



BUDAPEST UNIVERSITY OF TECHNOLOGY AND ECONOMICS
FACULTY OF CHEMICAL AND BIOENGINEERING

Structural study of metal halide molecules

Computational support for experimental analyses

Theses of PhD Dissertation

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I. Introduction

Metal halide molecules are usually simple symmetrical systems, consisting of only a few atoms. In spite of the apparent simplicity of their structural formulae they can still represent novelties to the structural chemists due to the variety of the possible electron configurations of their metals. This diversity is not only the result of the large number of metals in the periodic table, but also of the different possible oxidation numbers and electronic states of most metals. It is especially the occupation of the d and f orbitals that is important in this respect, because their variation may lead to molecular properties that are rather different from the expected trends.

Metal halides are not an easy target for structure determination. Under ordinary conditions most of them are crystals whose molecular forms can only be found in the gas phase. Most of them are of low volatility and can only be evaporated at high temperatures, often at over a thousand K. Under such circumstances the thermal effects on the structures cannot be neglected, and have to be taken into account in the analysis of experimental data.

Our group has been involved with the determination of molecular structures using the gas-phase electron diffraction technique. The study of metal halides has been performed by Magdolna Hargittai and her students. The electron diffraction experiments had ended almost a decade ago; and from that time only the structure analyses of previously recorded but not yet analyzed data have been performed. It is the most difficult complex systems that have been left over; those for which the analysis by electron diffraction alone did not seem to be promising. The elucidation of structures has often involved spectroscopic data as well in addition to the electron diffraction measurements, however, even so, the available information did not suffice for a reliable structure determination.

In addition to the experimental techniques, quantum chemical calculations have been included to an ever increasing extent. Due to the improvement of computational techniques and basis sets, it has become possible to produce computed structural information that is compatible with the level of precision of the experimental data. Accordingly, it has become increasingly feasible to combine the experimental and computed information aiming at a more reliable structure elucidation. The experimental data, however, continue to be an important reference point.

Our primary purpose has been the determination of molecular structures, but our aims were not limited to the mere structure determination. We have attempted interpreting the results and, accordingly, delve into the theoretical foundations of the information we have produced.

A focal question in the investigation of metal dihalides and trihalides has been whether or not these molecules are linear or bent and planar or pyramidal, respectively. A comprehensive review about these structures appeared in the year 2000.¹ Since then, additional structures kept appearing, often referring to compounds whose structures had previously been unknown. I would like to note that even some recent publications are based on data from a single technique and they often attempt generalizing their results without taking into account prior information. Recently, a misconception has appeared in the literature about the thermal expansion of molecules (see below).

We have already formed a general picture from computation of the molecular structures of both the main group metal halides and the transition metal halides. However, the recent much improved core potentials and basis sets have made it possible to refine their structural details and even find new structural features.

We have initiated computational investigation of aluminium monohalides (AlX, X = F, Cl, Br and I) in order to facilitate the structure analysis of AlX₃ molecules by electron diffraction and in particular to generate information about the bond asymmetry parameters.

Although iron trichloride is considered to be a rather common substance, and has figured in industrial processes (for example, in the manufacturing of printed circuits), nonetheless, its molecular structure had not been determined. A gradual decrease of stability has been observed in the series of iron trihalides (FeX₃, X = F, Cl, Br, and I), but this interesting phenomenon has not been interpreted.

We have taken a second look at the previous structure determination of vanadium dichloride and examined the vapor composition based on electron diffraction and mass spectrometric data, and augmented them with new and extensive quantum chemical calculations.

A relatively new area of research in our laboratory has been the study of lanthanide halides. In industrial processes they appear in the high-temperature extraction of lanthanide

¹ Hargittai, M., *Chem. Rev.* **2000**, *100* (6), 2233-2301.

metals in separation processes, in the treatment of nuclear waste, and in the halogen-lamp industry, in addition to their use as catalysts in organic chemistry involved with complexes possessing large cage-like cavities. The dysprosium trihalides (DyX₃, X = Cl, Br, and I) form complexes with alkali halides in the processes of the lamp industry.² The quantum chemical study of molecules of heavy metals was begun about two decades ago with the appearance of core potentials that involved the f electrons. This division between the core and the valence shell was justified by experience both in experimental and computational work, and it made it possible to carry out quantum chemical calculations for molecules of heavy atoms. There was a review about the structure of lanthanide trihalides in the year 2004.³ It is noted though that the results of these computations were not quite comparable with the available experimental results. Good-quality basis sets that have made it possible to include the 4f orbital in the valence shell have only appeared in recent years; moreover, the computational facilities have improved considerably and this made it possible to carry out calculations with those large basis sets. Thus, the time has become ripe for such studies.

II. Experimental and computational techniques

We have relied primarily on high-temperature electron diffraction and quantum chemical calculations and have augmented them by vibrational spectroscopic analyses for which the necessary experiments have been performed by our partner in cooperation.

Gas-phase electron diffraction is a unique technique for the experimental determination of the molecular structure of metal halides. The experiments (performed earlier) involved the combined electron-diffraction–quadrupole mass spectrometric techniques.

The quantum chemical calculations of open-shell systems require great care. Multi-reference techniques (CASSCF, MRCI, and CASPT2) need be used for the determination of electron configurations and relative energies of systems with partially filled d and f orbitals. However, these methods do not provide geometrical data that would be compatible with the precision of the experimental data for their geometries. Therefore, based on the results of the

² Haverlag, M., *Phys. Scripta* **2005**, *T119*, 67-70.

³ Kovács, A.; Konings, R. J. M., *J. Phys. Chem. Ref. Data* **2004**, *33* (1), 377-404.

multireference calculations, we used single-determinant techniques (MP2, CCSD(T), and DFT) to determine the geometrical parameters.

In addition to choosing the right quantum chemical technique, the choice of the basis sets is also very important. Developing proper basis sets for the description of many-electron atoms is a difficult task, and only a few basis sets are available for heavy atoms. Most of these basis sets take relativistic effects into account only partially and with varying success, whereas their proper inclusion in the computation is necessary. We have made efforts—while observing the need of compromises—to utilize such method/basis set combinations that well approximated the level of experimental parameters.

Geometries were obtained by standard analytical gradient techniques when available; otherwise, the equilibrium structures were calculated manually. The calculations of equilibrium structures of different electronic states always included testing of the stability of the wave function as well as frequency calculations.

To model the temperature effects we calculated the potential energy curves along the normal vibrational modes and on this basis we calculated the Boltzmann distribution at the experimental temperature and utilized the structural variations expressed by the discrete points of the curves for the so-called dynamic electron diffraction analysis.

Population, NBO, and Mayer bond index analyses were carried out in order to uncover the properties of the electronic structure of molecules.

In presenting the results of the calculations of thermodynamic parameters, in each case we noted whether or not BSSE corrections have been applied.

The quantum chemical calculations were performed using the GAUSSIAN 98 and 03, MOLPRO, and GAMESS program packages.

We determined the anharmonic frequency shifts on the basis of the potential energy curves of the normal vibrations by means of the one-dimensional Hamilton operator (FGHID program).

For two of the systems under study (DyBr_3 and DyI_3), we augmented our investigation by gas-phase infrared and matrix-isolation infrared and Raman spectroscopic studies. In principle, vibrational spectroscopy can establish molecular symmetry. In addition, the calculated mean vibrational amplitudes can greatly facilitate the electron diffraction structure analysis. However, the thermal effects at the high-temperature experimental

conditions of the gas-phase infrared studies were just as problematic as those of the electron diffraction studies. In the matrix-isolation technique the molecules under investigation are „frozen” among the atoms of the inert gas, be it krypton or xenon, and, accordingly, the molecules can be considered as isolated from each other, like in the gaseous state.

For the electron diffraction structure analysis the harmonic vibrational amplitudes were determined by using the programs ASYM and SHRINK on the basis of the geometry, vibrational frequencies, and force constants.

III. Results

The results of quantum chemical calculations for metal halides are sensitive to the conditions under which the respective programs are being used. To test the level of correlation in the post-HF calculations, a series of simple molecules (AlX , $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) were used. It was found that the most widely used quantum chemistry program package does not always treat two aspects of the calculations in a consistent manner and according to the program description. These two important aspects are the basis set and the level of electron correlation. These problems occur primarily for systems in which at least one of the atoms is described by an effective core potential/basis set combination. We have pointed out that the correlation space used in any given calculation should not be larger than for what the basis set had been optimized. These problems might cause a discrepancy of 0.01 to 0.02 Å in the computed bond lengths that is an order of magnitude larger than the expected accuracy. We have even found such a case, in which the above problem results in a change of molecular shape. At the same time, in some cases it was unavoidable to revise the „official” level of correlation (for example, in case of an empty valence shell) in order to ensure acceptable results.

Employing a combined analysis of electron diffraction and quantum chemical calculations, we have determined the high-temperature (900 K) vapor composition of iron trichloride and the structures of the monomeric and dimeric molecular species. We have utilized in this analysis the results of a prior study of lower temperature (460 K) experiments of our laboratory.

We have established a correlation between the stability of molecules and the occupation of the 3d subshell of the metal atom in the study of iron trihalides. For the heavier halides, the enhanced covalent character of the bonds increases the population of the 3d subshell to such an extent that the iron ion appears to be more like divalent rather than trivalent. This is why it has been observed that these trihalides stabilize by halogen loss as dihalides.

It has been known that a substance is more volatile if its crystal structure is closer to the gas-phase molecular structure. If the crystal structure retains the gaseous molecular structure, the changes during phase transition happen with saving a considerable amount of energy. We have uncovered a relationship as a result of our calculations on iron trichloride oligomers according to which the dimeric and tetrameric molecular species fit the crystal structure and it is supposed that this structural correspondence facilitates the process of crystallization.

We have performed quantum chemical calculations in order to further interpret the results of a previous electron diffraction investigation. We have established that in accordance with the mass spectrometric results, part of the evaporated vanadium dichloride species transforms into vanadium trichloride. This makes the vapor composition more complicated and this complexity is further enhanced by the occurrence of molecules in excited electronic states in the vapor. Our combined analysis of electron diffraction and quantum chemical computational data yielded information on the vapor composition and the structures of all molecules present in the vapor.

The identification of Jahn-Teller effect in the gas phase may be hindered by various difficulties. In case of vanadium trichloride, our quantum chemical study unambiguously established the presence of the Jahn-Teller effect that distorted its geometry.

We have determined the structure of dysprosium trihalides with a combined electron diffraction, spectroscopic, and quantum chemical investigation. Different core potentials and basis sets have been tested. The experimental electron diffraction bond lengths and the spectroscopic vibrational frequencies served as reference points. We have found that in agreement with previous studies the 4f sub-shell does not participate directly in chemical bonding; rather, they are non-bonding. In order to compute realistic bond lengths, however, the 4f sub-shell had to be treated as being part of the valence shell.

Contrary to expectations, we have found that the population of 4f orbitals played a role in determining the structure of dimeric species of dysprosium trihalides. Figure 1 shows this effect in the angular variations involving the terminal bonds. We have concluded that the structure depends on the occupation of 4f orbitals in the different electronic-state molecules.

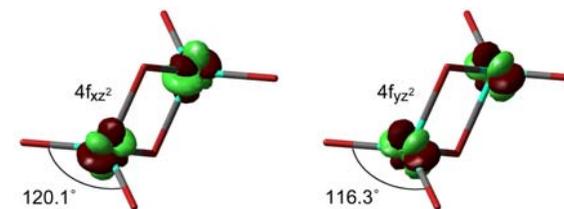


Figure 1. Illustration of the effect of 4f electrons on the molecular geometry.

Both ferro- and antiferromagnetic interactions are possible between the lanthanide atoms, since the 4f sub-shell is buried deep and shielded by outer shells. The structures of the high-spin and low-spin electronic state molecules often coincide both in their energies and geometries.

Different techniques often establish different symmetries for the same molecule. Thus, for example, matrix isolation spectroscopy may yield lower symmetry for some metal halides than other techniques. The probable reason is the formation of stable complexes in the matrix between the molecules and the atoms of the noble gas in the matrix. We have experienced in the work with dysprosium trihalides the appearance of additional transitions in the spectra beside those that were expected. The explanation was found in our quantum chemical calculations. The energies of stabilization pointed to an unambiguously pyramidal DyBr_3 structure and a multitude of structures for DyI_3 , corresponding to the formation of various complexes in the matrix.

We have corrected a statement that had appeared in the recent literature concerning the thermal expansion of molecules. The authors of a series of papers found the thermal expansion of certain types of molecules to be negligible, based on their theoretical calculations. We have analyzed their treatment and established that they did not consider the effect of asymmetric stretchings. Taking the asymmetric stretching into consideration, we

have shown that the amount of bond lengthening is consistent with the value determined from electron diffraction.

In conclusion, we can state that although we have applied the same experimental and theoretical methods to our various systems, almost in each case we had to solve unique problems. Table 1 illustrates that the joint analysis of experimental data and high-level computations results in highly accurate geometrical parameters.

Table 1. Summary of equilibrium bond lengths (\AA) of monomers from electron diffraction experiments (ED) and from computations.

	FeCl ₃	VCl ₂	VCl ₃	DyCl ₃	DyBr ₃	DyI ₃
	Fe-Cl	V-Cl	V-Cl	Dy-Cl	Dy-Br	Dy-I
ED, r_e^M	2.122(6)	2.185(21)	2.149(8)	2.443(14)	2.591(8)	2.808(7)
Comp. r_e	2.122	2.192	2.152	2.444	2.592	2.812

IV. Theses

1. We have determined the molecular structure (bond lengths, bond angles, and mean vibrational amplitudes) of nine metal halides using a joint experimental and theoretical analysis. (2–6)
2. We have shown that for molecules containing heavy atoms, the reliability of structure determination decreases when the applied level of electron correlation is too large, because the effect of the less accurate orbitals is unpredictable. This is contrary to the idea that the increasing level of electron correlation can improve the efficiency of any basis set. (1, 4–5)
3. We have determined by computations Jahn-Teller distortion in the molecular structure of VCl₃ manifested in symmetry-lowering. (2)

4. Our computations have shown that in certain cases the occupation of the 4f orbitals influences appreciably some of the geometrical parameters, contrary to general expectations. (4–6)
5. Based on our calculations, both ferro- and antiferromagnetic couplings are possible between the lanthanide atoms, because the 4f sub-shells are well isolated from each other. (4–6)
6. We have determined the vibrational frequencies of dysprosium tribromide and triiodide using a joint analysis of experimental and theoretical data. (5, 6)
7. We have established that in the matrix isolation studies the atoms of noble gases of the matrix may interact with the central atoms of the lanthanide halides, hence the molecular structure may change as compared with the isolated molecule. (5, 6)
8. We have interpreted the considerable decrease in the stability in the series of iron trihalides with increasing halogen size and increasing population of the 3d shells, as the consequence of the fact that the electron configuration approximates that of the iron dihalides and, accordingly, the systems may stabilize by halogen loss. (2)
9. We have corrected an erroneous claim in the literature according to which the thermal expansion of bonds is negligible even at high temperatures. We have shown that the estimated thermal bond lengthening corresponds to the results from the experiment, if the vibrational couplings that the original authors neglected, are taken into account. (7)

V. Possible applications

Our studies constitute fundamental research. Our results are important for extending knowledge about molecular structure and about the relationship between chemical bonding and electronic structure. Accordingly, they may find way into monographs and text books. They might also become useful for improved determination of thermodynamic functions that are applicable in industrial processes and their modeling.

VI. Publications

Sum of impact factor (IF): 52.998

Sum of citations (I): 115 (74 independent) [as of November 29, 2010]

Publications related to the theses

1. Molecular constants of aluminum monohalides: Caveats for computations of simple inorganic molecules
M Hargittai, **Z Varga**
J Phys Chem A 2007, 111(1), 6-8 (IF: 2.918, I: 6)
2. Gas-Phase Structures of Iron Trihalides: A Computational Study of all Iron Trihalides and an Electron Diffraction Study of Iron Trichloride
Z Varga, M Kolonits, M Hargittai
Inorg Chem 2010, 49(3), 1039-1045 (IF: 4.657, I: 1)
3. Molecular geometry of vanadium dichloride and vanadium trichloride: A gas-phase electron diffraction and computational study
Z Varga, B Vest, P Schwerdtfeger, M Hargittai
Inorg Chem 2010, 49(6), 2816-2821 (IF: 4.657, I: 0)
4. On the effect of 4f electrons on the structural characteristic of lanthanide trihalides. Computational and electron diffraction study of dysprosium trichloride.
G Lanza, **Z Varga**, M Kolonits, M Hargittai
J Chem Phys 2008 128(2) 074301 (IF: 3.149, I: 11)
5. Does the 4f Electron Configuration Affect Molecular Geometries? A Joint Computational, Vibrational Spectroscopic, and Electron Diffraction Study of Dysprosium Tribromide
CP Groen, **Z Varga**, M Kolonits, KA Peterson, M Hargittai
Inorg Chem 2009, 48(9), 4143-4153 (IF: 4.657, I: 4)
6. Curious matrix effects: a computational, electron diffraction, and vibrational spectroscopic study of dysprosium triiodide
Z Varga, CP Groen, M Kolonits, M Hargittai
Dalton Trans 2010, 39(27), 6221-6230 (IF: 4.081, I: 1)

7. On the thermal expansion of molecules

Z Varga, M Hargittai, LS Bartell

Struct Chem in print

Publications related to the field of the theses, but not directly included

8. The Elusive Structure of CrCl₂ - A Combined Computational and Gas Phase Electron Diffraction Study
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Struct Chem 2007, 18(5), 641-648 (IF: 0.888, I: 4)
11. Chemistry, commentary and community: Discussion of "The NaDyBr₄ complex: its molecular structure and thermodynamic properties" by Varga and Hargittai
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12. The NaDyBr₄ complex; its molecular structure and thermodynamic properties
Z Varga, M Hargittai
Struct Chem 2006, 17(2), 225-233 (IF: 1.510, I: 5)
13. Quasilinear molecule par excellence, SrCl₂: structure from high-temperature gas-phase electron diffraction and quantum chemical calculations; Computed Structure of SrCl₂.Argon complexes
Z Varga, G Lanza, C Minichino, M Hargittai
Chem Eur J 2006, 12(32), 8345-8357 (IF: 5.015, I: 12)

Other publications

14. Paradigms and paradoxes: the conformation of the fundamental unit of hyaluronic acid
Z Varga, I Hargittai
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16. Substituent effects on long-range interactions in the β -sheet structure of oligopeptides
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18. Long-range effects in oligopeptides. A theoretical study of the β -sheet structure of Gly_n (n = 2-10)
V Horváth, **Z Varga, A Kovács**
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19. Structure analysis of oligopeptides by means of quantum chemical calculations
Z Varga
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20. Computed long-range effects in Gly_n (n = 2-8) oligopeptides
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Conferences (l: lecture, p: poster)

1. Iron trihalides: An electron diffraction and quantum chemical study (p)
Z Varga, M Kolonits, M Hargittai
13th European Symposium on Gas Electron Diffraction (*Blaubeuren, Germany. 2009*)
2. Vas-halogenidek szerkezeti jellegzetességei (l)
Z Varga, M Kolonits, M Hargittai
XII. Anyagszerkezet-kutatási Konferencia (*Mátrafüred, Hungary 2009*)

3. Diszprózium-trihalogenidek szerkezetvizsgálata (l)
Z Varga, M Hargittai
XIV. Nemzetközi Vegyészkonferencia (*Kolozsvár, Romania 2008*)
4. Heterocomplexes of DyBr₃ with Alkali Halides: A Computational Study of Their Structures and Relative Stabilities (p)
Z Varga, M Hargittai
15th Conference on Current Trends in Computational Chemistry (*Jackson, Mississippi, USA 2006*)
5. Alkálihalogenidek és lantanida-halogenidek gázfázisú komplexei: Az AlkDyBr₄ komplexek (l)
Z Varga, M Hargittai
XI. Anyagszerkezet-kutatási Konferencia (*Mátrafüred, Hungary 2006*)
6. Távolható kölcsönhatások az oligopeptidekben (l)
KeMoMo-QSAR 4. miniszimpózium (*Szeged, Hungary 2005*)
7. Structure analysis of oligopeptides by means of quantum chemical calculations (p)
Z Varga, A Kovács
13th Conference on Current Trends in Computational Chemistry (*Jackson, Mississippi, USA 2004*)
8. Oligopeptidek szerkezetének analízise kvantumkémiaili számítások segítségével (l)
Z Varga, A Kovács
Tudományos Diákköri Konferencia (*Budapest, Hungary 2003*)