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NOTES

Infrared, Laser Raman Spectra and Normal Coordinate Analysis of Arsenous Oxide

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The vibrational spectra of arsenous oxide have been recorded in 625–4000 cm^{-1}, in i.r. region and 50–4000 cm^{-1} in the Laser Raman region. A vibrational analysis has been made on the basis of C_{3v} symmetry and the general quadratic valence force constants are reported.

A great majority of penta atomic molecules are based on tetrahedral arrangement, other possible shapes include square planar, tetragonal pyramidal, and trigonal pyramidal with an either apical or (more commonly) on equatorial position unoccupied. All these shapes correspond to formula XY_4 or its substituent derivatives, but there are some other formulae like X_2Y_3. In this paper we report the infrared spectrum and laser Raman spectrum of arseneous oxide. The frequencies of the molecule have been assigned on the basis of C_{3v} symmetry. Its vibration spectrum consists of six normal vibrations; three belonging to A_1 type symmetry species and three of doubly degenerate E type symmetry species.

Arseneous oxide was obtained from BDH Laboratory Chemicals, England. The infrared spectrum of As_2O_3 has been recorded on Perkin Elmer IH-257 double beam grating spectrophotometer in the region 625–4000 cm^{-1}. The Laser Raman spectrum has been recorded on CARE model 82 spectrophotometer equipped with argon laser of power 400 mW in the region 50–4000 cm^{-1}. The observed frequencies from these data are given in Table 1. The frequencies for all sharp bands are accurate to ± 1 cm^{-1}.

Siebert in his investigation of several polyatomic molecules has reported the spectra of S_2O_3 on the basis of C_{3v} tetrahedral symmetry. In analogy with this study we have assigned the C_{3v} point group for As_2O_3. Further an As-As stretching frequency band and two As-O stretching frequency bands also suggest a C_{3v} symmetry for As_2O_3. The two highest frequency bands centred at 711.2 cm^{-1} and 778 cm^{-1} are clearly to be assigned to the arsenic-oxygen stretching frequencies. ν_2 and ν_4 with the asymmetric stretch placed higher by analogy with numerous other oxygen coordinated compounds. This frequencies have been assigned on the basis of As-O stretching frequency in case of AsO_4 which is 813 cm^{-1}. From the knowledge of the diatomic As-As frequency, the band at 369 cm^{-1} has been assigned to As-As stretching frequency. The bands at 480 cm^{-1} and 555 cm^{-1} are clearly the bending modes. On the basis of the $\widehat{\text{O–As–O}}$ bending frequencies of arsenic-oxygen coordinated molecules, we have assigned 480 cm^{-1} to the deformation mode ν_3 and 555 cm^{-1} to $\widehat{\text{O–As–O}}$ bending frequency to ν_6. The remaining strong peak at 269 cm^{-1} has been assigned to $\widehat{\text{As—As—O}}$ bending frequency ν_5.

TABLE 1

OBSERVED FREQUENCIES OF ARSENEOUS OXIDE

	Frequency	Assignment
Laser Raman	135 w	$2\nu_4 - 2\nu_2$
	155 w	$2\nu_6 - 2\nu_3$
	182 m	$2\nu_3 - \nu_4$
	269 vs	ν_5
	369 vs	ν_1
	555 s	ν_6
	778 m	ν_4
Infrared	771.2 m	ν_2
	890 w	$2\nu_2 - 2\nu_5$
	1335 m	$\nu_4 + \nu_6$
	1375 w	$\nu_5 + 2\nu_6$
	1452 w	$2\nu_1 + \nu_2$
Far infrared	138 m	$2\nu_4 - 2\nu_3$
	153 m	$\nu_2 - 2\nu_3$
	255 w	$2\nu_1 - \nu_3$
	369 s	ν_1
	480 s	ν_3

A normal coordinate analysis of the observed bands has been carried out using Wilson's F-G matrix method[2]. The symmetry coordinates and other details are the same as reported earlier[3]. The kinetic constants of molecules appear to be of basic significance in the study of molecular vibrations[4,5]. The present set of kinetic constants and potential constants have been utilized to evaluate the vibrational mean amplitude, Coriolis coupling constants and centrifugal distortion constants of this molecule.

The mean square amplitude elements may be obtained[6] using the relations $\Sigma = L\Delta L'$ and hence the vibrational mean amplitudes of

298.16 K has been evaluated. The zeta matrix element has been evaluated from the relation $\zeta^{\alpha} = L^{-1}C^{\alpha}(L')^{-1}$,[7] where L is the normal coordinate transformation matrix. The centrifugal distortion constant for this molecule has been evaluated by making use of Kivelson and Wilson's expressions[8].

The kinetic constants and the potential constants are given in Table 2. The bond-angle interaction kinetic constants $k_{D\alpha}$, $k'_{d\alpha}$ and $k'_{d\theta}$ and the angle-angle interaction constants $k_{\alpha\alpha}$, $k'_{\alpha\theta}$ are uniquely negative for this molecule. The bond-angle interaction potential constants $f_{D\alpha}$, $f'_{d\alpha}$, $f'_{d\theta}$ and angle-angle interaction constant $f'_{\alpha\theta}$ are also negative for this molecule. It is interesting to note that $k_{D\alpha}$, $f_{D\alpha}$; $k'_{d\alpha}$, $f'_{d\alpha}$; $k'_{d\theta}$, $f'_{d\theta}$ and $k'_{\alpha\theta}$, $f''_{\alpha\theta}$ exhibit the same trend.

TABLE 2

VALUES OF KINETIC CONSTANTS (10^{-23} g); POTENTIAL CONSTANTS (10^5 dynes/cm) AND BONDED MEAN SQUARE AMPLITUDE (10^{-3} A^2) AT 298.16 K

Constants	D(As–As) d(As–0)	Dd dd	α θ	$\alpha\alpha$ $\alpha\theta'$	Dd dα'	dα'' dθ'
Kinetic constants	7.7296	0.3378	0.1772	−0.0499	−0.1826	0.0644
	2.4349	0.1482	0.2339	−0.0294	−0.0895	−0.0780
Potential constants	3.7343	0.1631	0.1181	0.0598	−0.0882	0.0336
	2.2603	0.2681	0.4942	−0.0287	−0.0059	−0.1620
Bonded mean square amplitude	1.6371	−0.0259	1.6189	−4.0603	1.3908	−0.3180
	2.1142	0.0290	1.5307	−1.4840	0.2568	0.2438

TABLE 3

VIBRATIONAL MEAN AMPLITUDE (10^{-2} A), CORIOLIS COUPLING CONSTANTS AND CENTRIFUGAL DISTORTION CONSTANTS (KHz)

Mean amplitudes	Coriolis coupling constants					Distortion constants
1_D(As–As)	ζ_4	ζ^z_{46}	ζ_{34}	ζ_{16}	ζ_{46}	D_J
1_d(As–0)	ζ_5	ζ^z_{56}	ζ_{15}	ζ_{26}	ζ_{56}	D_{JK}
1_p(As . . . As)	ζ_6	ζ_{14}	ζ_{25}	ζ_{36}		D_K
1_q(0 . . . 0)	ζ^z_{45}	ζ_{24}	ζ_{35}	ζ_{45}		
4.0461	0.2267	0.9046	0.6970	0.1867	0.2739	13.9600
4.5980	0.2595	−0.2044	−0.3291	−0.0553	0.3491	3.6400
	−0.3217	0.3078	0.6950	0.5030		65.3250
	−0.1824	−0.1654	0.1800	0.3617		

Table 3 deals with the bonded vibrational mean amplitude at 298.16 K, Coriolis coupling constants and centrifugal distortion constants. The bonded vibrational mean amplitudes obtained in the present work are in the characteristic range for As–As, As-0, As . . . 0 and 0 . . . 0. The important first order Coriolis coupling are those of the type E×E with respect to Z-axis. The second order couplings are those of the type $A_1 \times E$ and E×E with respect to X-axis and Y-axis. All the zeta constants obey the linear and quadratic sums rules of Boyd and Longuet-Higgins[9] and Oka[10] respectively. The high values of the constants ζ_{25}, ζ_{34} and ζ^{z}_{46} of this molecule suggest that the coupling between the vibrations concerned is more significant than the other couplings. The centrifugal distortion constants of this molecule are in the expected range.

REFERENCES

1. H. Siebert, *Z. Anorg. allgem Chem.*, **275**, 225 (1954).
2. E. B. Wilson, J. C. Decius and P. C. Cross, Molecular Vibration, McGraw-Hill, New York (1955).
3. S. Mohan and K. G. Ravikumar, *Acta Phys. Pol.*, **62A**, 133 (1982).
4. S. Mohan, *Acta Phys. Pol.*, **57A**, 433 (1980).
5. S. Mohan and K. G. Ravikumar, *Indian J. Pure & Appl. Phys.*, **20**, 417 (1982).
6. S. J. Cyvin, Molecular Vibrations, Mean Square Amplitudes, Elsevier Pub. Co., Amsterdam (1968).
7. J. H. Meal and S. R. Polo, *J. Chem. Phys.*, **24**, 1119, 1126 (1956).
8. D. Kivelon and E. B. Wilson, Jr., *J. Chem. Phys.*, **20**, 1575 (1953); **21**, 1229 (1954).
9. D. R. J. Boyd and H. C. Longust-Higgins, *Proc. Roy. Soc.*, **A213**, 55 (1952).
10. T. Oka, J. *Mol. Spectrosc.*, **29**, 84 (1969)

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