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Theoretical characterization and many-body expansion analysis of BF_3, BCl_3, AlF_3 and $AlCl_3$ interactions

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Summary. Metalloid–nonmetal and Metal–nonmetal interactions of BF_3, BCl_3, AlF_3 and $AlCl_3$ were examined at the matrix Hartree Fock level of *ab initio* theory. Structural and energetic properties, many-body expansion convergence, short- and long-range components of interaction energies, and group-theoretical parameters were found to uniquely characterize these interactions.

Key words: Metal–nonmetal–metalloid – BF_3, BCl_3, AlF_3, $AlCl_3$ – Theoretical characterization – Many-body expansion – Convergence – Group theoretical parameters

1. Introduction

Molecular interactions [1] contribute to our understanding of chemical and biochemical catalysis, the paths of chemical reactions, energy transfer in enzymes and phase transitions.

The development of new theoretical and experimental techniques as well as computer technology have led to a considerable progress in the study of molecular interactions. *Ab initio* molecular orbital calculations have played an especially important role. They have been successful in predicting geometries of molecular complexes prior to their experimental determinations, in predicting the distance and angular dependency of interaction potential energy surfaces, and in providing a theoretical basis for understanding the origin of molecular interactions [2].

Since the pioneering work of London, it had been assumed for a long time that perturbation approach is the most suited approach to intermolecular interactions. There is also the variational approach (SCF *ab initio* calculations) to the study of molecular interactions. A detailed information on the theoretical background of various approaches and their confrontation with experiment are reviewed in the literature [3a–e].

The determination of many-body effects had been proved to be a demanding theoretical and computational problem which provides a severe test for contemporary theoretical and computational methods [4]. For example, theoretical approaches in statistical physics and fluid dynamics start from independent particles.

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Molecular interactions is then introduced by potential energy functions which at first are based on the assumption of pairwise additive intermolecular forces. Three-body and four-body forces, or higher terms, account for the non-additivities. Consequently testing the convergence of the many body expansion may be considered as a prerequisite for constructing reliable model potentials for purposes of simulations of larger systems.

The most powerful form of the theory of molecular vibrations had been couched in terms of group theory. The fundamental frequencies of vibrations provide considerable information about the interionic forces in various molecules and consequently about the nature of intermolecular interactions.

In the present paper, an attempt is made for unique characterization and rationalization of metal–nonmetal and metalloid–nonmetal interactions using theoretical methods.

2. Theory

As far as the many-body expansion of the total interaction energy is concerned, the total energy $V(\text{tot.})$ for a finite cluster of (4) interacting ions may be written

$$V(\text{tot.}) = \sum_{m=1}^{4} V(m, 4),$$

where

$$\sum_{m=1}^{4} V(m, 4) = V(1, 4) + V(2, 4) + V(3, 4) + V(4, 4)$$

and

$$V(1, 4) = \sum_{i}^{4} V(1, 4)_i,$$

$$V(2, 4) = \sum_{i<j}^{4} V(2, 4)_{ij},$$

$$V(3, 4) = \sum_{i<j<k}^{4} V(3, 4)_{ijk},$$

$$V(4, 4) = \sum_{i<j<k<1}^{4} V(4, 4)_{ijkl}.$$

$V(1, 4)$ is the monomer energies and $V(2, 4)$, $V(3, 4)$ and $V(4, 4)$ are the two-body, three-body and four-body contributions to the total interaction energy $V(4)$. The total interaction energy $V(4)$ is obtained by subtracting the $V(1, 4)$ monomer energies from the total energy $V(\text{tot.})$

$$\begin{aligned} V(4) &= \sum_{m=1}^{4} V(m, 4) - \sum_{i}^{4} V(1, 4)_i \\ &= \sum_{i<j}^{4} V(2, 4)_{ij} + \sum_{i<j<k}^{4} V(3, 4)_{ijk} + \sum_{i<j<k<1}^{4} V(4, 4)_{ijkl} \end{aligned}$$

For the present many-body expansion to be convergent, the four-body term $V(4,4)$ should be negligible relative to the total interaction energy $V(4)$.

The calculations of molecular interactions by *ab initio* methods is particularly demanding computationally, requiring the careful selection of large flexible basis sets. Although electron correlation effects are important in studies of molecular interactions, the first priority must be to achieve an accurate description with the Hartree Fock approximation.

Group theory had proved to be of immense value in studying structures, energetics and interactions of polyatomic molecules [5]. A primary motive of these calculations is determining the potential functions of microclusters more accurately and over a wide range of co-ordinate space, particularly that withdrawing informations about equilibrium configurations and harmonic force fields from spectroscopic data is limited by the need to make corrections arising from the cubic and quartic anharmonic force fields. A secondary motive is understanding vibration–rotation intensities as well as interpreting data on isotopes.

The potential energy function V is written as a power series expansion in displacement co-ordinates from the equilibrium configuration with the coefficients of the expansion being considered to be the force constants.

$$V = \sum_{i,j} (1/2!) f^{ij}_{r_i r_j} + \sum_{i,j,k} (1/3!) f^{ijk}_{r_i r_j r_k} + \sum_{i,j,k,l} (1/4!) f^{ijkl}_{r_i r_j r_k r_l}.$$

For small displacements, the terms converge rapidly. The factor $1/n!$ on the nth-order terms ensures that the force constants are equal to the true derivatives of V in equilibrium. The quadratic, cubic, quartic, force constants are given by

$$\begin{gathered} f^{ij} = \delta V / \delta_{r_i} \delta_{r_j}, \\ f^{ijk} = \delta V / \delta_{r_i} \delta_{r_j} \delta_{r_k}, \\ f^{ijkl} = \delta V / \delta_{r_i} \delta_{r_j} \delta_{r_k} \delta_{r_l}, \\ \vdots \end{gathered}$$

The quantum mechanical treatment of group-theoretical analysis (vibrational analysis) does not require experimental data (experimental geometries and IR frequencies) but requires full geometry optimizations and becomes quite expensive as the size of the molecule and the basis set employed in the calculations increase. Group theory would then offer a wealth of knowledge (theoretical indices) that would be useful for characterizing metal–nonmetal and metalloid–nonmetal interactions with a reasonable degree of accuracy.

Calculations

Ab initio calculations were performed with the Gaussian 86 system [6] using the extended 6-311 + G(d) basis set at the Hartree Fock level of theory. Full geometry optimizations were carried out for the considered molecules, and optimum geometries were then used in the frequency calculations. Monomer energies were calculated to be: $V(\mathrm{Al}^{3+}) = -239.9938502 E_\mathrm{h}$, $V(F^-) = -99.4456557 E_\mathrm{h}$, $V(\mathrm{Cl}^-) = -459.565425 E_\mathrm{h}$ $V(\mathrm{B}^{3+}) = -21.9849005 E_\mathrm{h}$, $V(B) = -24.5303488 E_\mathrm{h}$, $V(\mathrm{Al}) = -241.8722624 E_\mathrm{h}$, $V(\mathrm{F}) = -99.3998926 E_\mathrm{h}$ and $V(\mathrm{Cl}) = -459.474232 E_\mathrm{h}$. Programs were run on the micro VAX 3800 VMS 5.4.

Table 1. Optimized geometries of BF_3, BCl_3, AlF_3 and $AlCl_3$

BF_3	$r_{BF} = 1.298$ Å	BCl_3	$r_{BCl} = 1.748$ Å
	⟨FBF = 120°		⟨ClBCl = 120°
	⟨FBFF = 180°		⟨ClBClCl = 180°
AlF_3	$r_{AlF} = 1.631$ Å	$AlCl_3$	$r_{AlCl} = 2.073$ Å
	⟨FAlF = 120°		⟨ClAlCl = 120°
	⟨FAlFF = 180°		⟨ClAlClCl = 180°

3. Results and discussions

Binding energies of BF_3, BCl_3, AlF_3 and $AlCl_3$ were calculated to be $-2.9629364E_h$, $-2.658772E_h$, $-2.2225089E_h$ and $-1.7088045E_h$ for interactions between ions; and $-0.5547774E_h$, $-0.3867082E_h$, $-0.4813860E_h$ and $-0.3769716E_h$ for interactions between neutrals. Clearly, interactions between ions are stronger than the corresponding interactions between the neutral atoms. Moreover, metal–nonmetal interactions (BF_3, BCl_3) are stronger than metalloid–nonmetal (AlF_3, $AlCl_3$) interactions. It is also evident that the major component of these ionic interactions is the coulomb energy. Coulomb energies were calculated to be $-2.9627768E_h$, $-2.2003437E_h$, $-2.3571835E_h$ and $-1.855273E_h$ for BF_3, BCl_3, AlF_3 and $AlCl_3$, respectively. As shown, coulomb energies predominate the interactions of B with F and Cl and greater than the interaction energies of Al with F and Cl. Subtracting the coulomb energies from the total interaction energies gives an attractive potential for the interactions of B with F and Cl, and a repulsive potential for the interactions of Al with F and Cl. Characterization of metal–nonmetal and metalloid–nonmetal interactions is thus feasible.

Characterization of interactions from structural informations was also possible. In Table 1, optimized geometries of the considered molecules at the Hartree Fock 6-311 + G(d) level are given. All the molecules belong to the same D_3h point group symmetry. They only differ in bond lengths. r_{BF} is 0.334 Å shorter than r_{AlF} and r_{BCl} is 0.325 Å shorter than r_{AlCl}. In other words, bond length between a metal and nonmetal is considerably shorter than the corresponding metalloid and the same nonmetal as a logical consequence of the larger size of the metalloid compared to the metal.

The many-body expansion convergence

In Table 2, total energies V, total interaction energies $V(4)$, two-body terms $V(2, 4)$, three-body terms $V(3, 4)$ and four-body terms $V(4, 4)$ are given. The covergence of the many-body expansion may be viewed as the percentage contribution of the four-body term $V(4, 4)$ to the total interaction energy $V(4)$. The four-body terms contribute 2.647%, 1.150%, 10.606% and 9.534% to the total interaction energies of BF_3, AlF_3, BCl_3 and $AlCl_3$. The result suggests that the many-body expansion of metal–nonmetal interaction is more converged than the corresponding metalloid–nonmetal interaction. Meanwhile, interactions with chlorine were characterized by a very poor convergence in comparison with the corresponding interactions

Table 2. Total energy V, total interaction energy $V(4)$, two-body contribution $V(2,4)$, three-body contribution $V(3,4)$ and four-body contribution $V(4,4)$ to be the total interaction energy of BF_3, BCl_3, AlF_3 and $AlCl_3$ in a.u.

BF_3	$V = -323.284804$	BCl_3	$V = -1403.339753$
	$V(4) = -2.9629364$		$V(4) = -2.6585772$
	$V(2,4) = -3.6946287$		$V(2,4) = -3.9425895$
	$V(3,4) = 0.8101136$		$V(3,4) = 1.565988$
	$V(4\ 4) = -0.0784213$		$V(4,4) = -0.2819757$
AlF_3	$V = -540.5533262$	$AlCl_3$	$V = -1620.67193$
	$V(4) = -2.2225089$		$V(4) = -1.7088045$
	$V(2,4) = -2.485701$		$V(2,4) - 2.5548072$
	$V(3,4) = 0.2887397$		$V(3,4) = 0.6830873$
	$V(4,4) = -0.0255476$		$V(4,4) = 0.1629154$

with Fluorine. The latter observation points to a correlation between the bond polarity and the convergence of the many-body expansion.

Since the many-body expansions were not convergent, particularly for BCl_3 and $AlCl_3$, they would not be well expressed by the sums of two- and three-body terms and would not be useful for simulations of larger systems. The argument is in agreement with the view of Biswas and Hamann [7] that a potential which simultaneously fits a data for small clusters and solids, necessarily include $N \geqslant 3$ body terms. Consequently, testing the convergence of the many-body expansion is a prerequisite for constructing any reliable model potentials for interactions.

In Table 2, sign oscillation of successive terms in the series of the many-body expansion occurs for all of the molecules except $AlCl_3$. Since the negative sign points to the binding property of a particular term, the three-body terms are repulsive, while the two- and four-body terms are attractive except for $AlCl_3$ where the four-body term is clearly repulsive. This is explained on basis of the predominance of the short-range repulsive forces in $AlCl_3$ relative to the long-range attractive forces. This is in turn attributed to the intensive overlap of charge clouds of both Al and Cl ions.

Interaction components

Decomposition of interaction energies to components is profitable for understanding the nature of interactions, deriving rules for the selection of a basis set and for characterizing interactions.

In contrast to the perturbation treatment in which all components of interactions are obtained directly from explicit expressions, we follow the approach of Dreyfus and Pullman [8a] and Ahlrichs [8b] which may be performed in two steps: In the first step, the sum of the electrostatic and first-order repulsion energies is obtained. This term denoted as $V_s(n) = V_{\mathrm{coul.}} + V_{\mathrm{ex.}}$, results from the antisymmetrized product of the SCF wave functions of (n) subsystems. Computationaly, the term $V_s(n)$ (short-range repulsive component) is obtained from the energy in the first iteration of the SCF calculations, if orthogonalized occupied SCF orbitals of isolated (n) subsystems are used as starting vectors and if the energies of the isolated (n) subsystems are subtracted. In the second step, the SCF calculations are allowed to reach self-consistency (converged energy). The long-range attractive component

$V_l(n)$ is then calculated by subtracting the short-range repulsive component $V_s(n)$ from the total interaction energy $V(n)$ calculated using this converged energy.

In general, a detailed informations on the theoretical background of various approaches and their confrontation with experiment may be reviewed [9]. However, it should be noted that coventions for generating initial solutions for SCF procedures are by no means universal – practically any energy could be produced.

Further decomposition of interaction energies into components is also possible but has its own limitations. For instance, the distinction between charge transfer and polarization terms is in some cases questionable. Meanwhile, partial decomposition reduces the possibility of introducing misleading interpretations. As a logical consequence of these limitations, Kollman and Allen [10a] called the sum $V_{\text{ex+coul}}$. "electrostatic" and $V_{\text{CT+Pl}}$ "delocalization". Also, Jeziorski and Van Hemert [10b] introduced a collective term called $V_{\text{CT+Pl}}$ in their variation perturbation approach.

Variationally, decomposition of total interaction energy $V(n)$

$$V(n) = \sum_{m=1}^{n} V(m, n) - \sum_{i=1}^{n} V(l, n)_i,$$

where the first term at the right-hand side represents the total energy in terms of m-body contribution, and the second term represents the sum of monomer energies, may be expressed as follows:

$$V_s(n) = \sum_{m=1}^{n} V_{\text{scf}}(m, n) - \sum_{i=1}^{n} V(1, n)_i.$$

$V_s(n)$ is the short-range repulsive component and the first term on the right-hand side represents the energy of the first iteration in the SCF cycles. Consequently, the long-range attractive component $V_l(n)$ may be expressed as

$$V_l(n) = \sum_{m=1}^{n} V(m, n) - \sum_{m=1}^{n} V_{\text{scf}}(m, n).$$

Interaction energies, as well as the short-range repulsive and long-range attractive components are given in Table 3.

Despite of the fact that Boron and Aluminum are two adjacent members in the same IIIB group of the periodic table having the same outer valence shell electronic configuration, and should have more or less similar chemical properties, the transition from Boron (weak metal) to Aluminum (metalloid) is clearly reflected on their components of interactions with the same nonmetal Fluorine or Chlorine, which are also not too far from them in the periodic chart. As shown in Table 3,

Table 3. Totral interaction energy $V(4)$, short-range repulsive $V_s(4)$ and long-range attractive $V_l(4)$ components of BF_3, BCl_3, AlF_3 and $AlCl_3$ interactions in a.u.

BF_3	$V(4) = -2.9629364$ $V_s(4) = -1.214731$ $V_l(4) = -1.7482054$	BCl_3	$V(4) = -2.6585772$ $V_s(4) = 0.2212198$ $V_l(4) = -2.87797$
AlF_3	$V(4) = -2.2225089$ $V_s(4) = 0.9583041$ $V_l(4) = -3.180813$	$AlCl_3$	$V(4) = -1.7088045$ $V_s(4) = 1.7503995$ $V_l(4) = -3.459204$

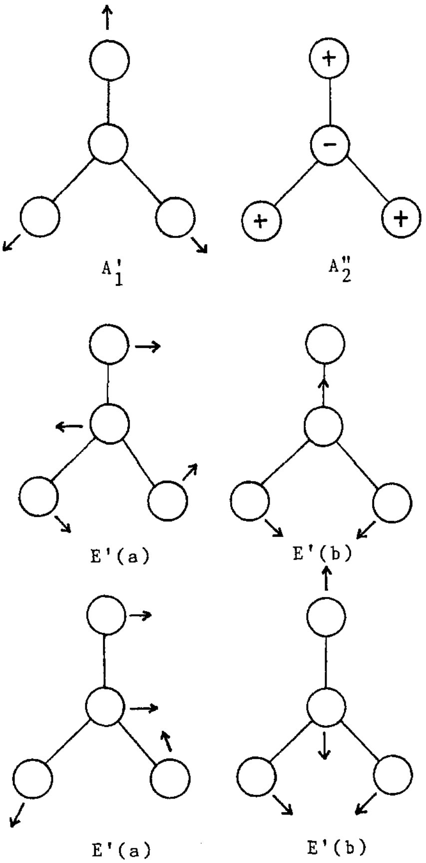

Fig. 1. Vibrational modes of MX_3 molecules

both short-range repulsive and long-range attractive components of metalloid–nonmetal interactions (AlF_3 and $AlCl_3$) are considerably greater than the corresponding components of metal–nonmetal (BF_3 and BCl_3) interactions. Moreover, the components of Chlorine interactions with B and Al are greater than the corresponding components of Fluorine interactions. This is definitely attributed to the sizes of halogen ions, electronegativities and the electron density overlap between the interacting ions. The negative sign of the short-range repulsive component of BF_3 is attributed to the magnitude of the delocalization energy component of interaction energy. The delocalization energy of BF_3 is considerably greater than the total interaction energy in contrast to other molecules.

Group-theoretical parameters

Group-theoretical analysis of the present molecules was carried out at the minimal energy configurations and proved to be valuable in providing two more indices for characterizing metal–nonmetal and metalloid–nonmetal interactions. Additional motives of group-theoretical analysis are: determining the potential functions of microclusters more accurately and over a wider range of co-ordinate space as well

Table 4. Harmonic frequencies (cm^{-1}), IR intensities (KM/mol), Raman scattering activities (A^4/amu), depolarizations ratios and force constants (m dyn/Å) of BF$_3$, BCl$_3$, AlF$_3$ and AlCl$_3$

	BF$_3$				BCl$_3$			
	A_1'	A_2''	E'	E'	A_1'	A_2''	E'	E'
F	930.7	743.7	504.2	1521.2	491.7	480.1	271.1	996.8
FC	9.696	3.850	2.675	16.772	4.981	1.600	1.353	7.182
IR	0.0	154.9	19.95	555.70	0.0	16.567	1.114	450.4
R	2.010	0.0	0.646	0.0560	6.764	0.0	2.708	0.040
D	0.055	0.0	0.750	0.7500	0.069	0.0	0.750	0.750

	AlF$_3$				AlCl$_3$			
	A_1'	A_2''	E'	E'	A_1'	A_2''	E'	E'
F	722.4	310.7	251.3	1000.5	401.5	212.9	154.4	641.7
FC	5.842	1.352	0.741	13.261	3.322	0.756	0.474	7.075
IR	0.0	201.9	49.60	245.80	0.0	60.686	11.952	231.7
R	2.251	0.0	0.435	0.2500	9.482	0.0	2.444	0.750
D	0.056	0.0	0.750	0.7500	0.081	0.0	0.75	0.75

F: harmonic frequencies
FC: force constants
IR: IR intensities
R: Raman activities
D: depolarizations

as understanding vibration-rotation intensities and interpreting data on isotopes as stated previously.

Despite the fact that the considered systems belong to the same D$_3$h point group symmetry, frequencies and force constants uniquely characterize their interactions. Vibrational modes are shown in Fig. 1. Harmonic frequencies, harmonic force fields, IR intensities, Raman activities as well as depolarizations are given in Table 4.

Each molecule displays 6 modes of vibrations according to the 3N − 6 rule. The modes are distributed as follows:

$$\Gamma_V = A_1'(\mathrm{R}) + A_2''(\mathrm{IR}) + 2E'(\mathrm{IR}).$$

A_1' mode is Raman active, while A_2' and E' modes are IR active (E' mode is a doubly degenerate mode). IR and Raman activities are given in Table 4. The representation of the vibrational mode Γ_V is obtained by subtracting the representations of the translational and rotational vectors Γ_{T+R} from the Γ_{3N} representation.

$$\begin{aligned}\Gamma_{3N} &= A_1'(\mathrm{R}) + 2A_2''(\mathrm{IR}) + 3E'(\mathrm{IR}) + A_2'(\mathrm{R}) + E''(\mathrm{R}),\\ \Gamma_{T+R} &= E'(\mathrm{IR}) + A_2''(\mathrm{IR}) + A_2'(\mathrm{R}) + E''(\mathrm{R}),\\ \Gamma_V &= \Gamma_{3N} - \Gamma_{T+R}\\ &= A_1'(\mathrm{R}) + A_2''(\mathrm{IR}) + 2E'(\mathrm{IR}).\end{aligned}$$

As shown in Table 4, metalloid–nonmetal (AlF_3 and $AlCl_3$) interactions are characterized by lower frequencies and force constants in comparison with metal nonmetal (BF_3 and BCl_3) interactions. The result follows from the greater mass of the metalloid compared to the metal (Al compared to B). However, IR intensities, Raman activities, and depolarizations were not discriminative for interactions. It may also be noted that frequencies are force constants of Chlorine interactions with both Boron and Aluminum were significantly smaller than the corresponding interactions of Fluorine.

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