Infrared Spectra and Molecular Parameters of Matrix-isolated Gallium(I), Indium(I), and Thallium(I) Oxides (Ga_2O, In_2O, and Tl_2O)

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Summary The ν_3 fundamentals are observed for ^{16}O and ^{18}O species, and these frequency ratios used directly to derive bond angles: principal stretching force constants are evaluated assuming a range of interaction constants, and the corresponding bond lengths estimated *via* the Laurie–Herschbach relationship.

IN recent years the combined techniques of matrix isolation and i.r. spectroscopy have provided valuable structural information on high-temperature chemical species.[1] We describe part of an investigation into the vaporisation and condensation of Group III oxides. It is known from mass-spectrometric studies[2] that the suboxides M_2O (M = Ga, In, Tl) are present in the vapour above samples of M_2O_3. However, apart from a brief communication describing the low-resolution vapour-phase i.r. spectra[3] of Ga_2O and In_2O, and an electron-diffraction study[4] of Ga_2O and In_2O, the interpretation of which has recently been questioned,[5] little is known about these species, and no force-constant data are available.

When the vapour species present above heated Ga_2O_3 are trapped in a nitrogen matrix at 15°K, the i.r. spectrum shows an intense band at 809·4 cm.$^{-1}$. ^{18}O-enrichment gives rise to only one additional band at 768·5 cm.$^{-1}$ and the relative intensity of these two bands reflects the original $^{16}O:^{18}O$ isotopic distribution. This molecular species evidently contains only one atom of oxygen. It cannot be diatomic GaO, since $Ga^{16}O$ is known[6] to absorb at *ca.* 755 cm.$^{-1}$, and on the basis of the mass-spectrometric data,[2] can only be Ga_2O. Similar results were obtained for the In/O and Tl/O systems, and the frequencies observed are listed in the Table. A number of very weak bands were also present in some spectra: these will be discussed in a later paper. The same results were obtained when oxygen gas was passed over the heated metals, and this proved the most satisfactory method of obtaining ^{18}O enrichment.

Matrix-isolation studies on the Al_2O_3/Al system[7] have shown that in the i.r. spectrum of Al_2O, the strongest band is the antisymmetric stretch ν_3. The bands observed in this work are therefore assigned as being the antisymmetric modes of Ga_2O, In_2O, and Tl_2O. For triatomic molecules M_2O with symmetries C_{2v} or $D_{\infty h}$, the zero-order antisymmetric vibration frequency ω_3 is given by:

$$4\pi^2\,\omega_3{}^2 = (F_r - F_{rr})(\mu_M + 2\mu_O\sin^2\theta) \qquad (1)$$

where μ_M and μ_O are the reciprocal masses of atoms M and O, and 2θ is the angle M–O–M. F_r is the principal stretching force constant, and F_{rr} is an interaction constant. From equation (1) it is evident that:

$$\left(\frac{\omega_3}{\omega_3^i}\right)^2 = \frac{[\mu_M + 2\mu(^{16}O)\sin^2\theta]}{[\mu_M + 2\mu(^{18}O)\sin^2\theta]} \qquad (2)$$

where $\omega_3{}^i$ refers to the isotopically substituted $M_2{}^{18}O$.

Although this equation holds rigorously only for zero-order frequencies, it may usefully be applied to estimate a value for θ from observed i.r. transitions provided that anharmonicity corrections and matrix shifts are small.[7,8]

TABLE

I.r. absorptions and molecular parameters of Ga_2O, In_2O, *and* Tl_2O

		ν_3 $M_2{}^{16}O$ (cm.$^{-1}$)	ν_3 $M_2{}^{18}O$ (cm.$^{-1}$)	MOM	F_r (mdynes/Å)	r_{M-O}(Å)
M = Ga	This work	809·4 ± 0·1	768·5 ± 0·1	143 ± 5°	3·05 ± 0·35	1·86 ± 0·03
	Previous work	770[a]	—	140 ± 10°[b] 150°[c]	—	1·84 ± 0·01[b]
M = In	This work	722·4 ± 0·1	684·3 ± 0·1	135 ± 7°	2·67 ± 0·3	2·04 ± 0·04
	Previous work	680[a]	—	150 ± 10°[b]	—	2·02 ± 0·01[b]
M = Tl	This work	625·3 ± 0·1	591·2 ± 0·1	131 ± 11°	2·12 ± 0·25	2·19 ± 0·05
	Previous work	—	—	130°[c]	—	—

[a] ref. 3 [b] ref. 4 [c] ref. 5

The M–O–M angles given in the Table are calculated directly from the observed frequencies using equation (2). They correlate well with a statement made by Rambidi *et al.*[5] in a re-assessment of the original electron-diffraction data,[4] although the observed trend may not be significant in view of the approximations involved. The principal force constant F_r may be obtained directly from equation (1) by setting $F_{rr} = \pm 0{\cdot}1 F_r$. This parameter may then be used to estimate the bond length r_{M-O} *via* the appropriate Laurie–Herschbach relationship.[9] The bond lengths listed in the Table have been derived in this way, and correspond closely to the values obtained from electron diffraction.

These results indicate that all three fundamental vibrations of Ga_2O, In_2O, and Tl_2O are i.r.-active. A knowledge of these frequencies will provide important thermodynamic data for these high-temperature species and will also allow a complete determination of the quadratic force field.

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