 200—200 cm^{-1}) obtained from a sample of arsenic(V) oxide heated to *ca.* 1 000 K. This spectrum shows features assigned to As_4O_6 (denoted by asterisks) and a small peak due to CO_2 impurity at 662 cm^{-1}, but the numerous additional bands indicate that new arsenic oxide species have been isolated. These new bands are found close to the (cage) modes of As_4O_6 and also in the spectral region 900—1 100 cm^{-1} which is characteristic of terminal As=O stretching modes.[11] The positions of these new bands are summarised in Table 1. Argon matrices yielded very similar spectra, but the bands were somewhat broader, leading to poorer resolution of the complex patterns at *ca.* 1 010 and *ca.* 850 cm^{-1}.

Terminal As=O *modes.* Figure 2(*a*)—(*c*) show medium-resolution spectra of the terminal As=O region obtained from three separate experiments on successive days from an initial sample of arsenic(V) oxide. Each experiment involved the complete cycle of cool down, deposition (*ca.* 30 min), spectral recording, and warm up, but the sample of arsenic oxide was not replenished. Six absorptions may be identified, at 1 011.6, 1 012.8, 1 014.7, 1 019.2, 1 025.1, and 1 026.8 cm^{-1}. However, it is evident that there are significant changes in relative band intensities between day 1 [Figure 2(*a*)] and day 3 [Figure 2(*c*)], and these variations can only be explained by assuming that at least four different molecular species are present.

In particular, the bands at 1 012.8 and 1 026.8 cm^{-1} each appear to show unique intensity variations, and are therefore assigned to separate species A and D. The two bands at 1 011.6 and 1 014.7 cm^{-1}, however, appear to retain the same relative intensity and are thus assigned to the same species B whilst the remaining two bands are similarly assigned to a single species C.

Figure 2(*d*) shows a typical spectrum obtained (on the first day) from a mixture of arsenic(V) and arsenic(III) oxide (molar ratio 1 : 1), whilst Figure 2(*e*) shows the spectrum obtained from a sample of arsenic(V) oxide + tantalum powder. Both these

---

† The general features of our matrix-isolation apparatus have been described elsewhere.[10]

‡ There is no consensus in the literature concerning the exact position of the T_2 fundamentals in the gas phase, but these matrix i.r. absorptions are consistent with the Raman data of Rytter *et al.*[4] and the i.r. data of Sakano.[5]

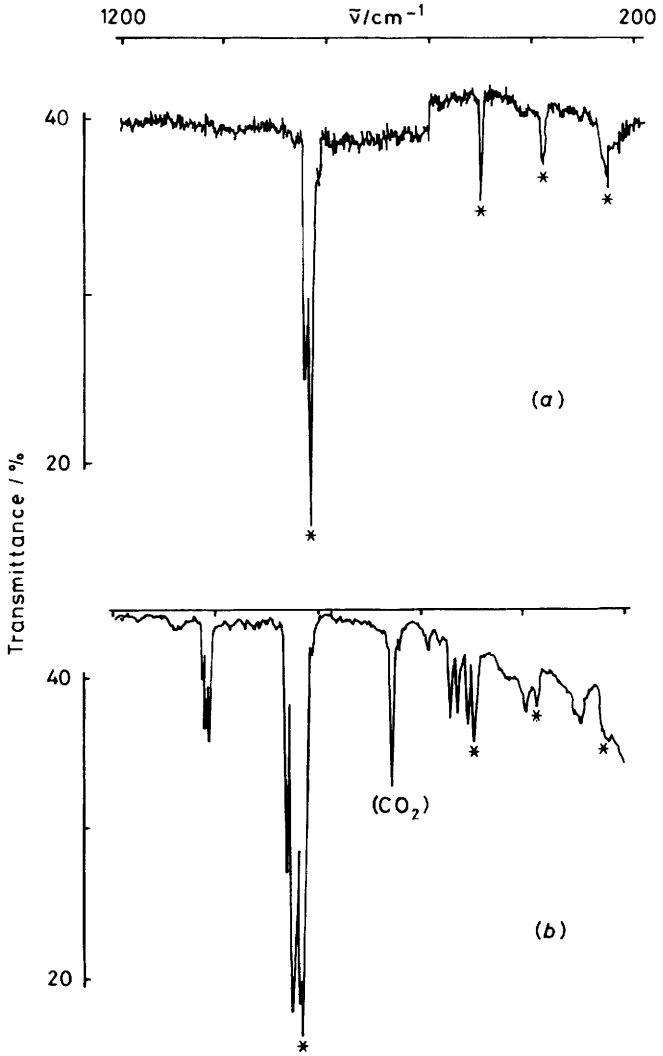


Figure 1. Nitrogen-matrix i.r. spectra (1 200—200 cm⁻¹) obtained from the vaporisation of arsenic(III) oxide (*a*) and of arsenic(v) oxide (*b*). Bands denoted by asterisks are due to As_4O_6

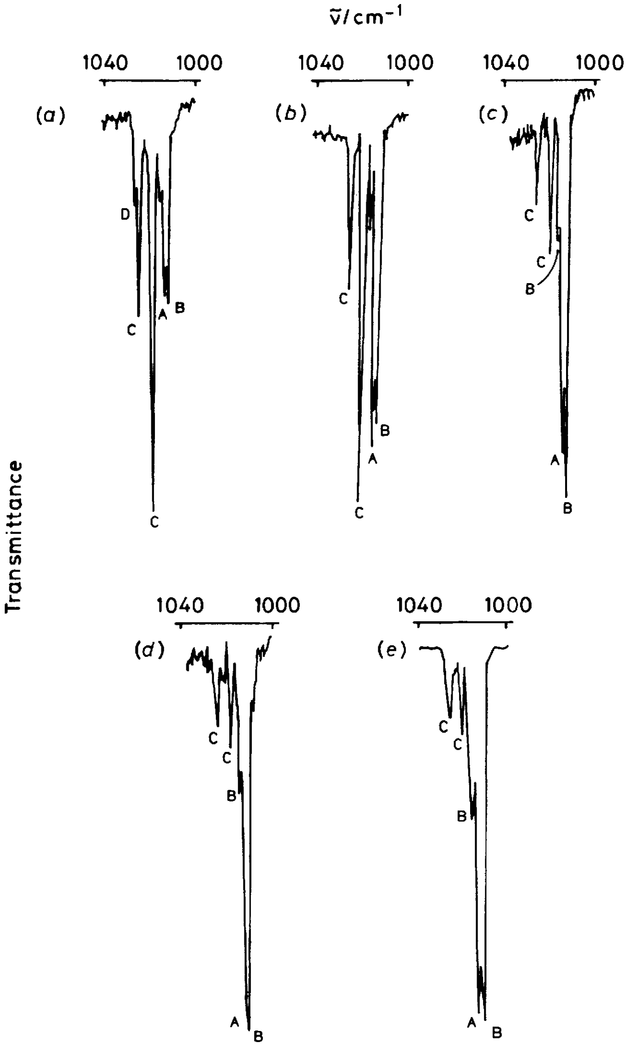


Figure 2. High-resolution i.r. spectra of the As=O terminal stretching region (1 040—1 000 cm⁻¹) obtained from (*a*) a sample of arsenic(v) oxide, (*b*) and (*c*) the sample as in (*a*) on subsequent days, (*d*) an equimolar mixture of arsenic(III) and arsenic(v) oxide, (*e*) an arsenic(v) oxide–tantalum powder sample

experiments clearly show that the bands assigned to A and B are relatively more prominent here than in the *initial* spectra obtained from pure samples of arsenic(v) oxide [Figure 2(*a*)].

A preliminary assignment of these bands is relatively straightforward. The mass spectrometric studies[8,9] indicate that As_4O_7, As_4O_8, As_4O_9, and As_4O_{10} are all expected to be present in the vapour above heated arsenic(v) oxide, and if one assumes that these species are isostructural with the corresponding phosphorus oxides, their point groups will be C_{3v}, C_{2v}, C_{3v}, and T_d respectively. Figure 3 indicates the proposed structures for these molecules, and summarises the i.r. activity expected for both terminal and cage stretching modes. In particular, we note that As_4O_7 and As_4O_{10} are each predicted to show only one i.r.-active terminal mode, whilst As_4O_8 and As_4O_9 should each show two.

Species D is characterised by one absorption at 1 026.8 cm⁻¹, which was only present in the initial stages of arsenic(v) oxide vaporisation [Figure 2(*a*)] and was not observed at all from the mixtures in 2(*d*) and (*e*); D is therefore identified as As_4O_{10}. In contrast, the single band which characterises A is most prominent where there is the possibility of reduction [As^V–O + Ta] or where the O:As ratio is lower [*e.g.* arsenic(III)–arsenic(v) oxide mixtures, or after prolonged vaporisation]; A is thus identified as As_4O_7. Similar arguments allow one to identify B as As_4O_8 and C as As_4O_9.

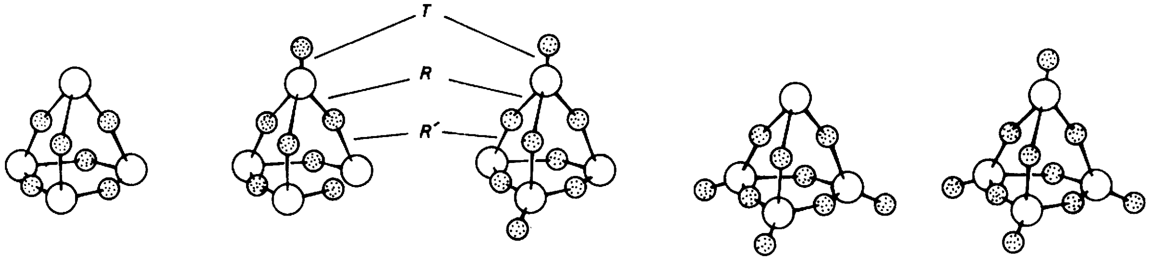
In addition, it is possible to assign each band observed for B and C to a specific symmetry. If one assumes that the structures of As_4O_8 and As_4O_9 are based on a tetrahedral cage unit, then to a first approximation the angles between terminal As=O groups will be *ca.* 109°. Even if this angle were to deviate by up to *ca.* 20°, a simple bond-dipole model would predict that the antisymmetric As=O stretches would be more intense than the symmetric stretches.[12] We therefore assign the A_1 and E modes of As_4O_9 as 1 025.1 and 1 019.2 cm⁻¹ respectively, and similarly identify the A_1 and B_2 modes of As_4O_8 at 1 014.7 and 1 011.6 cm⁻¹. Structural studies on P_4O_8 reveal an angle of *ca.* 106° between the terminal P=O vectors.[13]

The only terminal mode which remains unidentified is the (inactive) A_1 mode of As_4O_{10}. Two lines of argument indicate that this mode should lie slightly above the observed T_2 frequency. First we note that for P_4O_{10} the terminal A_1 mode lies just above the T_2 frequency[2] and that this order is found[14] for several (T_d) MO_4 species which contain a heavy central mass. Secondly, it would appear that for As_4O_9 and As_4O_8 the

Table 1. Observed and calculated vibrational frequencies (cm^{-1}) for As_4O_n (n = 7—10) species

As_4O_7			As_4O_8			As_4O_9			As_4O_{10}		
Observed[a]	Calculated[b]	Assignment	Observed[a]	Calculated[a]	Assignment	Observed[a]	Calculated[b]	Assignment	Observed[a]	Calculated[b]	Assignment
1 012.8	1.012.8	A_1 As=O	1 014.7	1 014.7	A_1 As=O	1 025.1	1 025.1	A_1 As=O		(1 036.0)	A_1 As=O
			1 011.6	1 011.6	B_2 As=O	1 019.2	1 019.2	E As=O	1 026.8	1 026.8	T_2 As=O
848.3	848.3	E	851.2	852.2	B_2	862.0	862.0	E			
841.5	841.5	A_1		849.6	B_1	851.0	851.0	A_1			
			846.2				845.7	A_2			
	835.7	A_2		845.3	A_1						
				844.5	A_2						
833.0	832.7	E	838.3	838.7	B_1	839.6	839.5	E			
				823.1	B_2						
509.1	509.1	E	543.2	543.2	A_1	529.6	529.6	E			

[a] Nitrogen matrix. Frequency accuracy ±0.5 cm^{-1}. [b] Based on force-constant parameters listed in Table 3.



Molecule	As_4O_6	As_4O_7	As_4O_8	As_4O_9	As_4O_{10}
Symmetry	T_d	C_{3v}	C_{2v}	C_{3v}	T_d
Γ terminal		A_1*	A_1* + B_2*	A_1* + E*	A_1 + T_2*
Γ cage	A_1 + E + T_1 + $2T_2$*	$3A_1$* + A_2 + $4E$*	$4A_1$* + $2A_2$ + $3B_1$* + $3B_2$*	$3A_1$* + A_2 + $4E$*	A_1 + E + T_1 + $2T_2$*

Figure 3. Structures and i.r. activities for the species As_4O_{6-10}; * i.r.-active bands

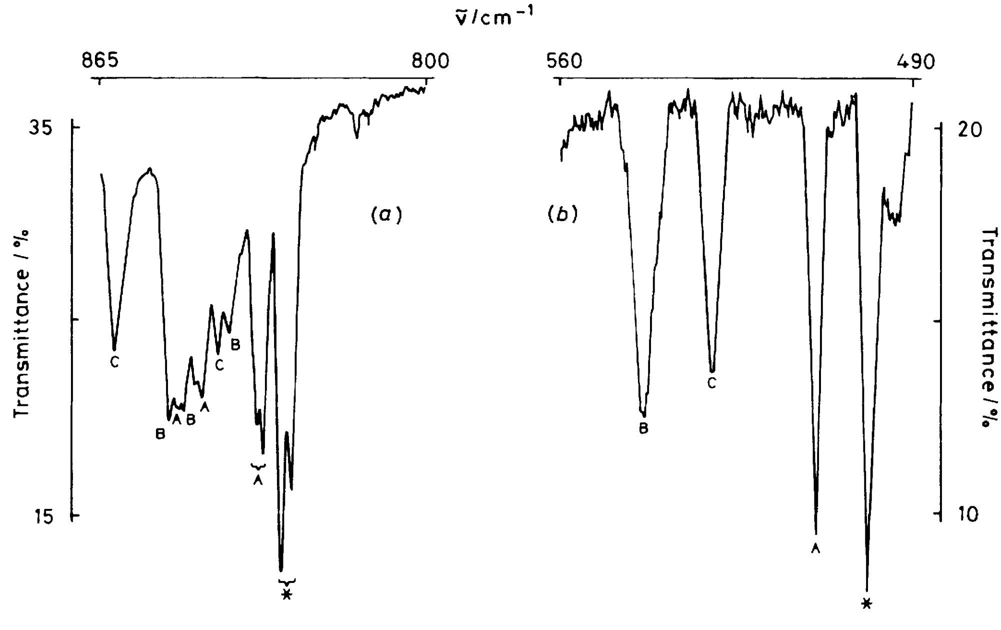


Figure 4. High-resolution spectra of the As–O cage stretching region: (a) 865—800 cm^{-1} and (b) 560—490 cm^{-1} showing bands due to As_4O_6 (*), As_4O_7 (A), As_4O_8 (B), and As_4O_9 (C)

symmetric terminal stretches similarly lie above the anti-symmetric stretches. This order is also found for several C_{3v} MO_3 and C_{2v} MO_2 moieties where M is a heavy atom.[15,16] The reasons for this lie basically in the greater importance of off-diagonal F matrix elements (compared with off-diagonal G matrix elements) in the vibrational analysis of such systems. We therefore estimate that the A_1 mode of As_4O_{10} will lie at *ca.* 1 035 ± 10 cm^{-1}.

Cage modes. Figure 1(*b*) shows that the vaporisation of arsenic(V) oxide also results in intense new absorptions in the same spectral regions as As_4O_6, and it would seem reasonable to assign these to cage modes of the four higher oxides As_4O_{7-10}. Figure 4(*a*) and (*b*) show the more significant bands in these regions under better resolution. In principle, the assignment of these bands to specific higher oxides should be possible by correlating their intensities with corresponding absorptions in the As=O terminal region, using, for example spectral subtraction. However, this strategy ideally requires several 'primary' spectra in which the proportions of As_4O_7, As_4O_8, As_4O_9, and As_4O_{10} all differ significantly, and also requires both accurate frequency reproducibility (generally good) and uniform band widths.

This latter constraint was not always realised (perhaps due to varying amounts of molecular oxygen trapped in the matrix), but it was nevertheless possible to identify prominent cage modes of As_4O_9 at 862, 851, 840, and 530 cm^{-1} with some confidence using this approach (see Table 1). Spectra in which there were widely differing proportions of As_4O_7 and As_4O_8 were difficult to obtain, and the cage modes of these molecules are identified (Table 1) with somewhat less confidence. However, no cage modes for As_4O_{10} could be positively identified, and there are perhaps two reasons for this. First, As_4O_{10} was never present in a sufficiently large proportion (judged by the intensity of its terminal T_2 mode) for its absorptions to dominate the spectrum; and secondly, as a result of its high symmetry, only one i.r.-active cage mode would be expected in each of the two regions considered here. The possibility of accidental overlap in the region 800—900 cm^{-1} is clearly very high, whilst in the lower-frequency region (*ca.* 450—550 cm^{-1}) bands are generally found to be much less intense. Finally, it should be noted that there is no *a priori* method of establishing the symmetry of a particular cage mode from this work.

Relative abundances. If one assumes that the bond-dipole derivatives for terminal As=O vibrations are the same in the four molecules As_4O_{7-10}, and that these modes are effectively uncoupled from cage motion, it is possible to estimate[12] the relative abundances of As_4O_{7-10} by measuring the integrated i.r. intensities of the terminal modes. Thus, to a crude approximation, the integrated intensities of equimolar amounts of As_4O_9 and As_4O_8 would be in the ratio 3:2.

Figure 2(*a*)—(*c*) clearly show that the relative proportions of these oxides vary during deposition, and using the above approach we estimate that in the initial stages the species As_4O_7, As_4O_8, As_4O_9, and As_4O_{10} are present in approximate percentage ratio 27:23:45:5. As deposition proceeds, the continuous loss of molecular oxygen from the system results in a decreasing proportion of higher oxides, and the ratio estimated after *ca.* 3 h of deposition is found to be *ca.* 42:40:15:3 respectively.

Both earlier mass spectrometric studies have attempted to establish the proportions of neutral species by considering ion intensities. Plies and Jansen[8] reported a ratio of *ca.* 30:60:10: <1 for $As_4O_{7-10}^+$, whilst Drowart[9] estimated the relative proportions of *neutral* As_4O_{7-10} to be *ca.* 34:60:6: <1 from small orifices (diameter *ca.* 0.1 mm). The agreement between these two mass spectrometric studies is good, and differs significantly from our ratios only in the relative importances of the two higher oxides. Our matrix spectra indicate significantly higher proportions of As_4O_9 and As_4O_{10} in the vapour, and there are perhaps three possible reasons for this. First, it is probable that, in the mass spectrometric studies, samples were outgassed for a longer period of time prior to making measurements. This would inevitably result in a low concentration of As_4O_{10}. Secondly, the higher oxides may be subject to excessive fragmentation even at low electron energies, and thirdly, there is an undoubted difference in orifice size between our studies and the mass spectrometric work. In our matrix experiments we employed holders with large orifices (diameter *ca.* 4 mm) and vaporisation conditions much closer to free evaporation than to Knudsen effusion.

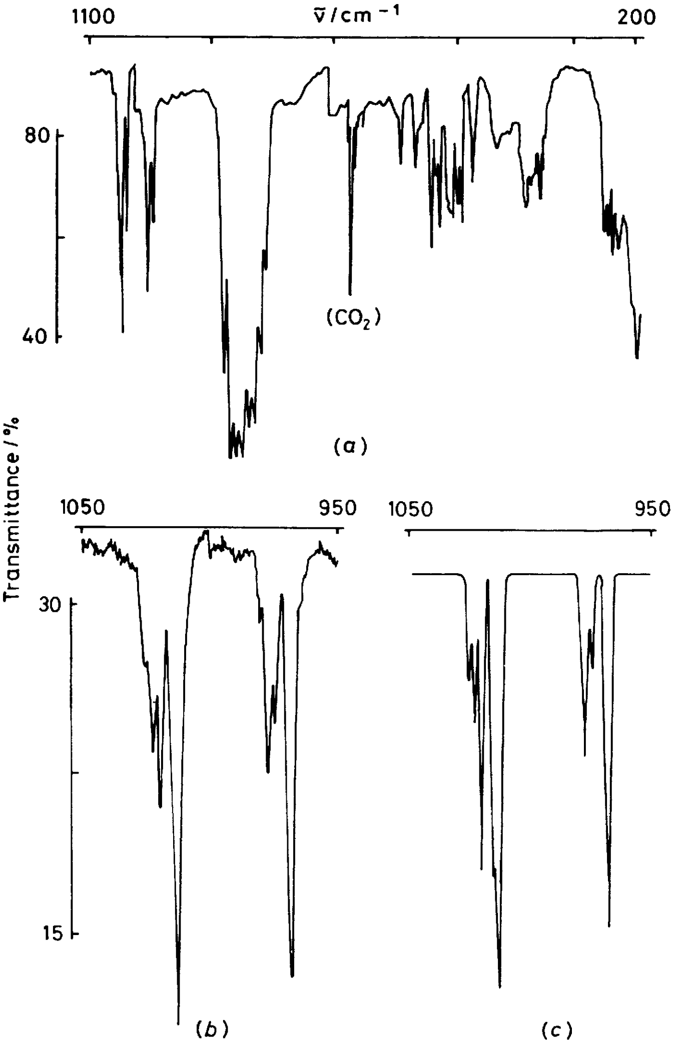


Figure 5. (*a*) Nitrogen-matrix i.r. spectrum obtained from ^{18}O-enriched arsenic(V) oxide, (*b*) high-resolution spectrum (1 050—950 cm^{-1}) of the As=O terminal stretching region, and (*c*) isotope pattern calculated for (*b*) based on 28% ^{18}O enrichment

^{18}O-*Enrichment Studies.—Vibrational analyses.* The preliminary assignment of the absorptions shown in Figures 1 and 2 was made on the basis of relative band intensities observed over a range of experimental conditions, and rested heavily on the structures proposed for the higher oxides. It is therefore desirable to confirm these assignments independently, and in principle this can be achieved using the additional spectroscopic data available from ^{18}O-enriched samples.

Figure 5(*a*) shows a typical early spectrum obtained from the vaporisation of ^{18}O-enriched arsenic(V) oxide. As one might anticipate, a large number of absorptions may be identified, and in view of our somewhat limited success in disentangling the cage modes of the all-^{16}O species, no attempt was made to unravel the spectral regions below 900 cm^{-1}. However, in the terminal As=O region we obtain a comparatively simple spectrum. This region is shown under higher resolution (after longer deposition) in Figure 5(*b*) and two points are worth

Table 2. Observed and calculated terminal As=O stretching modes (cm^{-1}) for isotopically substituted As_4O_n (n = 7—10) species

Observed[a]	Calculated[b]	Species	Assignment (terminal atoms)		Symmetry
—	1 036.0	T_d	As_4O_{10}	($^{16}O_4$)	A_1
1 026.8	1 026.8	T_d	As_4O_{10}	($^{16}O_4$)	T_2
1 025.1	1 025.1	C_{3v}	As_4O_9	($^{16}O_3$)	A_1
1 022.7	1 023.4	C_s	As_4O_9	($^{16}O_2{}^{18}O$)	A'
1 021.8	1 021.0	C_s	As_4O_9	($^{16}O^{18}O_2$)	A'
1 019.2	1 019.2	C_{3v}	As_4O_9	($^{16}O_3$)	E
1 014.7	1 014.7	C_{2v}	As_4O_8	($^{16}O_2$)	A_1
1 012.8	1 012.8	C_{3v}	As_4O_7	(^{16}O)	A_1
1 011.6	1 011.6	C_{2v}	As_4O_8	($^{16}O_2$)	B_2
985.6	983.4	C_{3v}	As_4O_{10}	($^{16}O_3{}^{18}O$)	A_1
978.9	975.6	C_s	As_4O_9	($^{16}O_2{}^{18}O$)	A'
976.0	975.0	C_s	As_4O_9	($^{16}O^{18}O_2$)	A''
971.1	969.2	C_{2v}	As_4O_8	($^{18}O_2$)	A_1
968.0	968.1	C_{3v}	As_4O_7	(^{18}O)	A_1
967.8	968.0	C_s	As_4O_8	($^{16}O^{18}O$)	A'

[a] Accuracy ±0.5 cm^{-1}. [b] Based on force-constant parameters listed in Table 3.

Table 3. Calculated force constants (mdyn Å^{-1})* from cage and terminal vibrational analysis

Parameters used (see Figure 3) (distances in Å, angles in °)

$T(As^V{=}O)$	1.4	As^V–O–As^V	129.4	O–As^{III}–O	93.9
$R(As^V$–O)	1.77	As^{III}–O–As^{III}	135.6	O–As^V–O	97.9
$R'(As^{III}$–O)	1.79	As^{III}–O–As^V	132.1	O–As^V=O	119.4

	As_4O_7	As_4O_8	As_4O_9	As_4O_{10}
F_T	7.85	7.86	7.86	7.85
F_R	3.96	3.78	4.14	3.72
$F_{R'}$	3.62	3.46	3.38	—
F_{TR}	0.06	0.07	−0.07	−0.04
F_{RR}(As)	0.11	0.15	0.29	0.92
$F_{RR'}$	0.19	−0.02	−0.01	—
$F_{R'R'}$(As)	0.11	0.02	−0.08	—
F_{RR}(O)	—	1.27	0.67	0.76
F_{TT}	—	0.04	0.05	0.07
$F_{R'R'}$(O)	0.41	0.16	0.41	—

* 1 dyn = 10^{-5} N.

noting. First, absorptions occur in essentially two distinct spectral regions, 1 020—1 030 and 960—990 cm^{-1}, and secondly, the bands are relatively sharp. Experiments were also carried out on the vaporisation of [$^{16,18}O$]arsenic(v) oxide–tantalum mixtures in order to obtain ^{18}O data from systems known to favour the production of As_4O_7 and As_4O_8. The results of these ^{18}O studies are summarised in Table 2.

If one considers the number of different isotopic species which must contribute to these spectra, it is evident that there must be several *exact*, or *almost exact*, band overlaps, and this in turn suggests that the frequencies of the terminal As=O modes are relatively *insensitive* to ^{18}O substitution in the cage. Furthermore, as the effect of the latter will be to produce frequency shifts of up to *ca.* 30 cm^{-1} in certain of the cage modes, one might anticipate that uncertainties of this magnitude in the position of the cage modes of all-^{16}O species will also *not substantially affect* isotope patterns in the terminal region. In this event, it may be possible to interpret the $^{16,18}O$ isotope pattern in the terminal region using a force field based only on a small number of known fundamentals.

We therefore carried out a series of vibrational analyses using the program SOTONVIBP[17] in which the principal aim was to simulate the observed $^{16,18}O$ pattern in the terminal region [Figure 5(*b*)]. For each of the species As_4O_7, As_4O_8, and As_4O_9 we derived sets of principal and interaction stretching constants which generated the observed ^{16}O fundamentals (Table 1) and produced a very satisfactory simulation of $^{16,18}O$ terminal modes. Figure 5(*c*) shows the result of one such calculation using the parameters defined in Table 3, whilst Table 2 compares the observed and calculated band positions. In view of the assumptions made, the values of these parameters are by no means unique, and depend upon an essentially arbitrary assignment of cage modes. However, almost identical spectra in the terminal region may be generated using force constants based on different cage assignments, and these calculations also allowed us to explore the effect of ^{18}O enrichment in the cage on the terminal As=O frequencies. Several isotopomers, including the statistically most abundant, were studied, and typical shifts in terminal frequencies were found to be *ca.* 0.1—0.2 cm^{-1}.

The significance of these calculations lies not in the values of the actual parameters obtained (although they seem reasonable in comparison with other arsenic oxide species[5,7,11]) but in the fact that despite uncertainties in the positions of many of the cage modes, the principal features of the terminal region may be understood. Indeed, moderate agreement can even be achieved by ignoring *all* cage modes, and considering the terminal region to be derived from the overlap of $^{16,18}O$ patterns for the four species MO_4 (T_d), MO_3 (C_{3v}), MO_2 (C_{2v}), and MO, where M is a single mass chosen to represent the cage.

Conclusions

These experiments have shown that the vaporisation of arsenic(v) oxide leads to the formation of at least five arsenic oxide species: As_4O_6, As_4O_7, As_4O_8, As_4O_9, and As_4O_{10}. In particular, characteristic i.r. absorptions have been obtained for each of the higher oxides, and their spectra are interpreted on the basis of a central As_4O_6 cage structure with appropriate numbers of terminal As=O bonds. The spectra of the ^{18}O-enriched species have been interpreted for the terminal region using restricted force fields, and these calculations support the experimental observation that the high-frequency terminal stretching modes in these molecules may be effectively 'factored off' from the cage modes.

The proportions of these vapour species vary with time, and may also be altered by mixing arsenic(v) oxide with arsenic(III) oxide or a reducing agent such as tantalum powder. However, it proved impossible to obtain spectra containing only one of these higher oxides, and we believe it would be difficult to study these species without the advantages of spectral subtraction and the narrow linewidths available through the use of matrix isolation.

Acknowledgements

We gratefully acknowledge the financial support of the S.E.R.C. and Central Electricity Generating Board for this work.

References

1 L. R. Maxwell, S. B. Hendricks, and L. S. Deming, *J. Chem. Phys.*, 1937, **5**, 626; see also, K. S. Krasnov, V. S. Timoshinin, T. G. Danilova, and S. V. Khandozhko, 'Handbook of Molecular Constants of Inorganic Compounds,' Israel Program of Scientific Translations, Jerusalem, 1970.
2 I. R. Beattie, K. M. S. Livingston, G. A. Ozin, and D. J. Reynolds, *J. Chem. Soc. A*, 1970, 449.
3 S. B. Brumbach and G. M. Rosenblatt, *J. Chem. Phys.*, 1972, **56**, 3110.
4 E. Rytter, S. K. Goates, and G. N. Papatheodorou, *J. Chem. Phys.*, 1978, **69**, 3717.
5 T. K. Sakano, Dissertation, University of Wisconsin, 1966 (quoted in ref. 4).
6 See, for example, C. Sourisseau and R. Mercier, *Spectrochim Acta, Part A*, 1978, **34**, 173 and refs. therein.
7 See, for example, M. L. Walker, D. E. Peckenpaugh, and J. L. Mills, *Inorg. Chem.*, 1979, **18**, 2792.
8 V. Plies and M. Jansen, *Z. Anorg. Allg. Chem.*, 1983, **497**, 185.
9 J. Drowart, 29th Annual Conference on Mass Spectrometry and Allied Topics, 24—29th May, 1981.
10 I. R. Beattie, H. E. Blayden, S. M. Hall, S. N. Jenny, and J. S. Ogden, *J. Chem. Soc., Dalton Trans*, 1976, 666.
11 See, for example, J. S. Ogden, T. J. Sibley, and S. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1983, 851; B. J. Van der Veken, F. K. Varsant, and M. A. Herman, *J. Mol. Struct.*, 1977, **36**, 225.
12 See, for example, E. B. Wilson, jun., J. C. Decius, and P. C. Cross, 'Molecular Vibrations,' McGraw-Hill, New York, 1955.
13 See, for example, B. Beagley, D. W. J. Cruikshank, T. G. Hewitt, and K. H. Jost, *Trans. Faraday Soc.*, 1969, **65**, 1219.
14 See, for example, I. R. Beattie, H. E. Blayden, R. A. Crocombe, P. J. Jones, and J. S. Ogden, *J. Raman Spectrosc.*, 1976, **4**, 313.
15 See, for example, I. R. Beattie, R. A. Crocombe, and J. S. Ogden, *J. Chem. Soc., Dalton Trans.*, 1977, 1481 and refs. therein.
16 See, for example, W. Levason, R. Narayanaswamy, J. S. Ogden, A. J. Rest, and J. W. Turff, *J. Chem. Soc., Dalton Trans.*, 1982, 2009.
17 I. R. Beattie, N. Cheetham, M. Gardner, and D. E. Rogers, *J. Chem. Soc. A*, 1971, 2240.

Received 13*th January* 1986; *Paper* 6/087