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# High-Resolution He I and He II Photoelectron Spectra of the Indium Trihalides: Structure of $InI_3$ from In 4d Ligand Field Splittings and MS–X$\alpha$ Calculations

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High-resolution He I and He II photoelectron spectra of the gas-phase indium(III) trihalides have been recorded. The absence of any resolvable ligand field splitting in the In 4d spectra of indium triiodide shows that this compound is a dimer with pseudotetrahedral geometry about each In, rather than having the planar monomeric structure as postulated in earlier gas-phase He I photoelectron studies of the valence band. X$\alpha$–SW calculations on indium triiodide are also consistent with a dimeric structure. The structure of indium tribromide and indium trichloride cannot be obtained unambiguously from the In 4d, valence-band spectra or X$\alpha$–SW calculations. However, the overall evidence indicates that the tribromide is a dimer in our measurements, while the trichloride is probably mainly a monomer.

## Introduction

Over the past 15 years, a number of He I photoelectron studies of halides of the trivalent group III (13)[1] (B, Al, Ga, In) have been reported.[2-7] While the boron trihalides are gaseous at room temperature, elevated temperatures are required to vaporize the halides of the heavier group III metals. Although the boron compounds are monomeric molecules of $D_{3h}$ symmetry, the Al, Ga, and In analogues are often dimeric in the gas phase but generally dissociate at higher temperatures.[6] For example, in previous photoelectron studies of the indium trihalides,[4,6] it was claimed that dimeric species were discriminated against by vaporizing the samples at temperatures near 427 °C,[4] and the spectra were interpreted with the assumption that monomers were present.

Recent high-resolution He II (and in some cases He I) photoelectron spectra of the outer-core d levels in gas-phase zinc, cadmium, and thallium compounds[8,9] of $D_{\infty h}$ and $C_{\infty v}$ symmetries and monomeric $Me_3In$ of $D_{3h}$ symmetry[10] have shown five major peaks due to the combined effects of spin–orbit and ligand field splittings. The ligand field splitting is due mainly to the noncubic part of the ligand field (the $C_2{}^0$ term) and is proportional to the electric field gradient seen at the nucleus. The $C_2{}^0$ values are sensitive to metal–ligand bonding and structure. For example, the $R_2M$ (R = Me, Et) compounds give larger $C_2{}^0$ values than $MX_2$ (X = Cl, Br, I) compounds, while the signs of $C_2{}^0$ are opposite for $D_{\infty h}$ $Me_2Cd$ and $D_{3h}$ $Me_3In$.

In this paper, we wished to extend our studies of ligand field splittings to the indium trihalides. The lack of significant broadening or observable ligand field splitting on the In 4d levels of indium triiodide strongly indicates this compound is dimeric in this and previous photoelectron studies. The evidence for the tribromide and trichloride is not as conclusive. We have also reexamined the indium trihalide valence-band spectra; and we report MS–X$\alpha$ calculations for the triiodide valence levels that are also consistent with a dimeric structure for this molecule.

## Experimental Section

The high-resolution gas-phase UV photoelectron spectra were obtained on a McPherson ESCA-36 spectrometer using a heated inlet system described previously.[11,12] The source employed was a hollow cathode discharge He lamp.[13] The commercially obtained samples (Alfa) were loaded under $N_2$ due to their hygroscopic nature and heated slowly in situ until a reasonable count rate was achieved. The data presented were collected at 192, 268, and 378–385 °C for the triiodide, tribromide, and trichloride, respectively. The In 4d spectra were multiscanned in order to obtain reasonable counting statistics. Scans were added together with a provision for shifting in order to minimize line broadening due to differential charging effects. The spectra obtained were computer-fitted to Lorentzian–Gaussian peak shapes by using an iterative procedure.[14] He I spectra were calibrated with argon (Ar $3p_{3/2}$ = 15.759 eV) while He II spectra were calibrated with $He^+$ (He 1s = 24.587 eV).

## Results and Discussion

**Table I.** Experimental In 4d Binding Energies, Widths, and Spin–Orbit Splittings[a]

| | $^2D_{5/2}$ | | $^2D_{3/2}$ | | SO splitting, eV | |
|---|---|---|---|---|---|---|
| compd | BE, eV | fwhm, eV | BE, eV | fwhm, eV | obsd | free atom[b] |
| $In_2I_6$ | 26.58 | 0.17 | 26.46 | 0.21 | 0.87 | 0.849 |
| $In_2Br_6$ | 26.21 | 0.29 | 27.08 | 0.23 | 0.87 | 0.849 |
| $InCl_3$ | 26.60 | 0.30 | 27.44 | 0.24 | 0.84 | 0.849 |

[a] Errors are ~±0.02 eV otherwise noted. [b] Reference 15.

**In 4d Levels.** The previously unpublished He II spectra of the In 4d levels of $InX_3$ (X = I, Br) are presented in Figure 1. The experimental binding energies and assignments for all three halides are outlined in Table I. Unlike the In 4d spectra of $Me_3In$,[10] the 4d spectrum of indium triiodide shows two reasonably narrow, symmetrical components of the spin–orbit doublet with no obvious fine structure due to ligand field splitting. In fact, the width of the $^2D_{5/2}$ peak of indium triiodide ($4d_{5/2}$ = 0.169 eV) approaches the inherent In 4d line width (≤0.13 eV),[10] compared with the total $4d_{5/2}$ line width in $Me_3In$ of 0.33 eV. The line widths for the tribromide are broader than those for the triiodide at least in part due to lower count rates and greater charge shifting. Indium(I) chloride was present in varying amounts in all indium trichloride spectra due to thermal decomposition. The higher photoionization cross section of the In 4d peaks for indium(I) chloride relative to that for indium trichloride made it difficult

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(1) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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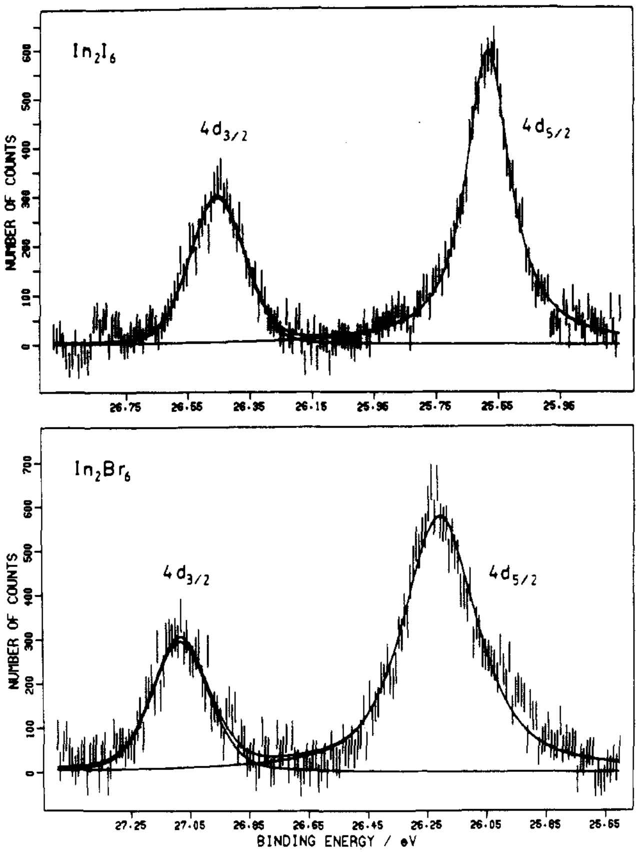

**Figure 1.** He II photoelectron spectra of the In 4d levels of $In_2I_6$ and $In_2Br_6$.

to obtain satisfactory In 4d spectra for indium trichloride. However, the line widths for the indium(I) chloride 4d spectra (In $4d_{5/2} = 0.49$ eV and $4d_{3/2} = 0.28$ eV) were much broader than those of the corresponding indium trichloride (In $4d_{5/2} = 0.30$ eV and $4d_{3/2} = 0.24$ eV).

Qualitatively, since $MX_2$ (M = Cd, Zn) compounds give smaller, but comparable, ligand field splittings and $C_2^\circ$ values relative to those for the corresponding $Me_2M$ compounds,[8] we would expect monomeric $InX_3$ compounds to have a ligand field splitting comparable to that for $Me_3In$. In contrast, the pseudotetrahedral dimeric $In_2X_6$ structure should give much smaller splittings. The lack of apparent ligand field splitting of the In 4d spectra of the indium triiodide and tribromide is thus more consistent with the dimeric structure.

For a more quantitative treatment, $C_2^\circ$ and $e^2q_nQ$ values must be examined more closely. As in previous papers, the complete Hamiltonian for the $d^9$ hole state in a linear $D_{\infty h}$ (e.g. $Me_2Cd$) or $D_{3h}$ (e.g. $Me_3In$) crystal field is[8-12]

$$\mathcal{H} = E_{4d} + C_2^\circ[3L_z^2 - L(L+1)] + C_4^\circ[35L_z^4 - 30L(L+1)L_z^2 + 25L_z^2 - 6L(L+1) + 3L^2(L+1)^2] + \lambda[\tfrac{1}{2}(L_+S_- + L_-S_+) + L_zS_z] \quad (1)$$

The Hamiltonian matrix has been diagonalized in the d-electron subspace, and equations for the five energies have been obtained.[16] These equations have the four variables $C_2^\circ$, $C_4^\circ$, $E_{4d}$, and $\lambda$, which are the axial and cubic[9] components of the crystal field and the Cd 4d or In 4d weighted average binding energy and the spin–orbit coupling constant, respectively. Using calculated values of these variables, it is possible to estimate the amount of ligand field splitting that should be observable in the indium 4d spectra due to the distorted tetrahedral symmetry about each metal atom in the dimeric complex. Since the contributions due to crystal field terms other than $C_2^\circ$ are very small, they are neglected.

**Table II.** $e^2q_nQ$ and $eq_n$ Values for Cd and In Compounds from NQR Measurements

| compd | $e^2q_nQ/h$, MHz | $Q$, cm$^2$ × 10$^{-24}$ | $eq_n$, esu cm$^{-3}$ × 10$^{16}$ |
|---|---|---|---|
| $Me_2Cd$ | 946[a] (77 K) | 0.50[a] | −2.61 |
| $Me_3In$ | 1101.7[b] (77 K) | 0.60[c] | +2.53 |
| $In_2Br_6$ | 291.1[d] (298 K) | 0.60 | 0.67[e] |
| $In_2I_6$ | 321.0[d] (298 K) | 0.60 | 0.74[e] |

[a] Reference 19. [b] Reference 20. [c] Reference 21. [d] Reference 18. [e] Sign not known.

**Table III.** Derived Crystal Field Parameters (eV) for the Indium Trihalides

| | | | | 5λ/2 | |
|---|---|---|---|---|---|
| compd | $C_2^\circ$ | $C_4^\circ$ | $E_{4d}$ | exptl | free atom[a] |
| $Me_2Cd$ | −0.0225 | −0.0008 | 17.747 | 0.685 | 0.699 |
| $CdBr_2$ | −0.020 | −0.0027 | 19.543 | 0.644 | 0.699 |
| $CdI_2$ | −0.023 | −0.0031 | 19.206 | 0.682 | 0.699 |
| $Me_3In$ | +0.024 | +0.0015 | 24.179 | 0.848 | 0.849 |
| $In_2Br_6$ | ~0.006 | | 26.557 | 0.875 | 0.849 |
| $In_2I_6$ | ~0.007 | | 25.931 | 0.873 | 0.849 |

[a] Reference 15.

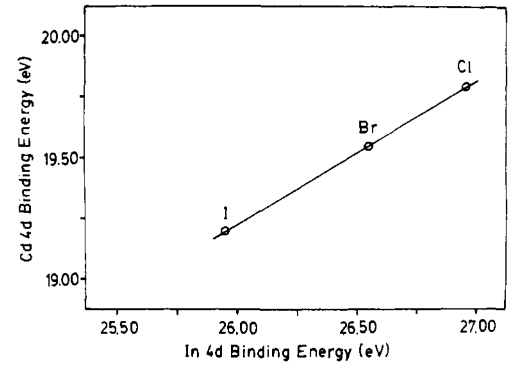

**Figure 2.** Correlation of the Cd 4d binding energies of the cadmium dihalides with the In 4d binding energies of the indium trihalides.

It is apparent[17] that the $C_2^\circ$ term transforms like the nuclear quadrupole Hamiltonian (neglecting the $\eta$ (or $C_2^2$) term):

$$\mathcal{H}_Q = \frac{e^2q_nQ}{4I(2I-1)}[3I_z^2 - I(I+1)] \quad (2)$$

where $eQ$ is the nuclear quadrupole moment of the nucleus, $eq_n$ is the field gradient set up by the ligands, and $I$ and $I_z$ are[10] the nuclear spin and nuclear spin momentum operators, respectively. It is immediately obvious from eq 1 and 2 that $C_2^\circ$ is proportional to $eq_n$. Values of $eq_n$ obtained from NQR measurements on solid $In_2X_6$ complexes that are known to be dimers for X = Br, I[18] are listed in Table II. Approximate values of $C_2^\circ$ for $In_2I_6$ and $In_2Br_6$ can be obtained from the $C_2^\circ$ value for $Me_3In$ and the ratio of $e^2q_nQ$ or $eq_n$ values of $In_2X_6$ and $Me_3In$:

$$C_2^\circ{}_{In_2X_6} \simeq \frac{e^2q_nQ_{In_2X_6}}{e^2q_nQ_{Me_3In}} C_2^\circ{}_{Me_3In} \quad (3)$$

These values (given in Table III) are very small. With the $E_{4d}$, $^5/_2\lambda$, and calculated $C_2^\circ$ values from Table III, the ligand field splittings were calculated from the energy equations[16] as being less than 0.05 eV in $In_2Br_6$ and 0.06 eV in $In_2I_6$. Since these values

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**Table IV.** Parameters Used in the X$\alpha$–SW Calculations

| region | $X$ | $Y$ | $Z$ | $R$ | $\alpha$ |
|---|---|---|---|---|---|
| In | 0.0 | 0.0 | 3.67 | 2.56 | 0.70102 |
| In | 0.0 | 0.0 | −3.67 | 2.56 | 0.70102 |
| I | 0.0 | 3.92 | 0.0 | 3.34 | 0.69984 |
| I | 0.0 | −3.92 | 0.0 | 3.34 | 0.69984 |
| I | 4.43 | 0.0 | 5.97 | 2.93 | 0.69984 |
| I | −4.43 | 0.0 | 5.97 | 2.93 | 0.69984 |
| I | 4.43 | 0.0 | −5.97 | 2.93 | 0.69984 |
| I | −4.83 | 0.0 | −5.97 | 2.93 | 0.69984 |
| outer | 0.0 | 0.0 | 0.0 | 10.36 | 0.70029 |

**Table V.** X$\alpha$–SW Calculated Binding Energies for Indium Triiodide

| peak | orbital | theor | exptl | peak | orbital | theor | exptl |
|---|---|---|---|---|---|---|---|
| A | $4b_{3u}$ | 10.05 | 9.52 | C | $1b_{1g}$ | 10.94 | 9.94 |
| | $3b_{2g}$ | 10.07 | | D | $2b_{2g}$ | 11.25 | 10.38 |
| | $2b_{1g}$ | 10.07 | | E | $2b_{2u}$ | 11.16 | 10.12 |
| | $1a_u$ | 10.10 | | | $3b_{1u}$ | 11.15 | |
| | $4b_{1u}$ | 10.09 | | F | $2b_{3u}$ | 11.58 | 10.87 |
| | $2b_{3g}$ | 10.09 | | G | $4a_g$ | 11.69 | 11.25 |
| | $5a_g$ | 10.13 | | H | $1b_{3g}$ | 11.74 | 11.72 |
| | $3b_{2u}$ | 10.18 | | I | $3a_g$ | 14.25 | 13.88 |
| B | $3b_{3u}$ | 10.71 | 9.74 | J | $2b_{1u}$ | 14.47 | 14.09 |

are much less than the full width of the component lines of the spin–orbit doublet, no ligand field splitting would be observed. If indium triiodide and tribromide were monomeric in the gas phase, one would expect splittings of the order of 0.2 eV, as observed for $Me_3In$, $Me_2Cd$, $CdBr_2$, and $CdI_2$.

The presence of InCl in the $In_2Cl_6$ spectrum indicates that mostly monomeric $InCl_3$ is present, which undergoes thermal decomposition to InCl and $Cl_2$, as previous work has indicated that $In_2Cl_6$ goes to $InCl_3$ before giving InCl.[22,23] Thus, the line broadening of the indium tribromide and particularly the indium trichloride spectra is probably due to the presence of monomer. However, the good correlation between the $E_{4d}$ of $CdX_2$ and the $E_{4d}$ of[12] $In_2X_6$, as shown in Figure 2, is probably surprising if the trichloride has a structure different from that of the tribromide and triiodide.

**Valence Bands.** In order to determine whether the valence-band spectra of the indium trihalides obtained are consistent with a dimeric structure, nonrelativistic X$\alpha$–SW calculations of $In_2X_6$ (X = Cl, Br, I) were undertaken. Only the triiodide results are reported here because the calculations for the tribromide and trichloride are not helpful in distinguishing dimer from monomer. The parameters used in the calculations are listed in Table IV. Unfortunately, gas-phase electron diffraction studies of the dimeric indium trihalides gave only average values of the metal–halide bond lengths.[24,25] However, a crystal structure of $In_2I_6$[26] gave bridging and terminal band distances whose average was in excellent agreement with Stevenson and Schomaker's gas-phase results.[25] Schwartz's $\alpha_{HF}$[27] values were used for the atomic exchange parameters. For the extramolecular and intersphere regions, a weighted average of the atomic values based on the number of valence electrons was used. The ratios of sphere radii were chosen so that the spheres overlap by 10%.[28] The calculations were done in $D_{2h}$ symmetry with the dimeric $In_2I_6$ molecule having a configuration of two approximate tetrahedra sharing a common edge. The core levels were never frozen during the iterations, and maximum $l$ values were $l = 0 \rightarrow 3$ for the metal center, the outer sphere, and the halogens. The valence-band binding energies calculated from the HOMO transition state are presented in Table V along with the experimental binding energies obtained from the He I spectra presented in Figure 3. The resolution of these spectra is similar to that published previously[6] except for our ability to resolve two components (I, J) in the lowest binding energy peak of $In_2I_6$. As noted below, this is the structurally important feature. In the $In_2Cl_6$ spectrum, the peaks labeled A′, B′, and C′ correspond to InCl peaks.[29,30]

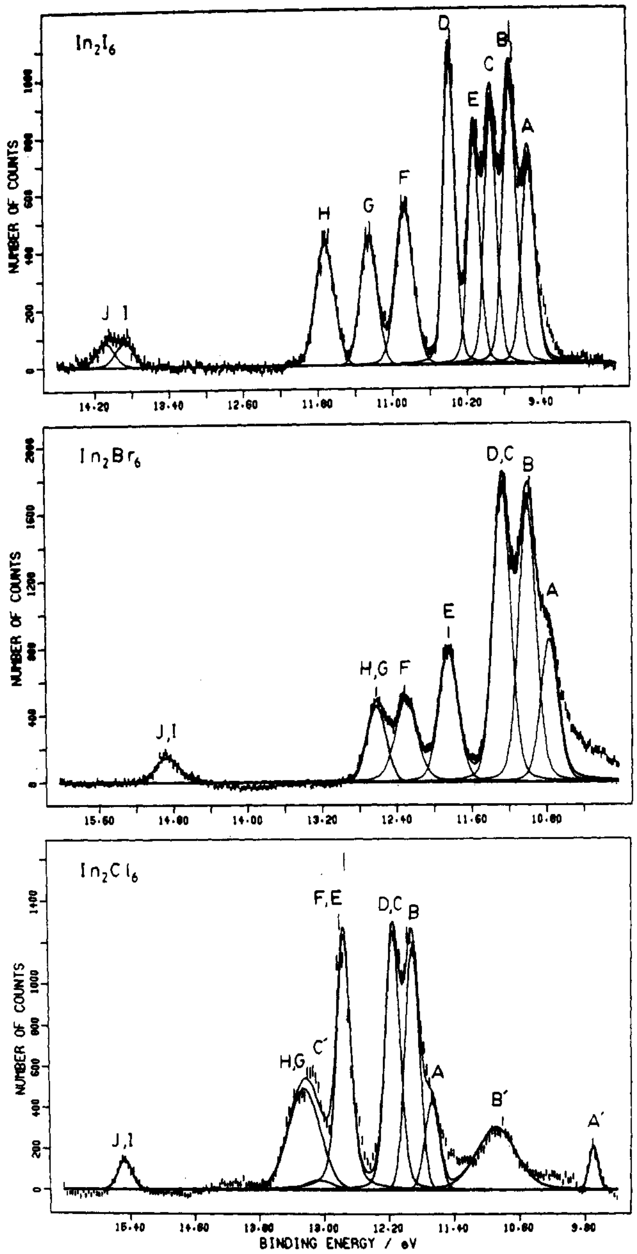

**Figure 3.** He I photoelectron spectra of $In_2I_6$, $In_2Br_6$, and $In_2Cl_6$. The poor fit in the low binding energy region is due to the contribution of He I$\beta$ valence-band peaks.

Calculations indicate that 18 orbitals should be accessible with He I radiation. However, only ten peaks are readily apparent in the valence-band spectrum of $In_2I_6$. The theoretical and experimental assignments in Table V seem reasonable; but, with the exception of peaks I and J, they are certainly not conclusive. For example, the first eight MO's (lone-pair p orbitals on the terminal halogens, Table VI) are assigned to the first peak (A) because they all have theoretical binding energies within 0.13 eV, while the $3b_{3u}$ molecular orbital (assigned to peak B) is calculated to

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**Table VI.** X$\alpha$–SW Calculated Valence Binding Energies and Charge Distributions (%) for $In_2I_6$[a]

| | | | In % | | | | $I_B$ % | | | | $I_T$ % | | | | % | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| peak | orbital | BE, eV | s | p | d | f | s | p | d | f | s | p | d | f | outer | inter |
| A | sum of 8[b] | 10.10 | | 0.05 | 0.38 | 0.12 | | 3.40 | 0.02 | | | 74.76 | | | 0.41 | 20.79 |
| B | $3b_{3u}$ | 10.71 | | 4.02 | 1.25 | 0.26 | | 45.09 | 0.04 | 0.01 | 0.08 | 36.32 | 0.24 | 0.01 | 0.65 | 11.94 |
| C | $1b_{1g}$ | 10.94 | | | 0.31 | 0.08 | | 82.84 | | | | 2.24 | 0.02 | | 0.02 | 14.48 |
| D | $2b_{2g}$ | 11.25 | | 13.26 | 0.94 | 0.22 | | | 0.21 | 0.11 | 0.71 | 68.45 | 0.70 | 0.23 | 1.06 | 14.11 |
| E | $3b_{1u}$ | 11.15 | 0.68 | 8.07 | 1.29 | 0.23 | | 43.59 | 0.13 | 0.10 | 0.21 | 32.17 | 0.36 | 0.13 | 0.34 | 12.68 |
| | $2b_{2u}$ | 11.16 | | 5.82 | 1.05 | 0.32 | 0.13 | 78.41 | 0.20 | 0.19 | | 3.31 | 0.07 | 0.03 | 0.04 | 10.43 |
| F | $2b_{3u}$ | 11.58 | | 9.40 | 0.11 | 0.04 | | 36.67 | 0.17 | 0.05 | 0.80 | 34.53 | 0.48 | 0.14 | 0.74 | 16.88 |
| G | $4a_g$ | 11.69 | 1.99 | 10.57 | 0.89 | 0.05 | 0.06 | 39.49 | 0.28 | 0.05 | 0.59 | 29.85 | 0.53 | 0.18 | 0.21 | 15.26 |
| H | $1b_{3g}$ | 11.74 | | 8.91 | 0.82 | 0.08 | | 71.19 | 0.50 | 0.08 | | 4.01 | 0.13 | 0.05 | 0.02 | 14.21 |
| I | $3a_g$ | 14.25 | 35.35 | 0.17 | 0.09 | 0.17 | 5.00 | 23.91 | 0.84 | 0.45 | 4.38 | 15.31 | 1.09 | 0.34 | 0.15 | 12.76 |
| J | $2b_{1u}$ | 14.47 | 40.63 | 0.10 | | 0.27 | | 18.73 | 2.54 | 0.67 | 5.90 | 16.61 | 1.25 | 0.38 | 0.27 | 12.64 |

[a] HOMO transition state. [b] Average value for each parameter.

be ~0.6 eV to higher energy. On the other hand, even though valence-band intensities are often not nearly proportional to the number of MO's, it is still surprising that peak A from eight MO's is less intense than peak B from one MO.

Bridging-halogen lone-pair orbitals ($1b_{1g}$ and $2b_{2u}$, Table VI) are assigned to peaks C and E in the valence-band spectra. Peaks B, D, E, F, G, and H correspond to bonding overlap between metal and halogen p orbitals. The highest binding energy peaks I and J are assigned to $3a_g$ and $2b_{1u}$ orbitals involving overlap between indium 5s and halogen p orbitals. Our valence-band assignments differ considerably from those given for the dimeric $Al_2Cl_6$ and $Al_2Br_6$ compounds by Lappert et al.[7] from their interpretation of ab initio calculations. If their reasoning is applied to the experimental and theoretical results for $In_2I_6$, then the five peaks A–E would be assigned to terminal-halogen lone-pair p orbitals with an experimental energy range of 0.86 eV. Peak F would be assigned to the $3b_{3u}$ and $1b_{1g}$ orbitals with a theoretical energy separation of 0.23 eV. Six orbitals involving overlap between the metal and halogen p orbitals would then be distributed among peaks G and H. Again, this assignment would not be consistent with the observed orbital intensities.

The important structural feature of the $In_2I_6$ valence-band spectrum is that the dimer calculation predicts a splitting of the $3a_g$ and $2b_{1u}$ orbitals of ~0.2 eV, in good agreement with the observed splitting of peaks I and J. Since the corresponding peak of the $InI_3$ monomer would be assigned to the nondegenerate $a_1'$ orbital, the experimental and theoretical I,J splitting provides strong evidence for the dimer structure. Unfortunately, for the tribromide and trichloride, no splitting of peaks I and J is obtained, experimentally or theoretically. The valence-band spectra are thus not useful in determining the structure of these two compounds.

Our evidence that the photoelectron spectra of the indium triiodide and tribromide indicate a dimeric structure is supported by other gas-phase studies. Brode's gas-phase electron diffraction studies[24] of the gallium and indium trihalides found all except gallium(III) iodide to be dimeric. A later study by Stevenson and Schomaker[25] supported these conclusions.

Several high-temperature Raman studies of the indium(III) halide melts and vapors have been reported.[31-33] Even at 627 °C, Radloff[31] found an appreciable contribution of the dimeric species to the gaseous spectra of indium(III) chloride and bromide. Beattie[32,33] found evidence of dimeric indium(III) iodide in the melt and the vapor at 480 and 675 °C.

From vapor-pressure and absorption studies, Kuniya[22,23] found that below 350 °C indium(III) chloride existed as a dimer and that between 350 and 400 °C progressively more monomer was obtained. At approximately 600 °C, the presence of indium monochloride was observed, suggesting a further decomposition of the monomer. Since relatively high temperatures were required for us to obtain indium(III) chloride spectra, this spectrum is probably due to the presence of monomer and its decomposition product, indium(I) chloride.

## Conclusions

The absence of ligand field splitting on the In 4d photoelectron peaks of gas-phase indium(III) triiodide provides strong evidence that this compound has the dimeric structure rather than the planar monomeric structure. X$\alpha$–SW calculations for $In_2I_6$ are consistent with the dimer assignment and provide a good explanation for the splitting of the ~14.5-eV peak. The valence-band spectra may now be readily assigned without postulating unusual pyramidal ground states[4] or second-order spin–orbit splitting.[6] Previous gas-phase electron diffraction, Raman, and absorption studies also indicate that, at our running temperatures, the dimeric structure should predominate for the triiodide and tribromide.

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