

High-Temperature Gas-Phase Electron Diffraction: Unexpected Dimer Structures Among Metal Halides¹

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Gas-phase electron diffraction (GED) studies at high temperatures have several special common features that justify their separate discussion. Due to the difficulties connected with the experiment this technique has developed only in a few laboratories. Most often inorganic systems are studied; lower-valence metal halides and metal oxides. Their low volatility requires high-temperature experimental conditions. Due to the complex vapor composition, other techniques, such as quadrupole mass spectrometry and, to an increasing degree, quantum chemical calculations accompany these GED studies. The analyses often reveal unanticipated structures. In this paper some unexpected and interesting structures of metal halide dimers will be shown, some from GED, others from computations carried out in connection with the high-temperature GED studies of metal halide systems of low volatility.

KEY WORDS: High-temperature gas-phase electron diffraction; metal halides; metal halide dimers; tin dihalides; alkaline earth dihalides.

INTRODUCTION

Most gas-phase electron diffraction (GED) studies are carried out on molecules, whose samples are easy to evaporate. There are, however, substances of low volatility and their gas-phase study requires high-temperature experimental conditions. Metal halides and especially oxides—or generally speaking, inorganic systems—are typical examples. Particularly, the lower-valence metal halides are ionic solids at ordinary conditions and their crystals do not contain molecules; they are only formed upon evaporation. Many industrial processes encounter vapor-phase metal halides, therefore, information on the vapor composition as well as the structure of the molecules present are important not only for fundamental knowledge but also for practical considerations [1].

In fact, metal halides were among the first objects to study by gas-phase electron diffraction, already in the very early days of the technique, in the 1930s [2]. Some metal halides, such as the aluminum halides evaporate at relatively low temperatures, at around 100°C, and as very

simple and symmetrical molecules, they were ideal targets for this new method. Then, during the 1950s, the first high-temperature electron diffraction group was established at Moscow State University mostly by Spiridonov (Fig. 1), Akishin, and Rambidi and they systematically determined the structure of large families of metal halides [3,4]. For a full reference to the early Russian literature on the electron diffraction studies of metal halides, see: Ref [3]. All these works used the so-called visual method of the technique. Although still often cited, the results of these early studies do not measure up to modern-day standards as far as the precision of the parameters is concerned; this is partly because of the rude approximation and data analysis and partly because the possible complexity of the vapor composition was not considered. Nonetheless, they were an important step in the history of molecular structure studies since for many decades these were the only geometrical data available on this large and important group of substances.

HIGH-TEMPERATURE GAS-PHASE ELECTRON DIFFRACTION

High-temperature GED poses special problems for the experiment as well as for the interpretation of the results, even if the basic principles of data reduction are the

¹Dedicated to the memory of Professor Victor P. Spiridonov.

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Fig. 1. Victor Spiridonov and some of his colleagues of the Moscow gas-electron diffraction group in 1969. Sitting from left to right: Victor Spiridonov, Lev Vilkov, M. Hargittai (on a visit), Natalya Tarasenko, and Vladimir Mastryukov. Standing from left to right: Leonid Khaikin, Alexei Golubinsky, Segei Smirnov, and Mikhail Anashkin.

same as for a room-temperature experiment. Therefore, it is prudent to summarize its development over the years. As mentioned above, pioneering work was carried out at the Moscow State University following some very early studies elsewhere [2b, 5,6]. Considerable development of the high-temperature GED technique was achieved at our laboratory starting from the 1970s [7,8]. High-temperature studies in Ivanovo, Russia [9] and in Oslo should also be mentioned [10].

The experimental difficulties of high-temperature electron diffraction were discussed in detail elsewhere [8], here only a short summary is given. The main problem concerns the technique of getting the high-temperature vapor into the diffraction chamber and into the way of the electron beam without creating a disturbing electromagnetic field. Different high-temperature nozzle systems have been developed. The first one, used by the Moscow GED Group used electron bombardment for heating the nozzle and it could reach as high a temperature as 2500°C. The structure of tungsten trioxide was determined by using this technique [11]. Another, more convenient nozzle system was the so-called radiation nozzle [12], used both in the Moscow and the Budapest laboratories. Metal

halides often evaporate at a few hundred centigrade as dimeric species. In order to get their monomers in the vapor in high-enough concentration but without getting too high vapor pressure in the diffraction chamber, the so-called double effusion chamber was developed [13]. Here the sample is put in the first part of the nozzle and heated and thus the species with higher volatility evaporate (e.g., the dimers). These molecules get into the second part of the nozzle that is heated to a much higher temperature and where the dimers dissociate into monomers. This system has been used in our laboratory to determine the structure of, e.g., monomeric Group 13 trihalides [14,15] and other monomeric metal halides and also in the Oslo Electron Diffraction Group [16]. Finally, special high-temperature nozzle systems were developed for carrying out diffraction experiments on reactive and unstable species prepared during the diffraction experiments [17,18]. Examples of structural studies include the unstable carbene analogues, SiCl_2 and SiBr_2 [19], GeCl_2 [20], and GeBr_2 [21].

Another problem that had to be dealt with in high-temperature experiments was the protection of the photographic plate from light emitted from the hot nozzle

tip. In the early experiments the plates were covered with India ink that was removed before developing. This technique was not very fortunate since it negatively impacted the signal/noise ratio. Applying different screening plates around the nozzle tip turned out to be a better solution in our laboratory.

Metal halides may evaporate in different forms and they might also decompose upon heating, or may even react with the container material. Therefore, monitoring the vapor composition during the actual experiment and before the time-consuming structure analysis is highly beneficial. The combined electron diffraction/quadrupole mass spectrometric experiment in our laboratory was an important development in this respect [22]. Later other laboratories also introduced this technique.

The interpretation of high-temperature experimental results also has its specificities, among them the most obvious ones are those related to the low-frequency, large-amplitude vibrations characteristic of most metal halides; the multiple scattering, and the complex vapor composition. Intramolecular multiple scattering is not specifically a high-temperature characteristic; rather one that manifests itself when a molecule has heavy atoms. It was recognized in connection with the GED study of the volatile rhenium hexa- and heptahalides relatively early [23]. The importance of other considerations in the structure analysis of high-temperature species, however, have only been realized gradually over the years. The available comprehensive review articles [1,24–26] about the GED studies of metal halides provide ample discussion of these effects. They also give information on a very large number of metal halide structures.

This paper is dedicated to the memory of Professor Victor P. Spiridonov, one of the pioneers of high-temperature electron diffraction and also a pioneer of the joint analysis of electron diffraction and vibrational spectroscopic data [27, 28]. The latter approach was developed partly because of the realization of several factors. One is the inadequacies of the usual structure analysis procedures applying the so-called rectilinear coordinate approximation. Another is that it was believed that for such small and symmetrical molecules as most metal halides are, the vibrational information present in the electron diffraction scattering data can be retrieved. Finally, the importance of taking into account the anharmonicity of vibrations for metal halide systems was also realized. Because of the complexity of the task the respective programs were developed only for simple metal dihalides and trihalides but the idea of the importance of using curvilinear rather than rectilinear coordinates in describing molecular vibrations was accepted and was addressed by others as well [29].

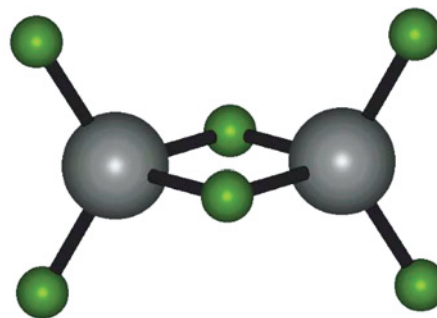


Fig. 2. D_{2h} -symmetry structure of most metal trihalide dimers with two distorted tetrahedra sharing an edge.

Metal Trihalide Dimers

Group 13 trihalides evaporate at a relatively low temperature as dimeric molecules. The only exception is their fluorides, which evaporate at around 1000 K as monomeric molecules [30]. The aluminum halides were among the first systems studied by GED [2]. They were followed by more up-to-date studies, Al_2Cl_6 [31], Al_2Br_6 [14, 31], Ga_2Cl_6 [32], Ga_2Br_6 [15]. These dimeric molecules have a well-known structure with D_{2h} symmetry in which two distorted tetrahedra share an edge (see Fig. 2).

Other metal trihalides also evaporate as dimers, as the examples of Au_2F_6 [33] and Au_2Cl_6 [34] indicate. Their electron diffraction study was carried out at 600 and 460 K, respectively. These molecules, as well as the other gold trihalide dimers [35], have a planar structure, also with two halogen bridges and D_{2h} symmetry (see Fig. 3). This structure is the result of relativistic effects [36]. As has been discussed, the primary effect of relativity is the contraction of all s orbitals, among them the valence shell 6s orbitals. These contracted s orbitals increase the shielding of the nuclear charge and that destabilizes the 5d orbitals that will expand. Due to these two effects, the 5d and 6s orbitals of gold get close to each other and the 5d orbitals become part of the valence shell and their shape prefers the planar arrangement over the tetrahedral

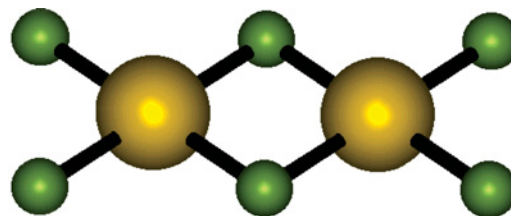


Fig. 3. D_{2h} -symmetry planar structure of gold trihalides.

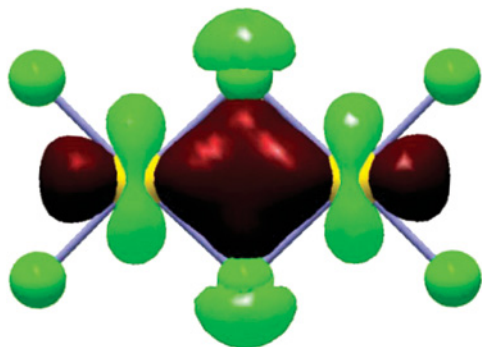


Fig. 4. One of the molecular orbitals of Au_2Cl_6 (after Ref. [34]).

one [34,35]. Figure 4 shows one of the molecular orbitals of Au_2Cl_6 , in which the role of the 5d orbitals is conspicuous.

Metal Dihalide Dimers

Irrespective of their shape, metal trihalides evaporate at relatively low temperatures as dimeric species. Metal dihalides are different in this respect. They evaporate as monomeric molecules at higher temperatures. It was realized only gradually, mostly as the result of mass spectrometric and vibrational spectroscopic studies, that often there were also dimeric species present in their vapors [1]. Sometimes their presence is only a few percent and in these cases the determination of their structure by GED is hardly possible. Even so, it is important to take them into consideration in the structure analysis as otherwise the precision of the geometrical parameters determined for the monomer may suffer [24]. Even if the dimer content of the vapor is relatively high, say, over 10%, the complete determination of their structure might pose problems due to the similar bond lengths in the monomer and dimer. To counter this problem the best solution is to calculate the structure of the dimer by quantum chemical calculations and then take over some parameters, such as the differences of bond lengths between the monomer and the dimer and within the dimer, from the calculation to the experiment and use these differences as constraints. It has been discussed [1, 37, 38] in detail before that the physical meanings of geometrical parameters coming from computation and from experiment are different. This is why the computed *differences* of distances rather than the computed geometrical parameters themselves are the ones to be carried over from the computation to the experiment. This is why it became essential that the structures of metal dihalide dimers be calculated at a high level of theory; they

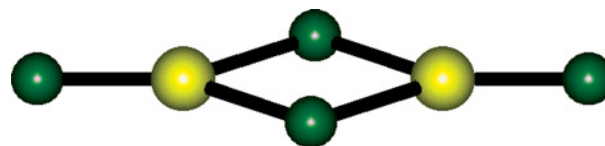


Fig. 5. D_{2h} -symmetry planar metal dihalide dimer structures.

had to be known in order to take their presence into consideration in the electron diffraction analysis—even if they were present in the vapor only in a relatively small amount.

In earlier studies where the presence of metal dihalide dimers was indicated, as a rule it was assumed that these molecules have a D_{2h} -symmetry planar structure with two halogen bridges (see Fig. 5) [39–41]. A computational study of the magnesium dihalide dimers and trimers probed other possibilities as well and concluded that the Mg_2X_4 molecules have a D_{2h} symmetry structure [42]. This observation was eventually accepted as applicable to all metal dihalide dimers. Only recently has it been realized that this generalization is not valid.

Alkaline Earth Dihalide Dimers

As indicated above, the general consensus has been that the dimers of all alkaline earth dihalides have a D_{2h} -symmetry geometry. A recent study [43], however, found that this is true only in those cases where the monomers are linear. It is well known by now, that only the dihalides of the lighter alkaline earth metals are linear [1]. Calcium difluoride and strontium dichloride are the most difficult cases with a very flat bending potential, and they can best be described as quasilinear molecules. All the barium dihalides and strontium difluoride are bent. The bent alkaline earth difluorides and dichlorides form dimers whose structure is very different from the D_{2h} -symmetry structure. These dimeric molecules have C_{3v} symmetry, with three halogen bridges and a rather polar, ionic nature (see Fig. 6)

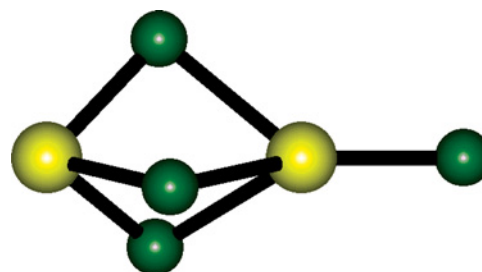


Fig. 6. C_{3v} -symmetry structure of the dimers of bent monomeric alkaline earth dihalide molecules (after Ref. [43]).

Table I. Geometrical Parameters (Bond Lengths in Å and Angles in Degrees) and Relative Energies (kJ/mol) of Alkaline Earth Difluoride and Dichloride Dimers from Computations after Ref. [43].^a

	Ca ₂ F ₄	Ca ₂ Cl ₄	Sr ₂ F ₄	Sr ₂ Cl ₄	Ba ₂ F ₄	Ba ₂ Cl ₄
M—X _t ^b	2.002	2.462	2.154	2.630	2.288	2.798
M—X _b	2.300	2.803	2.451	2.959	2.626	3.137
M ₂ —X _b	2.082	2.558	2.225	2.714	2.371	2.881
X _t —M—X _b	135.8	131.4	137.0	132.7	138.6	134.3
X _b —M—X _b	83.7	81.0	81.1	87.9	78.7	84.9
ΔE ^c	7.9	-2.5	28.9	13.0	45.8	27.3

^aDensity functional (B3LYP) calculations, Stuttgart quasirelativistic pseudopotentials, and a 6s6p5d1f basis for the metals and cc-pVTZ all electron bases for the halogens.

^bM is the four-coordinated metal atom in Figure 6.

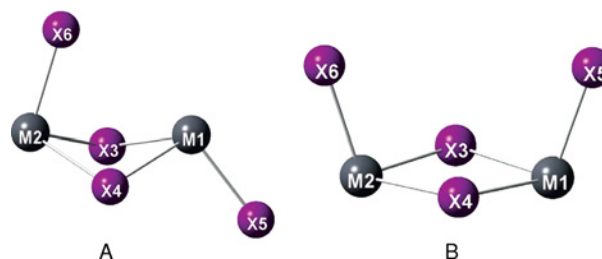
^cΔE = E(D_{2h}) - E(C_{3v}). Energy difference between the C_{3v} and D_{2h}-symmetry models.

[43]. For these molecules the D_{2h}-symmetry structure is not even a minimum, while, perhaps surprisingly, the C_{3v}-symmetry structure shown in Fig. 6 is a minimum for the linear dihalide dimers as well, even though with very high energy [43]. Table I shows some of the geometrical parameters together with the relative energies of the respective structures.

Apparently, the large polarizability of the heavy alkaline earth metals, which causes the bending of the monomers, makes the very symmetrical planar structure of D_{2h} symmetry unstable for the dimer.

Dimers of Group 14 Metal Dihalides

The vapors of tin dihalides have various practical applications; therefore their thermodynamic functions are of importance. In the mass spectrometric study of SnBr₂, for calculating their thermodynamic functions, again the above-mentioned D_{2h}-symmetry structure was assumed for the dimer [44]. However, even simple structural considerations question such an assumption. All tin dihalide molecules have a lone electron pair on the tin atom and its space requirement is the reason for their highly bent geometry. The presence of this lone electron pair is not in line with the supposed D_{2h}-symmetry planar dimer geometry. Many of the relevant crystal structures also conform with the space requirement of the lone electron pair. Tin difluoride, for example, has tetrameric units in the crystal with angles around the tin atom smaller than 90° indicating the stereochemical activity of the lone pair of electrons [45]. The same is true for the crystal of tin dichloride, which is a polymeric chain containing bent SnCl₂ molecules joined together by single chlorine bridges and with pyramidal three-coordination of tin [46].

**Fig. 7.** Stable minimum-energy structures of Group 14 metal dihalide dimers. Structure A is the global minimum (after Refs. [47, 48, 50]).

Recent computations found that, indeed, the structures of tin dihalide dimers differ considerably from the planar D_{2h}-symmetry shape [47,48]. In fact, two minimum structures were found with a rather small energy difference between them for both the chloride and the bromide. These structures are shown in Fig. 7. The global minimum is of C_s symmetry while the other minimum structure—only about 9 kJ/mol higher in energy—is of C_{2v} symmetry. Considering the fact that tin dichloride and tin dibromide vaporize only at several hundred degrees, we might assume that both species are present in the vapor, in perhaps somewhat different concentrations. An electron diffraction study of tin dichloride did not consider the presence of dimers [49]. In contrast, our recent electron diffraction study of tin dibromide found 2–3% of dimer present; alas this was too small to determine its structure [48a]. It was comforting that the thermodynamic calculations on tin dibromide suggested about the same concentration of dimers in the vapor phase. Such an agreement, of course, could be fortuitous. As part of our ongoing study of these dimers, the preliminary results for the Pb₂I₄ dimer [50] are also shown in Table II and these are in agreement with the findings for the tin dihalide dimers.

Dimers of Group 12 Metal Dihalides

The monomers of the zinc-group dihalides are linear molecules and there is no lone electron pair in their central atom to consider. Thus, D_{2h}-symmetry should be characteristic for the structure of their dimers. Because of the low relative concentrations of the dimeric species in the vapors of the zinc dihalides [51]—and the electron diffraction analyses of zinc dihalides [52] did not indicate any appreciable amounts either—their structure can only be determined by computations. As the results of Kaupp and von Schnering show [53], the dimers of zinc and cadmium difluoride and dichloride, indeed, have the expected shape of D_{2h} symmetry just as has the dimer of CdI₂ [54]. On the other hand, the mercury dihalides form very loose dimers with C_{2h} symmetry [55]. Figure 8 displays this structure.

Table II. Geometrical Parameters (Bond Lengths in Å and Angles in Degrees) and Relative Energies (kJ/mol) of Some Group 14 Metal Dihalide Dimers from Computations

M_2X_4	$Sn_2Cl_4^a$	$Sn_2Br_4^b$	$Pb_2I_4^c$
C_s model			
$r(M_2-X_3)$, Å	2.626	2.758	3.142
$r(M_1-X_3)$, Å	2.684	2.817	3.193
$r(M_2-X_6)$, Å	2.422	2.570	2.795
$r(M_1-X_5)$, Å	2.395	2.543	2.882
$\angle X_3-M_1-X_4$, deg	79.9	84.6	85.7
$\angle X_3-M_2-X_4$, deg	82.5	82.4	87.5
$\angle M_1-Y-M_2$, ^d deg	139.5	132.9	134.9
$\angle Y-M_1-X_5$, ^d deg	92.2	92.5	98.3
$\angle Y-M_2-X_6$, ^d deg	90.4	95.3	104.8
C_{2v} model			
$r(M_1-X_3)$, Å	2.662	2.792	3.176
$r(M_1-X_5)$, Å	2.383	2.528	2.875
$\angle X_3-M_1-X_4$, deg	81.9	85.7	88.5
$\angle M_1-Y-M_2$, ^d deg	170.6	167.7	173.2
$\angle Y-M_1-X_5$, ^d deg	93.4	96.8	105.0
ΔE^e	8.8	9.1	1.3

^aFrom Ref. [47]. MP2 level. Quasirelativistic ECP (Stuttgart) and a (14s10p2d1f)/[3s3p2d1f]-type valence basis set on Sn and all electron cc-pVTZ basis on Cl.

^bFrom Ref. [48a]. MP2 level. Quasirelativistic ECP (Stuttgart) and a (14s10p2d1f)/[3s3p2d1f]-type valence basis set on both Sn and Br atoms.

^cFrom Ref. [50]. Density functional (B3LYP) calculation. Quasirelativistic ECP (Stuttgart) on both Pb and I atoms, and a valence basis set (4s4p1d)/[2s2p1d] for Pb and (4s4p)/[2s2p] for I.

^dY is the midpoint of the $Br_3 \cdots Br_4$ distance.

^e $\Delta E = E(C_{2v}) - E(C_s)$. Energy difference between the C_{2v} and C_s -symmetry models.

Apparently, relativistic effects decrease the intermolecular interactions for the mercury dihalide dimers and thus they prefer the C_{2h} -symmetry structure to the more symmetrical D_{2h} structure. The role of relativistic effects in this is shown by the fact that the nonrelativistic (as well as the Hartree-Fock) calculations result in a D_{2h} -symmetry structure for the mercury halides as well. From the rela-

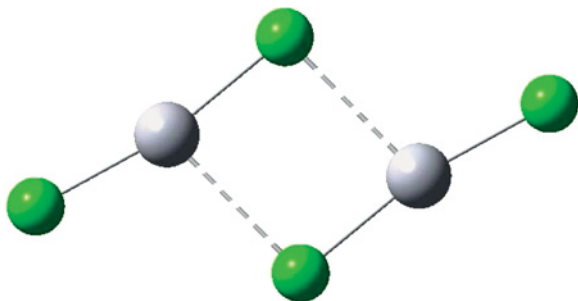


Fig. 8. C_{2h} -symmetry geometry of the mercury dihalide dimers (after Ref. [55]).

tivistic calculation, this appears to be a transition structure with one negative frequency. The geometrical parameters are shown in Table III.

CONCLUDING REMARKS

In 2005, the 75th anniversary of GED is being celebrated. During these 75 years, this technique has proved to be a beautiful and extremely useful technique to learn about intricate details of the innermost secrets of matter. The information it has provided about the structure of small free molecules has not only enriched our knowledge about these small building blocks of matter but also helped to determine the structure of larger biological systems—as, for example, the story of the discovery of the alpha-helix structure of proteins by Linus Pauling proved [56].

GED is a delicate and precise technique—but at the same time costly and the analysis is time-consuming. It would be self-deceiving not to accept the fact that for small simple organic molecules quantum computations have gradually taken over. They are cheaper, easier, and faster and their application does not require long and difficult learning periods from those who want to apply them as does GED. If there is a place, however, where GED is a uniquely important technique, it is the high-temperature studies of inorganic systems. Computations are still in the developing stage for molecules containing heavy atoms often with open electron shells. Here the geometrical information provided by GED cannot be replaced by other approaches in the foreseeable future. They not only provide reliable geometrical data but also serve as benchmarks for computations. Of course, in this role the different physical meanings of computed and experimental geometries [1,37] have to be taken into account—this is a feature of modern structure determination that needs to be brought to the attention of all computational chemists.

Above we referred to the complicated composition of metal halide vapors and in this regard the importance of having additional information from other sources for successful GED analysis. In this respect computations have proved to be an invaluable aid. Even if they are not yet at the best possible level for these heavy and floppy systems—and thus the actual computed geometrical parameters may be off more than what experimentalists would call an “acceptable experimental error”—they are very helpful. According to the usual practice—and as was discussed above briefly—it is differences of bond distances, and sometimes the bond angles, that can be taken over from the computation to the experimental analysis and used as constraints. Even if the physical meanings of the computed and experimental parameters are different

Table III. Geometrical Parameters of Group 12 Dihalide Dimers (Bond Lengths in Å, Angles in Degrees) After Refs. [53] and [55]^a

M ₂ X ₄	Symmetry	M—X _t	M—X _b	M ··· X _b	X _b —M—X _b	X _t —M—X _b
Zn ₂ F ₄	D _{2h}	1.763	1.937	1.937	80.0	140.0
Zn ₂ Cl ₄	D _{2h}	2.111	2.305	2.305	93.5	133.3
Cd ₂ F ₄	D _{2h}	1.977	2.146	2.146	75.5	141.2
Cd ₂ Cl ₄	D _{2h}	2.317	2.517	2.517	88.6	135.7
Hg ₂ F ₄	C _{2h}	1.972	2.023	2.506	72.5	173.5
Hg ₂ Cl ₄	C _{2h}	2.295	2.329	3.130	84.8	174.4
Hg ₂ Br ₄	C _{2h}	2.424	2.455	3.284	87.8	173.7
Hg ₂ I ₄	C _{2h}	2.629	2.659	3.444	91.5	170.0

^aMP2 level. Quisirelativistic (Stuttgart) pseudopotentials on all atoms. Valence basis sets on the metals: (8s7p6d)/[6s5p3d] and on the halogens: (5s5p1d)/[3s3p1d].

and even if the computed parameters might not be reliable enough yet, we might assume that these problems will cancel out in their *differences* as well as they do in the bond angles themselves. Experience with complicated vapor compositions such as was the case with copper chloride [57] and with vapors in which the concentration of one component is too small such as was the case with the dimer content in most metal dihalide vapors shows that this approach can be properly utilized. This joint use of the old high-temperature GED experiment and the new and constantly developing quantum chemical calculations, appears to be the most promising way for the structure determination of complicated inorganic systems. Invoking other experimental techniques, such as quadrupole mass spectrometry for monitoring the vapor composition and different spectroscopies for facilitating the vibrational analysis are additional and welcome possibilities.

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