Mössbauer Studies of Matrix-isolated SnO Molecules

By A. BOS and A. T. HOWE*
(*Inorganic Chemistry Laboratory, South Parks Road, Oxford* OX1 3QR)
B. W. DALE
(*Materials Physics Division, A.E.R.E., Harwell*)
and L. W. BECKER
(*Nuclear Physics Division, A.E.R.E., Harwell*)

Summary The Mössbauer spectrum attributed to matrix-isolated SnO molecules shows an unusually large quadrupole splitting, which has been related to possible bonding schemes.

CALCULATIONS of Mössbauer parameters are frequently complicated by the difficulties inherent in theoretical treatments of bulk solids. However, the study of isolated atoms or molecules trapped in inert solid matrices offers more promise, and Mössbauer parameters have recently been reported for several matrix-isolated species.[1-4] From the spectra of Fe[1,2] and Sn[4] atoms in their essentially free states a well-defined calibration point has been determined for the respective isomer shift scales, and from the quadrupole splittings observed for the Fe_2[1,2] and Sn_2[4] molecules estimates of the respective excited state quadrupole moments have been made.

We report here the ^{119}Sn Mössbauer spectrum attributed to matrix-isolated SnO molecules. In conjunction with calculated electronic configurations the results may provide a second calibration point on the Sn isomer shift scale. Since both the external and valence-electron environments of Sn in the SnO molecule are very asymmetric compared with those found in normal Sn^{II} compounds, the data should also help in resolving the conflicting interpretations of Sn^{II} quadrupole splittings.[5–7]

SnO molecules, effused from a modified alumina Knudsen cell containing SnO_2 at 1200—1300 K, were co-condensed with a large excess of argon or nitrogen on to a beryllium disk at 4·2 K. Mass spectrometric studies[8] have established that there is only *ca.* 1% of other Sn-containing species (mainly Sn_2O_2) in the vapour with the SnO molecules and O_2 under the above conditions.

The Figure shows the spectra obtained at various matrix ratios using either argon or nitrogen.

The parameters of the doublet present at high dilution in both argon and nitrogen (Figure, a and b) can be assigned to SnO molecules on the basis of both the high dilution used and the i.r. evidence. In dilute nitrogen matrices deposited at 15 K, i.r. studies have shown that molecular SnO is at least four times as predominant as any other species.[9] A computer fit to the spectra for two peaks plus baseline curvature showed that the isomer shifts, relative to $BaSnO_3$ at 300 K, did not differ significantly for the two matrices (3·02 and 3·04 mm s^{-1} for argon and nitrogen, respectively). However, the quadrupole splittings (4·10 and 4·40 mm s^{-1}, respectively) showed a slight dependence on the local matrix environment.

Matrix b after annealing at 34·5 K, showed peaks having a smaller quadrupole splitting superposed on the original doublet. These additional peaks correlate with the presence of simple polymers of the type found in the i.r. studies of similarly annealed matrices. The comparative area of the total resonance remained unchanged after annealing, indicating that the monomeric and polymeric species have similar Mössbauer *f* factors. The difference between the spectra of the SnO molecule and its polymers can be seen from spectra c and d. The predominant component in the most concentrated matrix has values of the isomer shift = 2·82 mm s^{-1} and quadrupole splitting = 2·33 mm s^{-1} approaching those of either of the two forms of bulk SnO (IS = 2·71 and 2·60 mm s^{-1} and QS = 1·45 and 2·20 mm s^{-1} for the tetragonal and orthorhombic forms, respectively[10]).

The most notable feature of the spectrum of SnO molecules is the large quadrupole splitting. In the case of a linear molecule possible electric field gradients at the Sn nucleus arising from non-bonding and σ-bonding p_z electrons and from the external effects of the charge polarisation of the molecule are of the same sign, and are opposed only by the effects of p_x and p_y π-bonding electrons. The magnitude of the dipole moment of the gas-phase molecule[11] suggests a structure $Sn^{+0\cdot5}O^{0\cdot5}$ intermediate between Sn^+–O^- and Sn=O. The valence electric field gradient V_{zz} in these structures has a maximum value when the 5*s* and 5*p* electrons are completely *sp* hybridised resulting in an imbalance of 1·5 and 1p_z electrons for the two forms, respectively. If the electric field gradient arising from the charge imbalance on the molecule is assumed to be small, as found in other highly asymmetric structures,[12] a lower limit of *ca.* 3·0 mm s^{-1} can be placed on the quadrupole splitting due to one p_z electron, which provides support for the previously estimated values of 2·97[5] and 3·5 mm s^{-1}.[4]

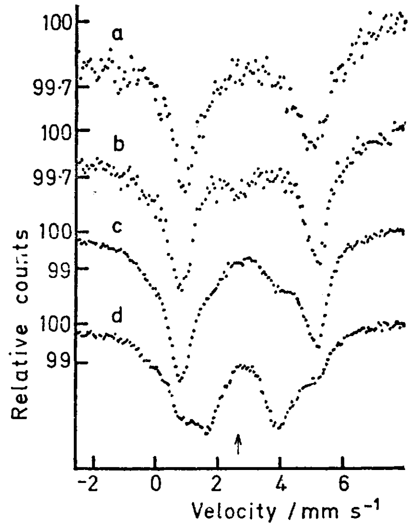

FIGURE. ^{119}Sn *Mössbauer spectra obtained at* 4·2 K *from matrices having* SnO : Ar ca. 1 : 10,000 (a) *and* SnO : N_2 *ca.* 1 : 3000 (b), 1 : 400 (c), and 1 : 100 (d). Sn *content* 20—400 μg cm^{-2} (90% ^{119}Sn). *The arrow indicates the position of a tin impurity peak derived from the thermocouple solder.*

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