# Infrared Spectroscopic Evidence for Molecular Tin(IV) Oxide ($SnO_2$)

By J. S. Anderson, A. Bos,* and J. S. Ogden
(*Inorganic Chemistry Laboratory, South Parks Road, Oxford* OX1 3QR)

*Summary* Molecular tin(IV) oxide ($SnO_2$) has been formed in a krypton matrix by reaction of the elements; isotopic splitting in the i.r. spectrum suggests that it is isostructural with carbon dioxide.

---

Apart from the well known linear molecule carbon dioxide, the simple triatomic Group IV dioxides are not well characterized. Small concentrations of silicon dioxide have been observed by mass spectrometry in the vapour over heated silica[1] and the electric deflection experiments of Klemperer *et al.*[2] suggest that this molecule is linear. However, the corresponding species $GeO_2$, $SnO_2$, and $PbO_2$ do not appear to have been observed. We present evidence that molecular tin(IV) oxide is formed when tin atoms are co-condensed at low temperatures in a krypton matrix containing a few mol % of oxygen.

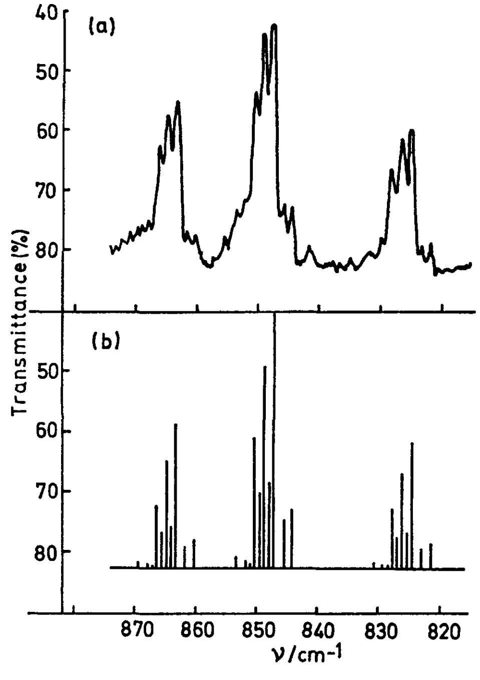

Figure (a) *Observed i.r. spectrum of* $SnO_2$ *with* $^{18}O$ *enrichment;* (b) *calculated spectrum.*

Mass spectrometric work on the vaporization of tin oxides[3] has shown that the species SnO, $Sn_2O_2$, $Sn_3O_3$, and $Sn_4O_4$ are all present in the vapour phase, and the i.r. spectra of these molecules have been obtained using the technique of matrix isolation.[4] The apparatus used for this work has been described elsewhere.[5] When tin atoms were condensed at 16 K in a matrix of 90% Kr and 10% $O_2$, a new i.r. band was observed at 863·1 $cm^{-1}$ in addition to peaks characteristic of SnO and its polymers.[4] Under high resolution, this new band was resolved into seven components, the intensities of which reflected the isotopic abundances expected for a molecule containing one atom of tin. When the experiment was repeated using $^{18}O$ labelling (90% Kr, 2·2% $^{16}O_2$, 5·3% $^{16}O^{18}O$, and 2·5% $^{18}O_2$), two additional bands were observed at 847·2 and 824·7 $cm^{-1}$. Under high resolution, the fine structure of these bands again indicated that there was a single tin atom in the molecule. The Figure shows both the basic triplet pattern observed on $^{18}O$ enrichment and the multiplet splitting on each band due to the tin isotopes. The observed frequencies are listed in Table 1.

The basic triplet pattern indicated that the molecule contained two equivalent atoms of oxygen, and the bands were thus assigned to molecular $SnO_2$ with symmetry $C_{2v}$ or $D_{\infty h}$. No other bands were observed which could be assigned to this species. If the molecule were linear, the symmetric stretch $\nu_1$ would not be active in the i.r., and although the bending frequency $\nu_2$ would be i.r. active, it could well lie below the limit of our spectrometer. The observed band would thus be identified as the antisymmetric stretch $\nu_3$. For a $C_{2v}$ structure, $\nu_1$ is active, but is expected to be much less intense than $\nu_3$. The observed band was therefore assigned as $\nu_3$ for either symmetry.

For a $C_{2v}$ or $D_{\infty h}$ structure, the ratio of the antisymmetric vibration frequencies on symmetric isotopic substitution is given by equation (1),[6] where $\omega$ is the zero order frequency,

$$\omega_3/\omega_{3i} = [(\mu_O + 2\mu_{Sn}\sin^2\alpha)/(\mu_O + 2\mu_{Sn}\sin^2\alpha)_i]^{\frac{1}{2}} \qquad (1)$$

$\mu_O$ and $\mu_{Sn}$ are the reciprocal masses of oxygen and tin respectively, $2\alpha$ is the angle ∠OSnO, and the subscript "i" refers to the isotopically substituted molecule. If anharmonic corrections and matrix shifts are small, the zero

Table 1

*Observed frequencies* ($cm^{-1}$) *and suggested assignments of peaks observed for matrix isolated* $SnO_2$

| Tin isotopes | 116 | 117 | 118 | 119 | 120 | 122 | 124 |
|---|---|---|---|---|---|---|---|
| Oxygen/oxygen isotopes | | | | | | | |
| 16/16 | 866·1 | 865·1 sh | 864·6 | 863·6 sh | 863·1 | 861·5 | 860·1 |
| 16/18 | 850·2 | 849·2 sh | 848·7 | 847·6 sh | 847·2 | 845·6 | 844·3 |
| 18/18 | 828·0 | 827·0 sh | 826·3 | 825·2 sh | 824·7 | 823·1 | 821·6 |

Absolute frequency accuracy, ±0·3 $cm^{-1}$; relative frequency accuracy, ±0·1 $cm^{-1}$.

TABLE 2

*Observed and calculated frequency ratios for isotopic* $SnO_2$ *species*

| | Molecules | Observed frequency (cm$^{-1}$) | Observed ratio | Calculated ratio For $D_{\infty h}$ | Calculated ratio For $C_{2v}$, $\alpha = 75°$ |
|---|---|---|---|---|---|
| Pair 1 | $^{16}O^{120}Sn^{16}O$ | 863·1 | 1·0466 | 1·0470 | 1·0477 |
| | $^{18}O^{120}Sn^{18}O$ | 824.7 | | | |
| Pair 2 | $^{16}O^{116}Sn^{16}O$ | 866·1 | 1·0069$_8$ | 1·00706 | 1·00668 |
| | $^{16}O^{124}Sn^{16}O$ | 860·1 | | | |
| Pair 3 | $^{18}O^{116}Sn^{18}O$ | 828·0 | 1·0077$_9$ | 1·00774 | 1·00733 |
| | $^{18}O^{124}Sn^{18}O$ | 821·6 | | | |

order frequencies ($\omega$) may be approximated[7] by the observed frequencies ($\nu$) in this expression. In Table 2 we have compared the ratio of the observed frequencies of selected pairs of molecules with the ratio calculated firstly for the $D_{\infty h}$ structure, and secondly for a $C_{2v}$ structure with $\angle$OSnO = 150° ($\alpha = 75°$). For pair 1 the calculated ratio increases for a decrease in angle $2\alpha$; the observed ratio is slightly less than predicted for a linear $SnO_2$. For pairs 2 and 3 the observed ratios are very close to those expected for a linear molecule. Like $CO_2$ and $SiO_2$, the $SnO_2$ molecule thus appears to be linear.

From the frequencies observed for the three isotopically substituted molecules, $^{16}O^{120}Sn^{16}O$, $^{16}O^{120}Sn^{18}O$, and $^{18}O^{120}Sn^{18}O$, the principal Sn–O force constant $F_r$ and the interaction constant $F_{rr}$ may be calculated, using standard expressions,[6,8] giving equations (2) and (3). In particular,

$$F_r = 536{\cdot}3 \pm 0{\cdot}2 \text{ N m}^{-1} \tag{2}$$

$$F_{rr} = -18{\cdot}1 \pm 0{\cdot}2 \text{ N m}^{-1} \tag{3}$$

the value for $F_r$ may be compared with the value of the force constant[9] in gaseous diatomic $^{120}Sn^{16}O$ of 562·3 N m$^{-1}$.

Financial support from the S.R.C. is acknowledged.

(*Received, August 26th,* 1971; *Com.* 1496.)

[1] R. F. Porter, W. A. Chupka, and M. G. Inghram, *J. Chem. Phys.*, 1955, **23**, 216.

[2] M. Kaufman, J. Muenter, and W. Klemperer, *J. Chem. Phys.*, 1967, **47**, 3365.

[3] R. Colin, J. Drowart, and G. Verhaegen, *Trans. Faraday Soc.*, 1965, **61**, 1364; J. Drowart and P. Goldfinger, *Angew. Chem. Internat. Edn.*, 1967, **6**, 581.

[4] J. S. Ogden and M. J. Ricks, *J. Chem. Phys.*, 1971, **53**, 896.

[5] J. S. Anderson and J. S. Ogden, *J. Chem. Phys.*, 1969, **51**, 4189.

[6] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, New York, 1959.

[7] J. W. Hastie, R. Hauge, and J. L. Margrave, *J. Inorg. Nuclear Chem.*, 1969, **31**, 281.

[8] J. L. Griggs, jun., K. N. Rao, L. H. Jones, and R. M. Potter, *J. Mol. Spectroscopy*, 1965, **18**, 212.

[9] G. Herzberg, "Molecular Spectra and Molecular Structure", Van Nostrand, New York, 1959, vol. 1.