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# Molecular Structure of SbI$_3$ and BiI$_3$ from Combined Electron Diffraction and Vibrational Spectroscopic Studies[†]

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The molecular structure of SbI$_3$ and BiI$_3$ have been studied by gas-phase electron diffraction and infrared spectroscopy, BiI$_3$ has been studied by electron diffraction, and SbI$_3$ has been studied by infrared spectroscopy for the first time. Both molecules are pyramidal ($C_{3v}$ symmetry), and their geometries are characterized by the following bond lengths ($r_g$) and bond angles ($\angle_\alpha$): Sb−I 2.721 ± 0.005 Å, I−Sb−I 99.0 ± 0.3°, Bi−I 2.807 ± 0.006 Å, and I−Bi−I 99.5 ± 0.3°. Three of the four normal modes of vibration were observed for both molecules: SbI$_3$, $\nu_2 = 74.4$ cm$^{-1}$, $\nu_3 = 193.6$ cm$^{-1}$, and $\nu_4 = 54.6$ cm$^{-1}$; BiI$_3$, $\nu_2 = 59.7$ cm$^{-1}$, $\nu_3 = 163.5$ cm$^{-1}$, and $\nu_4 = 47.0$ cm$^{-1}$. A joint electron diffraction/vibrational spectroscopic analysis was also carried out, from which the harmonic equilibrium geometries were estimated. Force field parameters from a normal coordinate analysis are reported for both molecules.

## Introduction

Although the Group 15 trihalides are among the simplest possible molecules, some of them have not yet been subjected to experimental structure determination. As part of our effort to remedy this situation, gas-phase electron diffraction and infrared vibrational spectroscopic investigations of SbI$_3$ and BiI$_3$ have been carried out. An electron diffraction study of SbI$_3$ was reported more then 30 years ago,[1] and we decided to carry out a new electron diffraction experiment with the aim of a joint electron diffraction/vibrational spectroscopic analysis in order to determine the harmonic equilibrium geometry; the gas-phase infrared spectrum of this molecule is reported here for the first time. As for BiI$_3$, the present work is the first investigation of its molecular geometry.

Joint electron diffraction/vibrational spectroscopic analyses for simple molecules have two advantages.[2−4] On the one hand, they can provide a harmonic equilibrium geometry that is preferable for comparison with quantum chemical calculations. On the other hand, this technique may also provide an estimate of not yet measured vibrational frequencies.

## Experimental Section

**Vibrational Spectroscopy.** SbI$_3$ was prepared from antimony metal (Highways, 6N) and iodine (Merck, pa) and purified by sublimation prior to use, as outlined by Brauer.[5] BiI$_3$ was purchased from Aldrich (purity >99%) and used without further treatment.

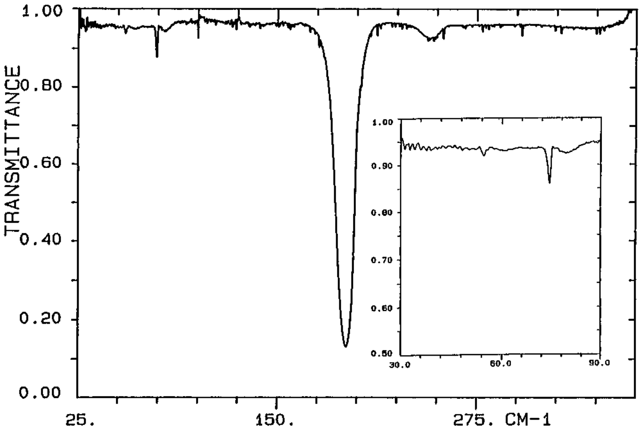

**Figure 1.** Gas-phase infrared spectrum of SbI$_3$ recorded in the 25−350 cm$^{-1}$ range.

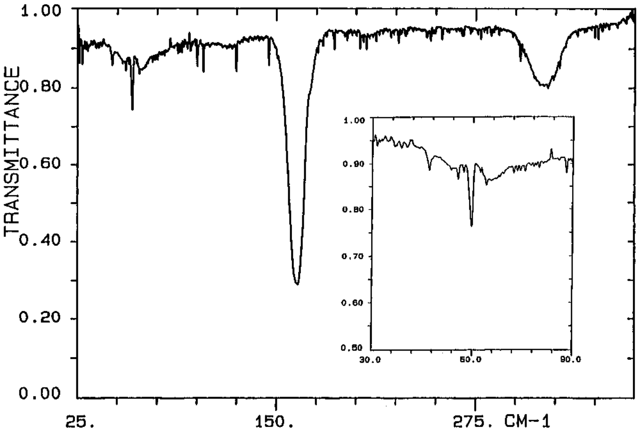

**Figure 2.** Gas-phase infrared spectrum of BiI$_3$ recorded in the 25−350 cm$^{-1}$ range.

The spectra (Figures 1 and 2) were recorded with a BOMEM DA3.02 Fourier transform spectrometer which was equipped with an optical

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[†] We dedicate this work to Professor Victor P. Spiridonov, who has pioneered the joint electron diffraction/vibrational spectroscopic analysis of molecular parameters, on the occasion of his 65th birthday.

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1996.

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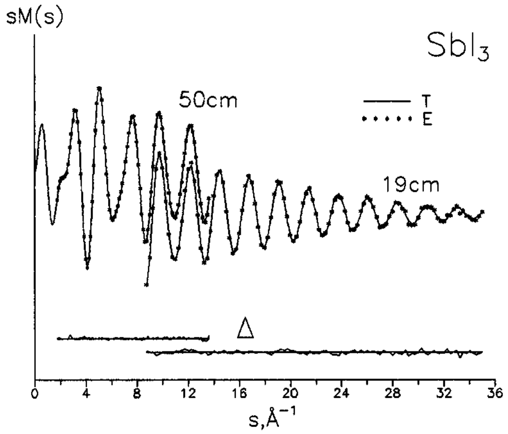

**Figure 3.** Electron diffraction molecular intensities for $SbI_3$: E, experimental; T, theoretical; Δ, difference curves.

gas cell (HTOC-2) constructed at ECN. Details of the equipment have been described previously.[6,7] The following experimental arrangements were used for the operation of the spectrometer: for the 375−100 cm$^{-1}$ range, a globar light source; for the 100−25 cm$^{-1}$ range, a Hg light source; and in both cases, a helium-cooled germanium bolometer operating at 4.2 and 1.6 K, respectively. In the whole range Si windows were used. The spectra were recorded at 0.5 cm$^{-1}$ resolution; 128 scans were coadded. The gas atmosphere in the cell was argon at a pressure of 15 mbar at room temperature. Loading of the cell was done in an argon-filled glovebox. During the measurements the cell temperature varied between 440 and 490 K for $SbI_3$ and between 590 and 760 K for $BiI_3$.

**Electron Diffraction.** Preliminary quadrupole mass spectrometric studies did not indicate the presence of any species other than the monomeric triiodide molecules in the vapor.[8] Electron diffraction experiments were carried out with the modified EG100A electron diffraction apparatus of the Budapest group[9] at two camera ranges, 50 and 19 cm. A high-temperature nozzle system[10] was used in both experiments. The nozzle material was stainless steel and molybdenum for $SbI_3$ and $BiI_3$, respectively. The nozzle temperature was 433 K for $SbI_3$ and 563 K for $BiI_3$. The accelerating voltage was 60 kV in both cases.

The electron scattering intensities were used in the following ranges, $s = 1.625-35.00$ Å$^{-1}$ for $SbI_3$ and $s = 1.75-34.50$ Å$^{-1}$ for $BiI_3$, respectively, where $s = (4\pi/\lambda)\sin(\sigma/2)$, $\lambda$ is the electron wavelength, and $\theta$ is the scattering angle. Scattering functions of ref 11 were used to calculate the theoretical molecular intensity curves presented in Figures 3 and 4.

## Structure Analysis

**Vibrational Spectroscopy.** At 473 K the spectrum of $SbI_3$ in the gas phase is dominated by a strong absorption band at 193.6 cm$^{-1}$, which we identify as the Sb−I stretch. Its value is close to that of the band at 186.5 cm$^{-1}$ in the Raman spectrum of $SbI_3$, which was assigned to the $\nu_1$ symmetric stretch by Clark and Rippon.[12]

The question now arises whether the stretching bands in the infrared and Raman spectra are overlapping $\nu_1$ and $\nu_3$ bands since both are IR active and Raman active for a pyramidal molecule of $C_{3v}$ symmetry. On the basis of existing data for group 15 trihalides, one expects $\nu_1$ and $\nu_3$ to be very close: $\delta(\nu_1-\nu_3) = 22$ cm$^{-1}$ for $SbCl_3$ and 7 cm$^{-1}$ for $SbBr_3$.[12] Also, for a pyramidal $XY_3$ molecule the $\nu_1$ fundamental is generally much less intense in the infrared than $\nu_3$, whereas the opposite holds for the Raman spectrum as can be deduced from the results of Clark and Rippon.[12] Combining this argument with the fact that the stretching band found here is highly symmetric (no indication for a shoulder around 186 cm$^{-1}$), we conclude that $\nu_3$ predominates in our infrared measurements and $\nu_1$ in the Raman measurements by Clark and Rippon.[12] With this assumption, $\delta(\nu_1 - \nu_3) = -7$ cm$^{-1}$ for $SbI_3$, which is consistent with the values found for $SbCl_3$ and $SbBr_3$.

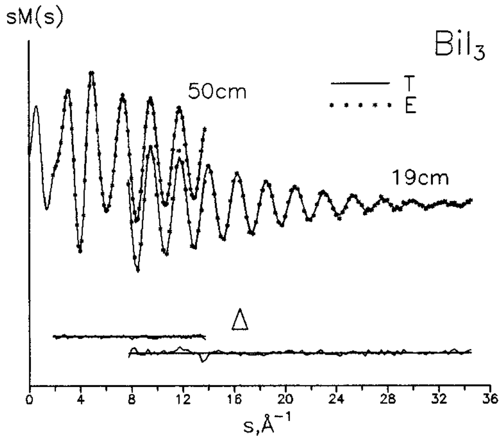

**Figure 4.** Electron diffraction molecular intensities for $BiI_3$: E, experimental; T, theoretical; Δ, difference curves.

**Table 1.** Vibrational Wavenumbers (cm$^{-1}$) of $SbI_3$(g) and $BiI_3$(g)

| | $SbI_3$ | | $BiI_3$ | |
|---|---|---|---|---|
| | Clark and Rippon, ref 12 (Raman/gas) | this study (IR/gas) | Zavalishin et al., ref 13 (IR/gas) | this study (IR/gas) |
| $\nu_1$ | 186.5 | | 158 | 162[a] |
| $\nu_2$ | 74.0 | 74.4 | 62 | 59.7 |
| $\nu_3$ | | 193.6 | 152 | 163.5 |
| $\nu_4$ | 54.3 | 54.6 | | 47.0 |

[a] Estimated on the basis of the equation of Figure 5.

When the spectrum was recorded at a higher temperature (550 K), no change in the band contour nor shift of the peak maximum was observed. However, at this temperature additional peaks were found at 246, 74.4, and 54.6 cm$^{-1}$. The peaks at 74.4 and 54.6 cm$^{-1}$ were sharp, the latter being of very low intensity. These values are almost identical with those found for $\nu_4$ and $\nu_2$ in the Raman spectrum,[12] and it is concluded that these peaks are the Q branches of these vibrations. Closer examination showed a very weak R wing for the 74.4 cm$^{-1}$ band. The peak at 246 cm$^{-1}$ is assigned to the combination band $\nu_3 + \nu_4$. All vibrational frequencies are given in Table 1.

Similar to $SbI_3$, the infrared spectrum of $BiI_3$ is dominated by a strong stretching band at 163.5 cm$^{-1}$, weak bending bands at 59.7 cm$^{-1}$ and 47.0 cm$^{-1}$, and a combination/overtone band at 317.4 cm$^{-1}$. In view of the marked similarity with the $SbI_3$ spectrum, the assignment is straightforward (Table 1). The major differences from $SbI_3$ are the much more pronounced PQR band structure of $\nu_2$ and the relatively strong combination/overtone band at 317 cm$^{-1}$. The most likely assignment of the latter is $2\nu_3$, but the peak width at half-height is too large compared to the $\nu_3$ fundamental. A possible explanation for the broadening of the $2\nu_3$ overtone is overlap with the $(\nu_1 + \nu_3)$ combination band. This would imply that, like in $SbI_3$, $\nu_1$ lies close to $\nu_3$. An Abstract, published earlier by Zavalishin et al.[13] on the gas-phase IR spectra of $BiI_3$, is in agreement with such a conclusion, although the actual values of the frequencies somewhat differ (see Table 1). It is difficult to comment on this difference due to the lack of any detail in ref 13 (nothing is given except the listing of the frequencies).

Plotting the two stretching frequencies of group 15 trihalides against each other gives a linear relationship, as shown in Figure 5. Using

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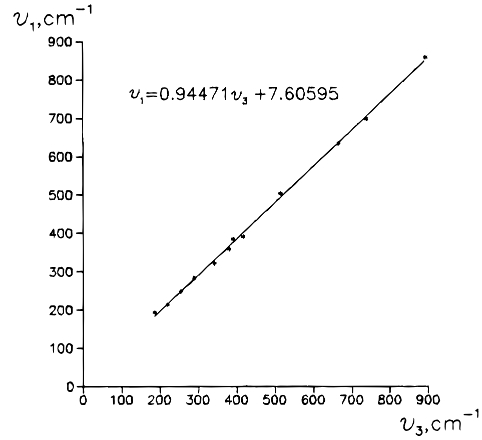

**Figure 5.** Symmetric versus asymmetric stretching vibrations of group 15 trihalides. (Data are from the following: Clark, R. J. H.; Rippon, D. M. *J. Mol. Spectrosc.* **1974**, *52*, 58. Adams, C. J.; Downs, A. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1745. Denchik, E.; Nyburg, S. C.; Ozin, G. A.; Szymanski, J. T. *J. Chem. Soc. A* **1971**, 3157 (all gas-phase data).)

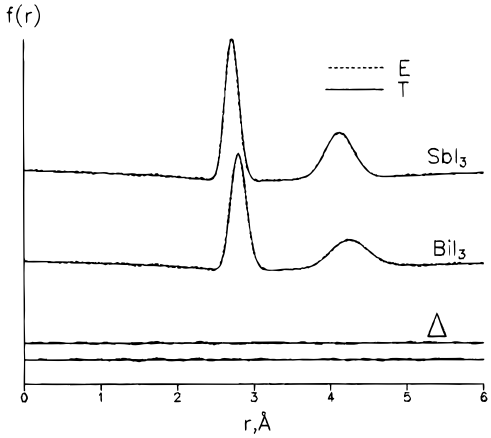

**Figure 6.** Radial distributions and difference curves of $SbI_3$ and $BiI_3$ from electron diffraction.

this empirical relationship and the measured $\nu_3$ frequency for $BiI_3$, $\nu_1$ appears to be 162 cm$^{-1}$.

**Electron Diffraction.** Since the molecular geometry of an $MI_3$ molecule is described by only two parameters, the metal−halogen and halogen−halogen distances, the assignment of their radial distribution curves (Figure 6) is straightforward.

There is appreciable vibrational anharmonicity, not only for the bond distances but also for the nonbonded distances. As expected, the vibrational amplitudes of neither distance were influenced by the asymmetry parameter, $\kappa$, but the distances themselves were. This is, of course, especially pronounced for the bond distance, but, for $BiI_3$, even the nonbonded distance changes noticeably and thus the bond angles are somewhat influenced as well.

Normal coordinate analyses have also been performed using the ASYM20 program.[14] All frequencies were available from experiment (this work and refs 12 and 13). Nonetheless, for the $\nu_1$ frequency of $BiI_3$ the value estimated by us (see Figure 5) was used instead of the value determined in ref 13 due to the disagreement between our asymmetric stretching frequencies. The underdetermined nature of such a normal coordinate analysis is well-known as far as the force field parameters are concerned. We have tried to find a set of force constants that gives the best agreement with all experimentally determined parameters, including the vibrational amplitudes. The good quality and long range of the electron diffraction intensity data and the absence of correlation among the parameters make these molecules an ideal object for such an analysis. The refinement of the force constants was carried out in a stepwise manner. The resulting force field is in good agreement with both the experimental and estimated frequencies and with the electron diffraction vibrational amplitudes. This agreement also reinforces the validity of our estimation of $\nu_1$ for $BiI_3$. Using the value communicated in ref 13 for $\nu_1$ changes the force constants only slightly. Table 2 contains the final set of force constants and the corresponding calculated vibrational amplitudes.

**Table 2.** Force Field Parameters and Vibrational Amplitudes from Normal Coordinate Analysis[a]

| parameter | $SbI_3$ | $BiI_3$ |
|---|---|---|
| $F_{11}$ | 1.589 | 1.364 |
| $F_{12}$ | 0.264 | 0.041 |
| $F_{22}$ | 0.774 | 0.659 |
| $F_{33}$ | 1.362 | 1.216 |
| $F_{34}$ | 0.253 | 0.166 |
| $F_{44}$ | 0.567 | 0.479 |
| $l_{calc}$(M−I) | 0.068 | 0.080 |
| $l_{calc}$(I···I) | 0.178 | 0.230 |

[a] Force constants ($F_{nn}$) in mdyn·Å$^{-1}$, vibrational amplitudes ($l_{ij}$) in Å. Frequencies used in the analysis are from this study, except for $\nu_1$, which is taken from ref 12 for $SbI_3$ and is estimated by the equation of Figure 5 for $BiI_3$.

**Table 3.** Structural Parameters of $SbI_3$ and $BiI_3$ from Electron Diffraction and from the Joint Electron Diffraction/Vibrational Spectroscopic Analysis[a]

| parameter (M = Sb or Bi) | $SbI_3$ this work | $SbI_3$ ref 1 | $BiI_3$ |
|---|---|---|---|
| $r_g$(M−I) | 2.721 ± 0.005 | 2.721 ± 0.005 | 2.807 ± 0.006 |
| $r_\alpha$(M−I) | 2.712 ± 0.005 | | 2.794 ± 0.006 |
| $r_e^h$(M−I) | 2.710 ± 0.006 | | 2.791 ± 0.006 |
| $l$(M−I) | 0.066 ± 0.002 | 0.066[b] | 0.080 ± 0.002 |
| $\kappa$(M−I) | $1.36 \times 10^{-5} \pm 1.8 \times 10^{-6}$ | | $2.78 \times 10^{-5} \pm 4.1 \times 10^{-6}$ |
| $r_g$(I···I) | 4.131 ± 0.009 | 4.145 ± 0.012 | 4.278 ± 0.014 |
| $l$(I···I) | 0.178 ± 0.006 | 0.173[b] | 0.234 ± 0.006 |
| $\kappa$(I···I) | $4.85 \times 10^{-5} \pm 6.03 \times 10^{-5}$ | | $4.62 \times 10^{-4} \pm 2.1 \times 10^{-4}$ |
| $\angle_a$ I−M−I | 98.6 ± 0.3 | 99.1 ± 1.0 | 99.0 ± 0.3 |
| $\angle_\alpha$ I−M−I | 99.0 ± 0.3 | | 99.5 ± 0.3 |
| $\angle_e^h$ I−M−I | 99.0 ± 0.2 | | 99.3 ± 0.3 |

[a] Distances ($r_{ij}$) and vibrational amplitudes ($l_{ij}$) are given in Å, bond angles in degrees, anharmonicity parameters ($\kappa_{ij}$) in Å$^3$. Indicated are estimated total errors, including systematic error, calculated according to ref 15. [b] Error limits not indicated.

## Results and Discussion

The geometrical parameters determined by electron diffraction are given in Table 3 for both molecules together with the earlier data[1] on $SbI_3$. The agreement of the two electron diffraction studies is excellent.

A joint electron diffraction/vibrational spectroscopic analysis has also been performed for both molecules. The results are also given in Table 3. Since the available program (see, for example, refs 3 and 4b) uses the harmonic approximation, the geometrical parameters determined by it will be the so-called "harmonic" equilibrium parameters, $r_e^h$. They are supposed to be the same as the $r_\alpha$ parameters calculated from the thermal average distances, $r_g$, with harmonic vibrational corrections ($r_\alpha = r_g - K - \delta r$, where $K$ is the perpendicular amplitude, $K = \langle(\Delta x)^2 + (\Delta y)^2\rangle/2r$, and $\delta r$ is the centrifugal distortion; see, for example, ref 16). Indeed, they agree within experimental errors.

We have tried to estimate the symmetric stretching frequency of $BiI_3$ from the joint analysis but without success. The reason

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for this may lie partly in the fact that $BiI_3$ appeared to be rather anharmonic and the available joint analysis program works only in the harmonic approximation.[4b] Another, possibly more important reason may be the unfortunate closeness of the $\nu_1$ and $\nu_3$ fundamentals. While $\nu_3$ belongs to an $E$ symmetry two-dimensional representation, $\nu_1$ is a one-dimensional $A_1$ symmetry vibration and as such has a smaller influence on the vibrational picture of the molecule, especially since the difference between $\nu_1$ and $\nu_3$ is very small. Fortunately, the harmonic equilibrium geometry is very stable and is virtually invariant to the choice of $\nu_1$.

Both molecular geometries follow the expected trend. Their bond angles are smaller than the tetrahedral angle, indicating the effect of the lone pair of electrons in the valence shell of the central atom, in accordance with the predictions of the VSEPR model.[17] Considering the molecular dimensions, the increase in bond length in going from the antimony to the bismuth trihalide is about the same for the iodides as for the chlorides[18] (0.088 and 0.082 Å for the trichlorides and triiodides, respectively, in $r_\alpha$ representation). A detailed discussion of the geometrical variations in group 15 trihalides is given in ref 19.

**Acknowledgment.** We are grateful to Prof. István Hargittai for helpful discussions. Orsolya Toke participated in the initial stages of the electron diffraction analysis of $BiI_3$. This work was supported by the Hungarian Scientific Research Fund (Grant No. OTKA T 014073).

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