Infrared Spectra and Structures of Matrix-isolated Disilicon, Digermanium, and Ditin Oxides (Si_2O_2, Ge_2O_2, and Sn_2O_2)

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IN recent years there has been considerable interest in high-temperature vapour species, and the combined techniques of matrix isolation and i.r. spectroscopy have proved particularly useful in determining molecular structures.[1] This Communication describes part of an i.r. investigation of the Group IV oxides. Mass spectroscopic studies[2] of the vapours above heated Group IV oxides indicate that in addition to diatomic molecules MO (M = Si, Ge, Sn), dimeric and higher polymeric species are present, whose spectra and structures are unknown.

In our experiments, samples of the solid dioxides, monoxides, or metal–dioxide mixtures were studied, and the vapours were trapped in argon or nitrogen matrices at 15° K. The apparatus used is similar to that described by previous workers,[3] and full experimental details will be given in a later paper. Several i.r. absorptions were observed in the range 5000—200 cm.$^{-1}$. These could readily be assigned to a number of distinct molecular species by varying the experimental conditions (*e.g.* furnace temperature, matrix ratio, diffusion). As expected, all spectra showed a peak with a vibration frequency very close to that predicted from the ultraviolet spectrum of the corresponding gaseous MO molecule. These "matrix shifts" were always less than 6 cm.$^{-1}$ and indicate that the molecular parameters are not significantly perturbed by the nitrogen and argon matrices. Two peaks corresponding to a second distinct species were also prominent in each oxide system. These were further investigated using ^{18}O substitution, and in the resulting spectra, each of the two peaks became a triplet with intensity ratios *ca.* 1 : 2 : 1 for *ca.* 50% ^{18}O enrichment. Evidently this species contains two symmetrically placed oxygen atoms and, on the basis of the mass spectrometric work, may correspond to dimer M_2O_2. No other peaks associated with this species were observed over the range 5000—200 cm.$^{-1}$. Figure 1 shows the two triplets observed in the Si–O system with *ca.* 50% ^{18}O enrichment, whilst Table 1 lists all the frequencies assigned to M_2O_2.

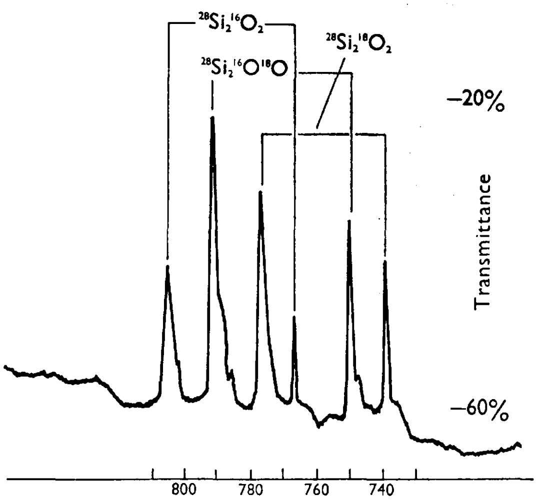

FIGURE 1. *Infrared spectrum of* Si_2O_2 *in a nitrogen matrix.*

White *et al.*,[4] and Berkowitz,[5] respectively, have shown that the structures of Li_2O_2 and several alkali halide dimers are based on a planar (V_h) rhombus, and have described the vibrational spectra in terms of a central force field. The remarkable similarity between the i.r. spectrum of Li_2O_2, and the spectra described here for M_2O_2 suggests that these three molecules also have V_h symmetry. Two i.r.-active stretching modes (B_{2u}

TABLE 1. *Infrared absorptions of* Si_2O_2, Ge_2O_2, *and* Sn_2O_2 *in nitrogen matrices*

	Frequencies (cm.$^{-1}$)			Observed ratios		Calculated ratio
M	$M_2{}^{16}O_2$	$M_2{}^{16}O^{18}O$	$M_2{}^{18}O_2$	$\frac{\nu_{B_{3u}}(^{16}O)}{\nu_{B_{3u}}(^{18}O)}$	$\frac{\nu_{B_{2u}}(^{16}O)}{\nu_{B_{2u}}(^{18}O)}$	$\left(\frac{\mu_M + \mu_{^{16}O}}{\mu_M + \mu_{^{18}O}}\right)^{\frac{1}{2}}$
Si ..	804·7 ± 0·5 766·3 ± 0·5	791·3 ± 0·5 749·4 ± 0·5	776·2 ± 0·5 739·0 ± 0·5	1·0367 ± 0·0005	1·0369 ± 0·0005	1·0373
Ge ..	667 ± 1 600 ± 1	652 ± 1 584 ± 1	636 ± 1 573 ± 1	1·049 ± 0·001	1·048 ± 0·001	1·0495
Sn ..	612·6 ± 0·3 523·2 ± 0·3	598·5 ± 0·3 507·3 ± 0·3	582·2 ± 0·3 496·9 ± 0·3	1·0530 ± 0·0005	1·0522 ± 0·0005	1·0529

TABLE 2. *Estimated molecular parameters for* Si_2O_2, Ge_2O_2, *and* Sn_2O_2

M_2O_2	$(F_r + 2F_\gamma/r^2)$ (millidynes/Å)	r_{M-O}(Å)†	Angle OMO
Si_2O_2	3·71	1·71	93°
Ge_2O_2	3·12	1·85	96°
Sn_2O_2	2·70	2·04	99°

† Estimated error ±0·05 Å.

and B_{3u}) are expected, together with one i.r.-active bending mode of symmetry B_{1u}. The form of the i.r.-active stretching vibrations is given in Figure 2a [assignment of the symmetry B_{2u} and B_{3u} between modes (i) and (ii) is arbitrary and depends on the choice of axes]. The model may also be considered in terms of a simple valence force potential function:—

$$2V = F_r(\Delta r_1^2 + \Delta r_2^2 + \Delta r_3^2 + \Delta r_4^2) + F_{\gamma_1}(\Delta\gamma_1^2 + \Delta\gamma_3^2) + F_{\gamma_2}(\Delta\gamma_2^2 + \Delta\gamma_4^2) \quad (1)$$

for the in-plane vibrations. F_r is the bond-stretching force constant, and F_{γ_1}, and F_{γ_2} are in-plane bending constants (Figure 2b). This is considered a more realistic function than that based on an ionic model. The frequencies of the two i.r.-active stretching modes derived in terms of these constants are:—

$$\lambda_{B_{2u}} = 4\pi^2\nu_{B_{2u}}^2 = 2(\mu_M + \mu_O)\left(F_r \cos^2\theta + \frac{2F_{\gamma_1}}{r^2}\sin^2\theta\right) \quad (2)$$

$$\lambda_{B_{3u}} = 4\pi^2\nu_{B_{3u}}^2 = 2(\mu_M + \mu_O)\left(F_r \sin^2\theta + \frac{2F_{\gamma_2}}{r^2}\cos^2\theta\right) \quad (3)$$

where μ_M, μ_O are the reciprocal masses of the atoms M and O respectively, and 2θ is the angle < OMO. These equations show that:

$$\frac{\lambda_{B_{2u}}(M_2{}^{16}O_2)}{\lambda_{B_{2u}}(M_2{}^{18}O_2)} = \frac{\lambda_{B_{2u}}(M_2{}^{16}O_2)}{\lambda_{B_{3u}}(M_2{}^{18}O_2)} = \frac{\nu^2(^{16}O)}{\nu^2(^{18}O)} = \frac{(\mu_M + \mu_{16_O})}{(\mu_M + \mu_{18_O})}$$

where $M_2{}^{18}O_2$ refers to the fully substituted ^{18}O species. Table 1 shows the observed and calculated frequency ratios for each of the two bands assigned to dimer M_2O_2. The low-frequency out-of-plane mode B_{1u} was not observed, and presumably lies below 200 cm.$^{-1}$. On the basis of the agreement between observed and calculated ratios for $\nu(^{16}O)/\nu(^{18}O)$ it appears that the molecules Si_2O_2, Ge_2O_2, and Sn_2O_2 all have planar rhombic structures.

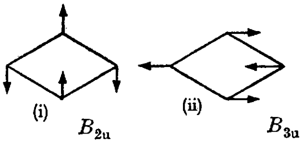

FIGURE 2a

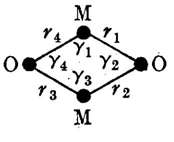

FIGURE 2b

Equations (2) and (3) contain four unknowns F_r, F_{γ_1}, F_{γ_2}, and θ. It is possible however to make certain approximations and thus to obtain molecular dimensions. Assuming $F_{\gamma_1} = F_{\gamma_2} = F_\gamma$ we have:

$$2\pi^2(\nu_{B_{2u}}^2 + \nu_{B_{3u}}^2) = (\mu_M + \mu_O)(F_r + 2F_\gamma/r^2)$$

Values for $(F_r + 2\,F_\gamma/r^2)$ are given in Table 2. These values are considerably lower than the corresponding force constants in the diatomic MO species, and this indicates a lower bond order and longer bond lengths. The latter may be estimated using the empirical relationships of Badger[6] or Allen,[7] together with data from SiO, GeO, and SnO,[8] and putting $2F_\gamma/r^2 = F_r/10$ one obtains an estimate for r_{MO} in the species M_2O_2 (Table 2). It is also possible to estimate the bond angles < OMO assuming that the terms $2F_{\gamma_1}\sin^2\theta/r^2$ and $2F_{\gamma_2}\cos^2\theta/r^2$ in equations (2) and (3) are both small. This gives $\tan\theta = \nu_{B_{3u}}/\nu_{B_{2u}}$. White *et al.*[4] have assumed that $\nu_{B_{3u}} > \nu_{B_{2u}}$ in Li_2O_2, and hence that $\theta > 45°$. The < OMO bond angles calculated on this assumption are given in Table 2.

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[8] See, *e.g.*, G. Herzberg, "Molecular Spectra and Molecular Structure. I.", D. van Nostrand, Toronto, 1950.