

Structure Determination of Metal Halides

Ph. D. Thesis

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1. General goals and methods of research

The scientific results in this thesis are based on the research I performed at the BUTE Institute of General and Analytical Chemistry then at the ELTE-MTA Structural Chemistry Research Group led by Professor István Hargittai. This electron-diffraction group has gained unique experience and international respect for the past decades. My Ph. D. Advisor was Professor Magdolna Hargittai.

In the course of my work, I examined the gas-phase molecular structure of metal halide molecules. High-temperature gas-phase electron-diffraction experiments were performed in our laboratory and I also regularly used vibrational spectroscopic and mass-spectrometric results from the literature. The experimental structure determination was augmented by high-level quantum-chemical calculations in all cases. Parts of the computational work were done by me while other parts of the theoretical results were fruit of international cooperation.

One of our main goals was the structure determination of several not yet examined molecules and of others about which there were contradictory data in the literature. Furthermore I always tried to determine the temperature dependence of the structural parameters.

Another goal was the structure determination of metal halides showing Jahn-Teller distortion in the gas-phase.

2.1. A usual case: ED study on gallium-tribromide

The molecular geometry of gaseous gallium tribromide has been determined by electron diffraction augmented with quadrupole mass spectrometry and quantum chemical calculations. Of the two experiments, at the higher temperature (638 K) only the monomeric form was present whereas at the lower temperature (357 K) the monomers and dimers were present in comparable amounts. The monomer is planar with bond lengths (r_g) 2.239 ± 0.007 Å at 357 K and 2.249 ± 0.005 Å at 638 K. The dimer has a halogen-bridged structure with bond lengths (r_g) of 2.250 ± 0.006 Å and 2.453 ± 0.005 Å and bond angles $\angle_a \text{Br}_b\text{-Ga-Br}_b$ $92.7 \pm 0.3^\circ$ and $\angle_a \text{Br}_t\text{-Ga-Br}_t$ $123.1 \pm 1.4^\circ$.

2.2 When I had only one experiment: structure determination of yttrium-trichloride

The molecular geometry of yttrium trichloride has been determined by high-temperature gas-phase electron diffraction. The vapor phase consisted of about 87% monomeric and 13% dimeric species. High-level quantum chemical calculations have also been carried out for both the monomer and dimer of yttrium trichloride, and their geometries, harmonic force fields and vibrational frequencies have been determined. The monomer YCl_3 molecule was found to be planar (D_{3h} symmetry) both by experiment and by computation. The bond length of YCl_3 from electron diffraction is 2.450(7) (r_g) or 2.422(12) (r_e) Å. It proved remarkably difficult to obtain a converged theoretical prediction for the bond length; large polarization bases are needed, and the published bases accompanying the pseudopotentials used appear to be overcontracted. The SCF method predicts bonds that are too long by some 0.043 Å, while the B3LYP method overestimates by about 0.03 Å. The B3PW91 prediction is almost within the experimental uncertainty for r_e . Amongst the traditional correlated methods, the MP2 distance with an infinitely large basis is probably indistinguishable from the experimental value, given the combined uncertainties, while the estimated CCSD(T) result of 2.423(10) Å is astonishingly close to the experimental result. The out-of-plane bending motion for YCl_3 is noticeably anharmonic, with the result that straightforward quantum predictions of its frequency are lower than the value observed in the gas phase at high temperature.

2.3. A real challenge: copper(I)-chloride oligomers

The molecular geometry of gaseous cuprous chloride oligomers was determined by gas-phase electron diffraction at two different temperatures. Quantum chemical calculations were also performed for $(\text{CuCl})_n$, $n = 1-4$ molecules. A complex vapor composition was found in both experiments. Cu_3Cl_3 and Cu_4Cl_4 molecules were present at the lower temperature (689 K), while dimeric molecules, Cu_2Cl_2 , were also found beside the trimers and tetramers at the higher temperature (1333 K). All Cu_nCl_n species were found to have planar rings by both experiment and computation. The bond lengths from electron diffraction (r_g) at 689 K are 2.166 ± 0.008 Å and 2.141 ± 0.008 Å and the Cu–Cl–Cu bond angles $73.9 \pm 0.6^\circ$ and $88.0 \pm 0.6^\circ$ for the trimer and the tetramer, respectively. At 1333 K the bond lengths are 2.254 ± 0.011 Å, 2.180 ± 0.011 Å, and 2.155 ± 0.011 Å and the Cu–Cl–Cu bond angles $67.3 \pm 1.1^\circ$, $74.4 \pm 1.1^\circ$, and $83.6 \pm 1.1^\circ$ for the dimer, trimer and tetramer, respectively.

2.4. A unique Jahn-Teller system – Electron diffraction – computational study of MnF₃

A new high-temperature gas-phase electron diffraction analysis of manganese trifluoride was carried out together with high-level quantum chemical calculations, providing direct geometrical evidence of a Jahn-Teller distortion in a free molecule. The potential energy surface of the molecule was scanned extensively by computation at the SCF level. CASSCF and CASPT2 calculations established that of the many C_{2v} symmetry stationary points on the potential energy surface the lowest energy ones are quintets. The global minimum is a quintet state of 5A_1 symmetry. In this planar C_{2v} symmetry structure there are two longer and one somewhat shorter Mn–F bond, with two bond angles close to 106° and one bond angle of about 148° . The second lowest energy state was of 5B_2 symmetry which turned out to be a transition state with an imaginary b_2 (in plane) bending frequency. A constrained planar structure of D_{3h} molecular symmetry has appreciably higher energy than the 5B_2 symmetry structure. The experimental data are in complete agreement with the results of the computations in giving the best agreement with a C_{2v} structure characterized by $r_g(\text{Mn–F})$ 1.728 ± 0.014 Å (once) and $r_g(\text{Mn–F})$ 1.754 ± 0.008 Å (twice), and $\angle_\alpha \text{F–Mn–F}$ $106.4 \pm 0.9^\circ$ (twice) and $\angle_\alpha \text{F–Mn–F}$ $143.3 \pm 2.0^\circ$ (once). Our computed infrared wavenumbers and intensities make an assignment possible for published vibrational spectra of MnF₃.

2.5. Jahn-Teller effect in complex vapor: structure determination of gold-trifluoride

The molecular geometry of monomeric and dimeric gold trifluoride, AuF₃ and Au₂F₆, has been determined by gas-phase electron diffraction and high-level quantum chemical calculations. Both experiment and computation indicate that the ground-state structure of AuF₃ has C_{2v} symmetry, rather than threefold symmetry, with one shorter and two longer Au–F bonds and an almost T-shaped form, due to a first order Jahn-Teller effect. CASSCF calculations show the triplet D_{3h} -symmetry structure, ${}^3E'$, to lie about 42 kcal/mol above the 1A_1 symmetry ground state and the D_{3h} -symmetry singlet, ${}^1E'$, even higher than the triplet state, by about a further 13 kcal/mol. The molecule has a typical “Mexican-hat” type potential energy surface with three equal minimum-energy structures around the brim of the hat, separated by equal-height transition structures, about 3.6 kcal/mol above the minimum energy. The geometry of the transition structure has also been calculated. The dimer has a D_{2h} -symmetry planar, halogen-bridged geometry, with the gold atom having an approximately

square-planar coordination, typical for d^8 transition metals. The geometries of AuF and Au₂F₂ have also been calculated. The very short Au...Au separation in Au₂F₂ is indicative of the so-called aurophilic interaction. This effect is much less pronounced in Au₂F₆.

2.6. What can we find after decomposition? Structure determination of gold-trichloriride

The molecular geometry of dimeric gold trichloride has been determined by gas-phase electron diffraction and high-level quantum chemical calculations. The molecule has a planar, D_{2h} -symmetry halogen-bridged geometry, with the gold atom in an almost square-planar coordination. The geometrical parameters from electron diffraction (r_g and \angle_α) are: Au-Cl_t 2.236±0.013 Å, Au-Cl_b 2.355±0.013 Å, \angle Cl_t-Au-Cl_t 92.7±2.5° and \angle Cl_b-Au-Cl_b 86.8±1.8° (t-terminal, b-bridging chlorine). Quantum chemical calculations have also been carried out on the ground state and transition state structures of monomeric AuCl₃; both have C_{2v} -symmetry structures due to Jahn-Teller distortion. CASSCF calculations show that the triplet D_{3h} -symmetry structure lies about 29 kcal/mol above the 1A_1 symmetry ground state. The Mexican-hat type potential energy surface of the monomer has three equal minimum-energy positions around the brim of the hat, separated by three transition state structures, about 6 kcal/mol higher in energy, at the CASSCF level. The distortion of AuCl₃ is smaller than that of AuF₃ and the possible reasons are discussed. The structure of the AuCl₄⁻ ion has also been calculated, the latter both in planar, D_{4h} , and tetrahedral, T_d , arrangements. The tetrahedral configuration of AuCl₄⁻ is subject to Jahn-Teller effect, which leads to a complicated potential energy surface. The factors leading to the planar geometry of AuCl₄⁻ and Au₂Cl₆ are discussed. The frequently suggested dsp^2 hybridization as a possible cause for planarity is not supported by this study. The geometries of AuCl and Au₂Cl₂ have also been calculated. The very short Au...Au distance in the latter, similarly to Au₂F₂, is indicative of the aurophilic interaction.

3. Most important scientific results

Gas-phase metal halide structures were determined in the course of the Ph.D. research. Gas-phase electron diffraction augmented with high level quantum-chemical calculations were used.

- The structure of 11 molecules in the vapor of 6 metal halides was determined
 - I determined the temperature dependence of the structure of the following molecules: GaBr₃, Au₂F₆, Cu₃Cl₃ and Cu₄Cl₄
 - It was found that the YCl₃ monomer has a planar equilibrium structure of D_{3h} symmetry
 - It was found that the Cu₄Cl₄ monomer has a planar equilibrium structure of D_{4h} symmetry
 - I determined the molecular symmetry and the geometrical parameters of the MnF₃, AuF₃ and AuCl₃ molecules
- I reported evidence of the presence of the Jahn-Teller effect in the gas-phase determining the geometrical parameters of the distorted ground-state molecules
- I determined the temperature dependence of the composition of the CuCl vapor along with the structure of the molecules present

List of publications

Scientific papers:

M. Hargittai, B. Réffy, M. Kolonits, C.J.Marsden, J.-L. Heully:

The Structure of the Free MnF₃ Molecule – A Beautiful Example of the Jahn-Teller Effect
J. Am. Chem. Soc., 119 (1997) 9042

B. Réffy, M. Kolonits, M. Hargittai:

Gallium Tribromide: Molecular Geometry of Monomer and Dimer from Gas-Phase Electron Diffraction
J. Mol. Struct., 445 (1998) 139

B. Réffy, M. Kolonits, A. Schulz, T. M. Klapötke, M. Hargittai:

Intriguing Gold Trifluoride – Molecular Structure of Monomers and Dimers: An Electron Diffraction and Quantum Chemical Study
J. Am. Chem. Soc., 122 (2000) 3127

M. Hargittai, A. Schulz, B. Réffy, M. Kolonits:

Molecular Structure, Bonding and Jahn-Teller Effect in Gold Chlorides: Quantum Chemical Study of AuCl₃, Au₂Cl₆, AuCl₄⁻, AuCl, and Au₂Cl₂ and Electron Diffraction Study of Au₂Cl₆
J. Am. Chem. Soc. 123 (2001) 1449

M. Hargittai, P. Schwerdtfeger, B. Réffy, R. Brown

The Molecular Structure of Different Species of Cuprous Chloride from Gas-Phase Electron Diffraction and Quantum Chemical Calculation
Chem. Eur. J. 9 (2003) 327

B. Réffy, C. J. Marsden, M. Hargittai

Molecular Geometry of Monomeric and Dimeric Yttrium Trichloride from Gas-Phase Electron Diffraction and Quantum Chemical Calculations
J. Phys. Chem. A 107 (2003) 1840

Conference abstracts:

M. Hargittai, B. Réffy, M. Kolonits, C. J. Marsden, J.-L. Heully

The Free MnF₃ Molecule - A Beautiful Example of the Jahn-Teller Effect
Fifth Conference on Current Trends in Computational Chemistry, Vicksburg, 1996. Abstracts, p.46-47.

M. Hargittai, B. Réffy, M. Kolonits, C. J. Marsden, J.-L. Heully

The Free MnF₃ Molecule – A Beautiful Example of the Jahn-Teller Effect
First UNCW Mini-Symposium on Chemical and Biochemical Structure and Function, Wilmington, 1997. Abstract, 13.

B. Réffy, M. Kolonits, T. M. Klapötke, A. Schulz, M. Hargittai

Molecular geometry of vapor-phase gold trifluoride
17th Austin Symposium on Molecular Structure, 1998.