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Thermodynamic Study of Tin Sulfide and Lead Sulfide Using a Mass Spectrometer*

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A mass-spectrometric investigation of the vapor in equilibrium with solid SnS, solid PbS, and a mixture of SnS and PbS has yielded the following reaction enthalpies:

$SnS(s) \rightarrow SnS(g)$	$\Delta H_{298}{}^0 = 52.6 \pm 1.6$ kcal/mole
$2SnS(s) \rightarrow Sn_2S_2(g)$	56.5 ± 5.0
$PbS(s) \rightarrow PbS(g)$	55.7 ± 1.6
$2PbS(s) \rightarrow Pb_2S_2(g)$	66.6 ± 5.0
$PbS(g) \rightarrow Pb(g) + \frac{1}{2}S_2(g)$	28.8 ± 2.6
$Sn_2S_2(g) \rightarrow 2SnS(g)$	48.7 ± 5.0
$Pb_2S_2(g) \rightarrow 2PbS(g)$	44.8 ± 5.0
$SnPbS_2(g) \rightarrow SnS(g) + PbS(g)$	$46.5 \pm 5.0.$

The dissociation energies of gaseous SnS and PbS were determined to be $D_0{}^0(SnS) = 110.1 \pm 3.0$ kcal/mole, $D_0{}^0(PbS) = 79.1 \pm 2.8$ kcal/mole and are compared with the spectroscopically determined values.

INTRODUCTION

THE vaporization of tin sulfide was studied and its vapor pressure determined as a function of temperature by different methods by Hsiao and Schlechten,[1] Richards,[2] St. Clair, Shibler, and Solet,[3] and Klushin and Chernykh.[4]

The vaporization of lead sulfide was noted by Pelouse and Fremp[5] and its vapor pressure measured by Schenck and Albers,[6] Veselowskii,[7] Hsiao and Schlechten,[1] Sudo,[8] and Miller and Abdeev.[9]

The molecule SnS has been the subject of several spectroscopic investigations[10–17] from which molecular constants for the ground and a number of excited states were derived. In particular, a dissociation energy $D_0{}^0(SnS) = 111 \pm 6$ kcal/mole was determined spectroscopically by Barrow, Drummond, and Rowlinson.[16] The latter authors suggested that a supposed predissociation[11,12] leading to a lower value, $D_0{}^0(SnS) \leq 68.5$ kcal/mole may well be reinterpreted as an interaction between neighboring excited states.

The molecule PbS was studied by optical spectroscopy by Rochester and Howell,[18] Bell and Harvey,[19] and Vago and Barrow.[20] While the electronic ground state was determined to be a $^1\Sigma$ state,[18,19] a convergence limit was obtained[20] for an excited state of this molecule at about 104.9 kcal/mole. From thermochemical data, Brewer[21] obtained 75 kcal/mole for the dissociation energy.

The present paper reports a mass-spectrometric investigation of the vaporization of tin sulfide, lead sulfide, and a mixture of tin and lead sulfides.

EXPERIMENTAL

The main features of the mass spectrometer and Knudsen effusion cell design have been described previously.[22–24] In the present work, small quartz cells containing the samples were placed inside molybdenum crucibles heated by radiation from a tungsten filament surrounding it. Temperatures were measured with a Pt–PtRh (10%) thermocouple. The thermocouple junction was placed beneath the quartz cell within the

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TABLE I. Approximate appearance potentials in eV (A.P.) and relative ion intensities for nominal 70 eV electrons (I).

MeS		S^+	S_2^+	Me^+	MeS^+	Me_2^+	Me_2S^+	$Me_2S_2^+$
SnS	(A.P.)	16.5 ± 2.0	...	12.5 ± 0.5	9.7 ± 0.5	16.5 ± 1.0	12.4 ± 1.0	9.4 ± 0.5
	(I)[a]	8×10^{-2}	$<10^{-4}$	8.2×10^{-2}	1	3.6×10^{-3}	6.7×10^{-3}	4.2×10^{-2}
PbS	(A.P.)	16.0 ± 2.0	9.6 ± 0.5	7.5 ± 0.5 and 11.6 ± 0.5	8.6 ± 0.5	...	...	9.2 ± 0.5
	(I)[a]	3.0×10^{-2}	2.1×10^{-2}	2.4×10^{-1}	1	$<10^{-4}$	$<10^{-4}$	6.0×10^{-3}

[a] Relative ion intensities are given at the mean temperature of the range investigated.

molybdenum crucible. To avoid temperature errors due to thermal conduction through the thermocouple wires, these were chosen very thin (0.1 mm in diameter), insulated by tiny quartz tubes and wound in several coils placed beneath the quartz cell, within the molybdenum crucible.

Effusion holes of 4 to 8×10^{-3} cm^2 were used in different experiments. Their area was small compared to the area of the sample. The finite thickness of the effusion hole was taken into account and an appropriate Clausing correction factor[25] applied. The weight of the samples was usually about 100 mg.

In the initial experiments with tin sulfide, commercial samples of SnS were used. As a result of oxidation these samples contain SnO, the vaporization of which was found to interfere with that of SnS. In subsequent experiments, commercial samples of SnS_2 or samples of pure SnS, prepared by reduction[26] of SnO by H_2S, were used. The reason for using SnS_2 is that this substance decomposes at low temperatures to SnS and a complex mixture of polyatomic sulfur molecules. If the SnS_2 samples contain oxides, these are simultaneously reduced to SnS, as shown by the effusion of SO_2 molecules. These processes were observed in the mass spectrometer at about 500°K.

The PbS samples were either prepared[26] from PbO or taken from natural galena crystals.

EXPERIMENTAL RESULTS

A. Composition of the Vapor

1. SnS

The atomic and molecular ions, characteristic of this system and their relative intensities for nominal 70-eV electrons used for the pressure measurements are given in Table I. All of the ions were identified from their mass, isotopic distribution, and appearance potential. It was further shown that the anteceding neutral species originate from the cell by intercepting the molecular beam.[27] Approximate ionization efficiency curves were obtained for each of these ions. The linear extrapolation method was used, the energy scale being calibrated with the appearance potential of water.[28] The corrected appearance potentials are given in Table I. These, as well as the relative intensities of the ions, indicate that SnS^+ and $Sn_2S_2^+$ are parent ions, while Sn^+, Sn_2^+, and Sn_2S^+ are fragment ions. Gaseous SnS and Sn_2S_2 are thus the major components of the vapor. The S_2 decomposition pressure was below the detection limit, in contradiction with data obtained by Albers and Schol.[29] Possible trimer Sn_3S_3 and tetramer Sn_4S_4 molecules, whose intensity relative to SnS was equal or smaller than 5×10^{-4}, could not be identified with certainty.

2. PbS

The appearance potentials and the relative intensities of the ions observed in this system and identified as above are given in Table I. The appearance potential of S_2^+ measured in this work is appreciably lower than the value of 10.7 ± 0.3 obtained by Smith and Blewett[30] in a study of thermally dissociated CS_2. A lower value 8.3 ± 0.2 eV was obtained by Bradt, Mohler, and Dibeler[31] who suggested that a comparison of the appearance potentials of S_2^+ and S^+ with those of O_2^+ and O^+ would lead to a value for S_2^+ lower than 10.7 eV. The first appearance potential of Pb^+ agrees within experimental error with the spectroscopic ionization potential of lead.[32] This appearance potential was therefore attributed to the direct ionization of atomic lead present in the vapor. This interpretation is supported by the simultaneous presence in the vapor of molecular sulfur as indicated by the appearance potential of S_2^+. The appearance potentials of PbS^+ and $Pb_2S_2^+$ and their relative intensity $[I(Pb_2S_2^+)/I(PbS^+)\simeq6\times10^{-3}]$ indicated direct ionization of the corresponding molecules. The second appearance potential of the ion Pb^+,

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TABLE II. Relative ionization cross sections and multiplier efficiencies.

Molecule	Cross section	Multiplier efficiency
S_2	21	1.14
SnS	44	0.65
Sn_2S_2	70	0.50
Pb	31	0.45
PbS	35	0.45
Pb_2S_2	56	0.41

11.6±0.5 eV was ascribed to fragmentation of the PbS molecule. The difference between the measured ionization and fragmentation potentials thus gave 4.1±0.7 eV as upper limit for the dissociation energy of the PbS molecule, a value which is much less reliable than, but compatible with, the thermodynamic value to be discussed below. Measurements of partial pressures of Pb were made with electrons of less than 11.5 eV to avoid the presence of Pb^+ fragment ions in the spectra. For the measurement of PbS, Pb_2S_2, and S_2 pressures, electrons with energies between 10 and 70 eV were used.

The analysis of the composition of the vapor indicates the Pb and S_2 decomposition pressures to be low compared to the total pressure as expected from thermochemical considerations based on the heat of formation of solid PbS. This calls for a revision of statements made in the literature in this connection.[33]

3. *SnS–PbS*

In addition to the atomic and molecular ions observed in the two separate systems given above, the molecular ion $SnPbS_2^+$ was identified, its appearance potential being 9±1 eV.

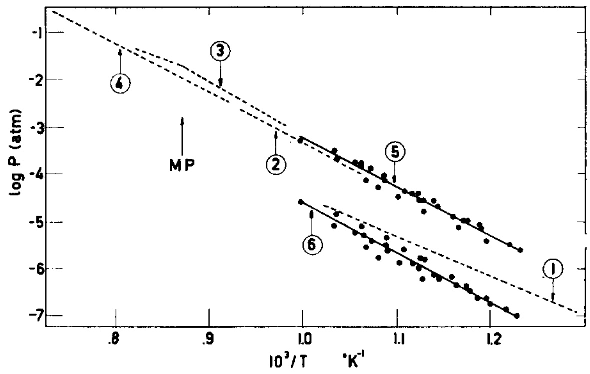

FIG. 1. Total and partial pressures above SnS. Total pressures: (1) Hsiao and Schlechten[1]; (2) Richards[2]; (3) St Clair, Shibler, and Solet[3]; (4) Klushin and Chernykh.[4] Partial pressures; this work: (5) gaseous SnS; (6) gaseous Sn_2S_2.

B. Pressure Data

Relative partial pressures were derived from the ion intensities by the relation

$$\frac{P_1}{P_2}=\frac{I_1\sigma_2(E-A_2/A_2)\gamma_2T_1}{I_2\sigma_1(E-A_1/A_1)\gamma_1T_2},$$

where P is the partial pressure, in atmospheres; I is the ion intensity in arbitrary units; σ is the relative cross section at the maximum of the ionization efficiency curve; A is the appearance potential in electron volts; E is the energy of the ionizing electrons in electron volts; γ is the secondary electron multiplier efficiency, corrected for molecular effects if necessary; and T is the absolute temperature.

TABLE III. Enthalpies of sublimation (ΔH_{298}^0).

Experiment	Molecule	Temperature range (°K)	2nd law	3rd law	Best average
63.02	SnS	835–1005	50.1±3.0	52.4±1.6	
63.03		840–965	52.5	53.3	52.6±1.6
63.04		815–970	52.1	52.0	
63.02	Sn_2S_2	835–1005	56.4±5.0	57.3±5.0	
63.03		885–965	57.0	58.2	56.5±5.0
63.04		815–970	53.0	57.1	
63.13	PbS	985–1080	52.5±4.0	56.9±1.6	
63.14		915–1080	49.7	55.1	55.7±1.6
63.15		865–1090	...	55.0	
63.18		995–1100	55.5	55.7	
63.18	Pb_2S_2	995–1100	64.5±5.0	67.8±5.0	
63.22		1129	...	66.7	66.6±5.0
63.27		1140	...	67.5	

By analogy with a number of dimeric molecules[34–37] the ratio 1.6 was used for the cross sections of S_2, Sn_2S_2, and Pb_2S_2 relative to S, SnS, and PbS, respectively. The relative ionization cross section of PbS was taken as eight-tenths of the sum of the cross sections of atomic lead and sulfur given by Otvos and Stevenson.[38] The secondary electron multiplier efficiency was estimated from the calibration[39] curve of a multiplier analogous to the one used here, which was in agreement

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TABLE IV. ΔH_{298}^0 (kcal/mole). Dissociation enthalpies of the SnS and PbS molecules from thermodynamic cycles.

	Sn	Ref.	Pb	Ref.
$MeS(g) \rightarrow MeS(s)$	-52.6 ± 1.6	this work	-55.7 ± 1.6	this work
$MeS(s) \rightarrow Me(s)+S(s)$	$+25.1\pm1.2$	44	$+22.5\pm0.5$	45
$Me(s) \rightarrow Me(g)$	$+72.0\pm0.6$	43	$+46.8\pm0.6$	43
$S(s) \rightarrow \frac{1}{2}S_2(g)$	$+15.4\pm1.5$	43	$+15.4\pm1.5$	
$\frac{1}{2}S_2(g) \rightarrow S(g)$	$+51.0\pm1.5$	46, 47, 48	$+51.0\pm1.5$	
$MeS(g) \rightarrow Me(g)+S(g)$	$+110.9\pm3.0$		$+80.0\pm2.8$	

with the curve given by Inghram, Hayden, and Hess.[40] Molecular effects were taken into account as suggested by Stanton, Chupka, and Inghram.[41]

The various relative cross sections and multiplier efficiencies including molecular effects are summarized in Table II.

In order to derive the absolute values of the pressure, a number of quantitative vaporization self-calibrations were carried out. Weighed quantities of either SnS or PbS (about 50 mg) were therefore vaporized completely and the SnS^+ or PbS^+ intensities integrated with time.

The average pressures obtained are summarized and compared with available literature data in Figs. 1 and 2. For both sulfides the pressures determinated here are in good agreement with the literature data, except for the measurements of Hsiao and Schlechten,[1] which are systematically low also for other sulfides by a factor of 5 to 10 and more.

C. Enthalpies of Sublimation and Dissociation

Enthalpies of sublimation were derived in the present study both from the second and third laws of thermodynamics and are summarized in Table III.

The necessary entropies and heat contents for solid and gaseous SnS and PbS were taken from Kelley,[42] while those of gaseous Pb and S_2 were taken from Stull and Sinke.[43] The entropies of gaseous Sn_2S_2 and Pb_2S_2 were taken identical to those of the molecules As_4 and Sb_4,[43] respectively. It was assumed that the moments of inertia are roughly the same and that the decrease in symmetry number for Sn_2S_2 and Pb_2S_2 compensates for an increase in the vibration frequencies. The entropy of $SnPbS_2$ was taken as the average of the preceding ones, corrected for the change in symmetry number.

The best average values chosen were based on the third-law results for SnS and PbS, since the entropies of these molecules are known from spectroscopic data.[10–20] In the cases of Sn_2S_2 and Pb_2S_2 the arithmetic average of all results was taken, while the agreement between second- and third-law results indicates the entropies used to be fairly accurate.

Dissociation enthalpies of both SnS and PbS molecules[44–48] were derived from the thermodynamic cycle given in Table IV.

In experiments with PbS, carried out with low-energy electrons, either Pb, S_2, or both Pb and S_2 partial pressures were measured in addition to the PbS pressure. The measurements, summarized in Table V, made it possible to calculate directly the enthalpy change for the reaction

$$PbS(g) \rightarrow Pb(g)+\tfrac{1}{2}S_2(g),$$

from the corresponding equilibrium constant. In those experiments where only Pb pressures were measured, the S_2 pressure (and vice versa) was deduced from the known fact that the sublimation is stoichiometric and

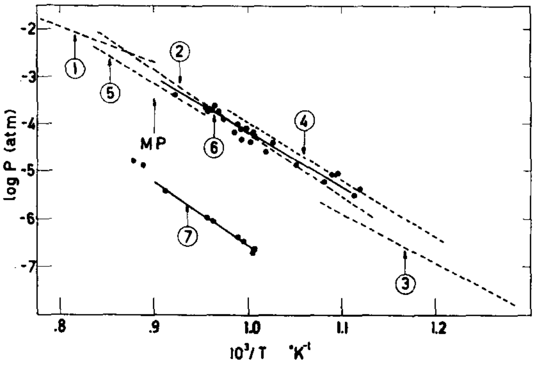

FIG. 2. Total and partial pressures above PbS. Total pressures: (1) Schenck and Albers[6]; (2) Veselowskii[7]; (3) Hsiao and Schlechten[1]; (4) Miller and Abdeev[9]; (5) Sudo.[8] Partial pressures, this work: (6) gaseous PbS; (7) gaseous Pb_2S_2.

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TABLE V. Dissociation enthalpy of the PbS molecule.

Experiment	T (°K)	log P(PbS) (atm)	log P(Pb) (atm)	log $P(S_2)$ (atm)	$D_{298}{}^0$ (PbS) (kcal/mole)
63.14	1002	−4.15	...	−5.98	79.6
63.14	1050	−3.60	...	−5.35	79.4
63.15	990	−4.30	...	−6.18	80.1
63.15	1040	−3.75	...	−5.54	79.6
63.18	1043	−3.70	...	−5.69	81.0
63.22	1007	−4.10	−5.20	...	78.6
63.22	1050	−3.62	−4.71	...	78.6
63.27	979	−4.45	−5.85	...	80.7
63.27	1118	−3.00	−4.12	...	79.2
63.27	1034	−3.80	−5.00	−5.74	79.8
63.27	1062	−3.50	−4.69	−5.36	79.0
63.27	1012	−4.02	−5.32	−6.05	80.4
63.27	1182	−2.60	−3.79	−4.72	81.4

Average $D_{298}{}^0 = 79.8 \pm 2.6$ kcal/mole

$D_0{}^0 = 78.9 \pm 2.6$ kcal/mole

hence that

$$\frac{Z(\mathrm{Pb})}{Z(S_2)} = \left[\frac{P(\mathrm{Pb})}{P(S_2)}\right]\left(\frac{64.14}{207.21}\right)^{\frac{1}{2}} = 2,$$

where Z is the number of atoms or molecules effusing per unit time.

The agreement between the dissociation energy $D_{298}{}^0$ of the PbS molecule obtained from the above thermodynamic cycle and from the partial pressure given in Table V is a verification of the sum of the heat of formation of PbS(s) and the heats of sublimation of gaseous Pb and S_2.

The dimerization energies of SnS and PbS calculated from the selected average of the sublimation enthalpies of SnS and Sn_2S_2, and PbS and Pb_2S_2 given in Table III are

$$Sn_2S_2(g) \rightarrow 2SnS(g) \qquad \Delta H_{298}{}^0 = 48.7 \pm 5 \text{ kcal/mole},$$

$$Pb_2S_2(g) \rightarrow 2PbS(g) \qquad \Delta H_{298}{}^0 = 44.8 \pm 5.$$

Finally, the dissociation enthalpy of the $SnPbS_2$ molecule into gaseous SnS and PbS, given in Table VI, was obtained from the reaction

$$2SnPbS_2(g) \rightarrow Sn_2S_2(g) + Pb_2S_2(g),$$

for which no pressure calibration is required and for which it was assumed that relative ionization cross sections and multiplier efficiencies compensate one another.

DISCUSSION

In a study of the absorption spectrum of the SnS molecule, Barrow, Drummond, and Rowlinson[16] derived the dissociation energy D_0'' of the ground state both from a repulsive state at about 56 000 cm^{-1} and from the extrapolated convergence limit at 40 850 cm^{-1} of the excited E state. Considering the only likely products forming the repulsive state to be $\mathrm{Sn}(^1D_2) + \mathrm{S}(^1D_2)$ the same authors obtained $D_0'' \simeq 56.100 - 17.853 = 38.247$ cm^{-1} or 109.4 kcal/mole. By analogy with the molecule SnO the above authors assumed the limit for the E state to correspond to dissociation into $\mathrm{Sn}(^3P)$ and $\mathrm{S}(^3P)$, and obtained $D_0'' = 111 \pm 6$ kcal/mole, the uncertainty being the spread of the ^3P sublevels of Sn and S, since it could not be decided which sublevels were involved.

These values may now be compared with the value obtained here, $D_0{}^0 = 110.1 \pm 3.0$ kcal/mole. If evaluated correctly, the experimental errors are such that the $^3P_0$ and $^3P_2$ sublevels of Sn can be excluded, since these lead to the values 116.8, 115.5, and 115.1, and 107.0, 105.8, and 105.3 kcal/mole for the $^3P_0$, $^3P_1$, and $^3P_2$ sublevels of S, respectively. The $^3P_1$ sublevel of Sn leads to the values 111.9, 110.8, and 110.3 for the same sublevels of S. The E state of SnS would thus dissociate into $\mathrm{Sn}(^3P_1) + S(^3P)$. Which ^3P sublevel of S is involved cannot be decided, although the best agreement between the two spectroscopic values derived from the repulsive state, the convergence limit of the E state and the thermochemical value might favor the $\mathrm{S}(^3P_0)$ sublevel. This agreement might be used to suggest a selected dissociation energy $D_0{}^0(\mathrm{SnS}) = 110.3 \pm 1.6$ kcal/mole.

The dissociation energy of the gaseous PbS molecule determined here is in agreement with the value obtained by Brewer[21] from the cycle given above, using a value of 60.2 kcal/mole for the heat of sublimation derived[49] from the measurements of Schenck and Albers.[6]

In an analysis of the vibrational spectrum of the PbS molecule, Vago and Barrow[20] obtained a convergence limit for an excited state of this molecule at about 4.55

TABLE VI. Dissociation enthalpy of the $SnPbS_2$ molecule.

$$SnPbS_2(g) \rightarrow SnS(g) + PbS(g)$$

Experiment	T (°K)	Ion intensities (arbitrary units) Sn_2S_2	Pb_2S_2	$SnPbS_2$	$\Delta H_{298}{}^0$ (kcal/mole)
63.25	1200	2380	100	1710	48.2
63.26	1062	3920	134	1050	46.2
	1090	4020	182	1135	46.6
	1098	947	254	614	45.8
	1115	150	1910	643	45.7
63.28	1043	1280	178	790	46.5
	1079	6060	401	2630	46.4

Average 46.5 ± 5.0

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[49] K. K. Kelley, U. S. Bureau of Mines Bull. **383** (1935).

eV or 104.9 kcal/mole. By analogy with PbO,[50] the corresponding level can presumably be correlated[51] with the elements in their $^3P_1$ state. Accordingly, if the corresponding excitation energies, 22.36 kcal/g atom for Pb($^3P_1$) and 1.13 kcal/g atom for $S(^3P_1)$, are subtracted from the convergence limit, a dissociation energy D_0^0 (PbS) of 81.4 kcal/mole is obtained in agreement with the value D_0^0 (PbS) $=79.1\pm2.8$ kcal/mole obtained here.

For the dimeric molecules Sn_2S_2 and Pb_2S_2 it is interesting to notice that the enthalpy for dissociation into SnS and PbS diatomic molecules is roughly the same and that for SnPbS, is the average of the two. Speculations about the structure of these dimeric molecules on this basis and the fact that there is no direct relation between the dimerization energies and the dissociation energies of the homonuclear metallic molecules[22] tend to favor a closed rather than a linear structure. Supporting this conclusion is the fact that these molecules have the same outer electronic structure as P_4, As_4, and Sb_4, which molecules should have either a tetrahedral or a plane square structure. Of these molecules, P_4 is indeed known to be tetrahedral.[52]

It must be emphasized however that there exists a characteristic difference in properties between Y_4 molecules of group V and $(MeX)_2$ dimers of group IV–group VI compounds. The ratio $\Delta H^0(\text{sub } Y_2)/D^0(Y_2-Y_2)=\alpha<1$ in the former case; whereas the ratio $\Delta H^0(\text{sub MeX})/D^0(\text{MeX}-\text{MeX})=\alpha'>1$ in the latter. Here ΔH^0 is the heat of sublimation and D^0 the dimerization energy. This means that in equilibrium with the condensed phase $P(Y_4)/P(Y_2)$ decreases, whereas $P(\text{MeX})_2/P(\text{MeX})$ increases with increasing temperature. This implies that for the group V elements, the bonding energy decreases from the diatomic molecules to the tetratomic molecule and to the lattice, whereas for the group IV–group VI compounds the reverse is true. The consequence is that higher polymers have to be expected for group IV–group VI molecules, as indicated by the probable presence of $(SnS)_3$ and $(SnS)_4$ molecules. For the analogous system SnO, such polymers, including $(SnO)_2$ to $(SnO)_6$ have been identified.[53] Further implications of the difference in behavior of group V and isoelectronic group IV–group VI molecule are beyond the scope of this paper and will be discussed elsewhere.

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[50] R. F. Barrow, J. L. Deutsch, and D. N. Travis, Nature **191**, 374 (1961).

[51] R. F. Barrow (private communication).

[52] G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1945).

[53] R. Colin, G. Verhaegen, and J. Drowart (to be published).