Journal of Solid State Chemistry **146,** 239–244 (1999)
Article ID jssc.1999.8344, available online at http://www.idealibrary.com on IDEAL®

Application of an Improved Point-Charge Model To Study the Crystal Hg_2F_2

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Received August 27, 1998; in revised form April 8, 1999; accepted April 22, 1999

An improved point-charge model has been applied to study the relatively close-packing crystal Hg_2F_2 compound. For this model, the point-charge values used for defining the Madelung potential are based on Mulliken population analysis, and then spherical expansions are made for the point charges. Bond lengths, bond energies, force constants, and vibrational frequencies have been determined. The calculated various properties are in reasonable agreement with the experimental crystalline data, which indicates the success of the model. We have also shown that this model is applicable to the Hg_2Cl_2 crystal as well. © 1999 Academic Press

Key Words: **Hg_2F_2 crystal compound; point-charge model; density functional calculations.**

INTRODUCTION

A series of studies (1–7) have shown that crystal compounds that contain rather localized building blocks can, in most cases, be well treated by the "embedded cluster approximation." That is, a group of atoms is treated by a molecular quantum mechanical method, while the environment is simulated in an approximate manner. A number of theoretical approaches (1, 2, 6–9) to account for the crystal environment have been established for ionic compounds. One of the practical methods is based on the point-charge model (1), in which the interactions due to the other atoms in the crystal are simulated by a potential of point charges. To obtain more accurate results, one may sum the effects of all point charges up to convergence by a Madelung-type treatment. The procedure is that the Madelung potential (MP) is evaluated on a point grid in the spatial region of the molecular group and is then simulated by fitted charges at a finite number of surrounding points of the crystal lattice. Therefore, the MP can be given by

$$V_{\mathrm{MP}}(\mathbf{r}_1) = \sum_p \frac{Z_p}{(\mathbf{r}_1 - \mathbf{r}_p)}, \qquad [1]$$

where Z_p are the (extra) point charges and $\mathbf{r}_p$ the corresponding position vectors.

The simple point-charge model can only take into account the long-range electrostatic interaction, but neglects the short-range overlap from the nearest neighbors. In practice (2), we made a slight modification for the MP by using a Coulomb cut off-type pseudopotential

$$V_{\mathrm{effective}}(\mathbf{r}_1) = \mathrm{Max}(V_{\mathrm{MP}}(\mathbf{r}_1), C). \qquad [2]$$

Equation [2] accounts for the fact that the valence electrons of the "molecular" group must not penetrate into the electrostatically attractive core regions of the surrounding anions or cations because of the Pauli exclusion repulsion. C is a constant used in cut off-type effective core potentials (10) to balance the nuclear attraction.

We have applied the point-charge model to a number of crystal compounds (2, 3). In most cases, the model has been very successful in rationalizing the properties observed in the solid state. So far, the method has not been used extensively and its scope is yet unknown. We found that, among the isostructural mercurous crystal halides (Hg_2F_2, Hg_2Cl_2, Hg_2Br_2, and Hg_2I_2), the point-charge model is quite suitable for the study of Hg_2Cl_2, Hg_2Br_2, and Hg_2I_2 (2). However, the model is not so adequate for Hg_2F_2. The MP of Hg_2F_2 strongly expands the Hg–Hg bond so that the calculated Hg–Hg distance is unexpectedly large. The exceptional nature of Hg_2F_2 in the MP was attributed to the more pronounced interactions between molecules in the fluoride (see next section), i.e., to the rather strong short-range overlap effect.

The point-charge model is an attractive simple approach to calculate solids. In a number of cases (1–5), satisfactory results have been obtained. We feel that it is necessary to

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0022-4596/99 $30.00

further explore the crystal field approach so that its application scope would become wider. In this paper, we have made an improvement on the previously used point-charge model and will show that the improved model is adequate for Hg_2F_2. For comparison, the Hg_2Cl_2 crystal has also been included in the investigation.

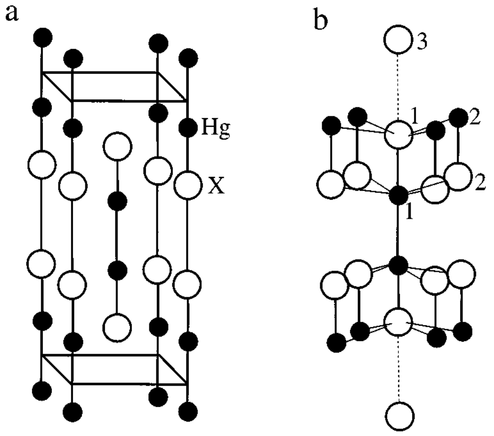

FIG. 1. Structure of crystal Hg_2X_2: (a) the unit of the cell; (b) the local environment of a Hg_2X_2 molecule in the crystal.

CRYSTAL STRUCTURES OF Hg_2X_2

All the crystal structures of the mercurous halides are equivalent (isostructural) (11–13). They are tetragonal with space group I_4/mmm and with lattice constants given in Table 1. The unit cell is shown in Fig. 1a. One unit cell contains two molecules of Hg_2X_2 (i.e., $Z = 2$). The discrete linear molecule is oriented along (001). The local environment of one Hg_2X_2 molecule in the structure is shown in Fig. 1b. The two halogen atoms of the shortest Hg–X distance represent the characteristic coordination. Each Hg atom is surrounded by four other halogen atoms, and vice versa for X.

We see that the packing conditions are similar for Hg_2Cl_2–Hg_2I_2. However, the parameter a ($= b$) of Hg_2F_2 is especially short compared with that of Hg_2Cl_2, while c remains actually the same. There is a close approach of 2.71 Å between the mercury and the fluorine atoms of neighboring molecules. The constituent atoms in the crystal are so near that this compound exhibits some unique properties.

CALCULATIONAL DETAILS

The calculations were carried out with the Amsterdam Density-Functional (ADF) program (version 2.0.1 (1995)] developed by Baerends *et al.* (14). The simple X_α potential ($\alpha = 0.7$) was chosen since more sophisticated potentials were shown not to improve the results for this kind of system (2). For Hg, a triple-ζ STO basis was used for the $5d$ and $6s$ valence orbitals augmented by two $6p$ polarization functions ($\zeta = 2.60$, 1.35) and one $5f$ polarization function ($\zeta = 2.70$). For F and Cl, we used a triple-ζ basis for the ns and np orbitals plus one $3d$ polarization function ($\zeta_{3d}^{F} = 2.00$, $\zeta_{3d}^{Cl} = 1.80$). The other shells of lower energy, i.e., [Xe $4f^{14}$] for Hg, [He] for F, and [Ne] for Cl were considered as core shells and kept frozen according to the frozen-core technique (14). Relativistic corrections of the valence electrons were calculated using the quasirelativistic method (15). Previously (2), one $5f$ polarization function was not included for Hg and relativistic corrections were calculated by the first-order perturbation approach (16).

TABLE 1
Structural Data[a] (Å) of Hg_2X_2

Compound	Hg_2F_2	Hg_2Cl_2	Hg_2Br_2	Hg_2I_2[b]
$a = b$	3.673	4.482	4.663	4.92
c	10.884	10.910	11.113	11.61
Hg–4X	2.71	3.21	3.32	3.51

[a] Ref. (11). [b] Ref. (12).

We have now made two modifications for the point-charge model. (i) The point-charge values used for creating the MP are based on Mulliken population analysis on Hg_2F_2. Previously (2), formal charges of $+1$ (for Hg) and -1 (for F) were attached in defining the MP. The calculations show that the Mulliken atomic charges are significantly less than ± 1. It was argued (4) that defects in the point-charge model would be dominated by the point-charge values. Lü (17) showed that for solid compounds like MgO, it is necessary to use Mulliken atomic charges in the point-charge model. (ii) A spherical expansion is made for the point charge (18). The idea was suggested by Rys *et al.* (19) and Yanez *et al.* (20). The charge density $\rho_p(r)$ is given by

$$\rho_p(r) = Q_p(\phi_s(r))^2. \qquad [3]$$

Here, we take $\phi_s(r)$ as a normalized spherical STO,

$$\phi_s(r) = \frac{1}{\sqrt{\pi}}\alpha^{3/2}e^{-\alpha r}. \qquad [4]$$

In Eq. [3], Q_p is the point-charge value and α is a parameter. For different ions, the ionic radii and also the spherical charge distribution may be different. So, one should use different α's for different ions. We calculate the average radius of the spherical charge,

$$\langle r \rangle = \int \phi_s^*(r) r \phi_s(r)\, d\tau = \frac{3}{2\alpha}. \qquad [5]$$

One obtains

$$\alpha = \frac{3}{2\langle r \rangle}. \quad [6]$$

In practice, the ionic radius R^{ion} is used to replace $\langle r \rangle$. From Eq. [3], the spherical charge has the form

$$q_p(r) = \int_0^r 4\pi r^2 \rho_p(r)\, dr = Q_p(1 - e^{-2\alpha r} - 2\alpha r e^{-2\alpha r} - 2\alpha^2 r^2 e^{-2\alpha r}). \quad [7]$$

RESULTS AND DISCUSSION

The linear symmetric X–Hg–Hg–X molecule contains two types of bonds, Hg–Hg and Hg–X. The equilibrium bond lengths, R_{HgHg} and $R_{\text{Hg}X}$, and the corresponding force constants, k_1(Hg–Hg) and k_2(Hg–X), were determined from a two-dimensional, complete second-order polynomial fit to a large number ($\sim$20) of calculated energy points around equilibrium. We then set up the secular equation to determine the frequencies ω_1, ω_2, and ω_3. The form of the vibrations is illustrated in Fig. 2.

The Hg–Hg bond energy (E_{HgHg}) is defined as

$$E_{\text{HgHg}} = 2E(\text{Hg}X) - E(\text{Hg}_2X_2), \quad [8]$$

where $E(\text{Hg}_2X_2)$ is the total energy of the molecule Hg_2X_2 and $E(\text{Hg}X)$ the total energy of the free HgX fragment (the Hg–X distance of the free HgX fragment is independently optimized).

The bond energy in the crystal field (CF) is defined as $AB(\text{in CF}) \rightarrow A(\text{free}) + B(\text{free})$. It now consists of two parts,

$$E_{\text{bond}}^{\text{total}} = \tfrac{1}{2}\, E_{\text{latt}} + E_{\text{bond}}^{\text{internal}}, \quad [9]$$

where $E_{\text{bond}}^{\text{internal}}$ is the bond energy of the molecule, as calculated in the crystal field. E_{latt} is the electrostatic interaction between the fragments and the lattice,

$$E_{\text{latt}} = \sum_A \left[\int \rho_A(\mathbf{r}) \cdot \text{MP}(\mathbf{r}) \cdot d\mathbf{r} + Z_A \cdot \text{MP}(R_A) \right]. \quad [10]$$

There are no direct measurements of the Hg–Hg bond energies E_{HgHg} for the crystal Hg_2X_2. The concerned thermodynamic data are available (21) and can be used to estimate E_{HgHg} in the compounds. We consider the standard enthalpies of formation and take the values at the same temperature of 298 K. According to the definition (Eg. [8]), we obtain the Hg–Hg bond energy as

$$\text{Hg}_2X_2(\text{solid}) \rightarrow 2\text{Hg}X(\text{gas}):$$

$$E_{\text{HgHg}} = 2\Delta H^\circ(\text{Hg}X) - \Delta H^\circ(\text{Hg}_2X_2) \quad [11]$$

The calculated various properties are given in Table 2. The results of free Hg_2X_2 have also been listed. There are no experimental data in the gas phase for comparison. Only the calculated values from the PP–HF, PP-MP2, and ANO-QCISD methods (22, 23) can be compared. In Table 2, we give the ANO-QCISD values, which were taken as a reference to judge the other more approximate methods (23). It is shown that our calculated Hg–Hg bond lengths and bond energies are in good agreement with the available ANO-QCISD data. Thus, the use of the X_α potential and the use of the basis sets are justified.

Hg_2F_2

The Hg–Hg bond length in the free Hg_2F_2 molecule is 0.05 Å longer than the experimental crystalline value. However, the Hg–F bond length in the free molecule is considerably shorter (by 0.12 Å) than that in the crystal. This is not surprising because, on one hand, the Hg–F moiety in the free molecule has quite more covalency than that in the solid state. On the other hand, the Hg–Hg bond energy in the free molecule is much smaller (by 2.3 eV) than that in the crystal. Similar situations can be found for Hg_2Cl_2.

We now put Hg_2F_2 in the crystal field. Hg_2F_2 has been treated in three cases. (i) The formal point charges of +1(Hg) and −1(F) are used to define the MP (here, denoted as $q = \pm 1$). (ii) The point charges used for defining the MP are based on Mulliken population analysis ($q = \pm 0.71$). (iii) Spherical expansions are made for the point charges ($q = \pm 0.71$ sph).

Let us first look at the results for $q = \pm 1$. The MP expands the Hg–Hg bond. So the calculated Hg–Hg bond length is 0.13 Å longer than the experimental crystalline value. Correspondingly, the Hg–Hg force constant is greatly reduced so that the calculated Hg–Hg frequency is considerably smaller than the experimental one (24). The other properties calculated in the MP are shown to compare favorably with the experimental value. In the crystal field, the MP shows a strong lengthening on the Hg–F bond (by 0.09 Å). Corresponding to the Hg–F bond lengthening, the force constant k_2 and frequencies ω_2 and ω_3 are greatly decreased. The crystal field enhances the Hg–Hg bonding strongly. In the MP of $q = \pm 1$, the Hg–Hg bond energy is calculated as 5.55 eV, which is 0.4 eV larger than the thermodynamic value.

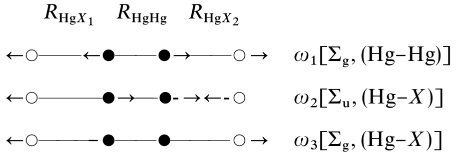

FIG. 2. Three parallel vibrational modes for Hg_2X_2. ●, Hg; ○, X.

TABLE 2

Calculated Properties[a] for Hg_2F_2 and Hg_2Cl_2 (FM = Free Molecule, MMP = Molecule in Madelung Potential)

		R_{HgHg}	E_{HgX}	E_{HgHg}	k_1	k_2	$k_{12}{}^b$	ω_1	ω_2	ω_3
Hg_2F_2	FM	2.56	2.02	2.83	1.87	3.04	−0.023	168	547	544
		2.56^c		2.91^c						
	MMP:									
	$q = \pm 1$	2.64	2.11	5.55	1.51	1.84	−0.063	149	429	423
	$q = \pm 0.71$	2.59	2.10	4.74	1.64	1.90	−0.048	156	435	430
	$q = \pm 0.71$ sph	2.58	2.10	5.23	1.67	1.90	−0.045	158	435	430
	Exptl (solid)[d]	2.51	2.14	5.16^e	—	—	—	186	387	—
	$-(FHg)_8$ (FM)	2.79	2.22							
	$-(FHg)_8$ (MMP)	2.59	2.17							
		2.57^f	2.19^f							
Hg_2Cl_2	FM	2.61	2.37	2.47	1.54	1.94	−0.002	145	339	332
		2.59^c		2.67^c						
	MMP:									
	$q = \pm 1$	2.60	2.45	4.42	1.66	1.40	0.020	149	290	282
	$q = \pm 0.58$ sph	2.60	2.42	4.12	1.64	1.51	0.010	149	301	292
	Exptl (solid)[g]	2.53	2.43	4.37^e	2.13	1.21	0.03	167	275	261
	$-(ClHg)_8$ (FM)	2.63	2.64							
	$-(ClHg)_8$ (MMP)	2.60	2.56							

[a] Bond length R in Å, bond energy E in eV, force constant k in N/cm, and vibrational frequency ω in cm^{-1}. [b] Force constant representing the interaction between adjacent bonds r_1 and r_2. [c] From ANO-QCISD calculations of Kaupp and von Schnering (23). [d] Experimental bond lengths are from Ref. (11); experimental frequencies are from Ref. (24). [e] Values from thermodynamic calculation. [f] From (quasi-relativistic) periodic Hartree–Fock calculations (23). [g] Experimental bond lengths are from Ref. (11); experimental force constants and frequencies are from Ref. (26).

We now look at the results for $q = \pm 0.71$. From $q = \pm 1$ to $q = \pm 0.71$, the Hg–Hg bond length is reduced significantly, by 0.05 Å. The Hg–Hg bond energy is also reduced considerably (by 0.8 eV). In this case, the calculated E_{HgHg} is now 0.4 eV smaller than the thermodynamic value. However, the other calculated properties (R_{HgF}, k_2, ω_2, ω_3) are only slightly changed by the modified MP.

Then, spherical expansions are made for the point charges. The ionic radii of Hg^+ and F^- are 1.11 and 1.15 Å, respectively (25). Therefore, α_{Hg^+} and α_{F^-} are obtained as 0.72 and 0.70, respectively. With the spherical charge model, the Hg–Hg bond length is again shortened by 0.01 Å, but the shortening is not pronounced. The calculated R_{HgHg} is still larger than the experimental crystalline value by 0.07 Å. We will give further discussion for this problem (Section 4.3). The calculated properties related to the Hg–F bond remain unchanged. The main effect of the spherical charges is to increase the Hg–Hg bond energy; E_{HgHg} is increased by 0.5 eV in the MP of the spherical charges as compared to the result for $q = \pm 0.71$. This implies that the spherical expansion brings about a nearly vertical stabilization of the point-charge potential, equivalent to a global molecule–lattice attraction. We see that the calculated bond energy is now very close to the thermodynamic value. So overall the calculated results are improved by using the spherical point-charge model.

Hg_2Cl_2

We now turn to the discussion of Hg_2Cl_2. Two cases have been considered, viz. $q = \pm 1$ and $q = \pm 0.58$ sph. The complete vibrational spectra of the Hg_2X_2 unit are known for Hg_2Cl_2 (26).

Hg_2Cl_2 experiences a bond contraction (by 0.01 Å) in the MP when compared to the Hg–Hg bond length of free Hg_2Cl_2. This is in contrast to Hg_2F_2. In the MP of $q = \pm 1$, the calculated Hg–Hg bond length is 0.07 Å longer than the experimental crystalline value. Correspondingly, the Hg–Hg force constant or frequency is significantly underestimated. The other calculated properties, E_{HgHg}, R_{HgCl}, k_2, ω_2, and ω_3, agree well with the experimental data.

From $q = \pm 1$ to $q = \pm 0.58$ sph, the Hg–Hg bond lengths remain unchanged, again, in contrast to Hg_2F_2. According to the calculations based on the spherical point-charge model, the Hg–Hg bond length in Hg_2Cl_2 is 0.02 Å longer than that in Hg_2F_2. This is in full agreement with the experimental data. Note that the Hg–Hg bond length in free Hg_2Cl_2 is 0.05 Å longer than that in free Hg_2F_2. The Hg–Cl bond length is shortened by 0.03 Å and the Hg–Hg bond energy is reduced by 0.3 eV. Because the calculated R_{HgCl} and E_{HgHg} for $q = \pm 1$ are slightly larger than the experimental data, the calculated values for $q = \pm 0.58$ sph are now slightly smaller than the experimental data. The force constants or frequencies calculated with the different models are close. Therefore, we conclude that the "conventional" point-charge model and the spherical point-charge model are all adequate for Hg_2Cl_2.

Hg_2X_2 *in Halide and Crystal Field Surrounding*

As shown above, the calculated Hg–Hg bond lengths are 0.07 Å too long. So one question is raised, i.e., what are the factors responsible for the short Hg–Hg bond length? It may be assumed that the Hg–Hg bond length is influenced by two factors: the short-range overlap interaction from the nearest X–Hg groups (see Fig. 1b) and the long-range electrostatic potential. In the above sections, we have only accounted for the lowest-order electrostatic interactions in the lattice (Coulomb and induction). Therefore, we have also performed another set of computations by including the (X2–Hg2) groups explicitly in the quantum mechanical treatment. All other atoms are still approximated by the point-charge model. We found that the calculated Hg–Hg bond length in Hg_2F_2 is no longer dependent on the point-charge values. This means that the calculated Hg–Hg bond length in Hg_2F_2 is sensitive only to the point-charge values used for the neighbors. The results are given in Table 2. In calculating the Hg_2X_2–$(X\mathrm{Hg})_8$ complex, only the Hg–Hg and Hg–$X(1)$ bond lengths were optimized and the positions of the surrounding (XHg) were fixed. For the sake of comparison, we have also calculated the free complexes, the results of which allow us to see the effect of the short-range overlap interaction on the bond lengths.

In free Hg_2F_2–$(FHg)_8$, the Hg–Hg bond length is calculated to be 2.79 Å, which is 0.23 Å longer than that in free Hg_2F_2. A rather long Hg–F bond length (2.22 Å) is also obtained. So the neighbouring (FHg) groups can strongly expand the Hg–Hg and Hg–F bonds.

Upon the complex being embedded in the MP, the Hg–Hg bond length is reduced from 2.79 to 2.59 Å and the Hg–F bond length is reduced by 0.05 Å. Therefore, the long-range electrostatic potential plays an important role in contracting the bonds. We see that the Hg–Hg bond length calculated by including halides and crystal field surrounding is equal or nearly equal to the bond length of Hg_2F_2 in the MP. However, the Hg–F bond length calculated in Hg_2F_2–$(FHg)_8$–MMP is significantly longer (by 0.07 Å) than the bond length in Hg_2F_2–MMP; it is now 0.03 Å longer than the experimental crystalline value.

We now turn to the situation of $X = \mathrm{Cl}$. The Hg–Hg bond length in free Hg_2Cl_2–$(ClHg)_8$ is only slightly longer (by 0.02 Å) than that in free Hg_2Cl_2, whereas the Hg–Cl bond in the free complex is remarkably lengthened (by 0.27 Å). So in the Hg_2Cl_2 crystal, the neighboring (ClHg) groups strongly expand the Hg–Cl bond, but only weakly expand the Hg–Hg bond. The MP contracts the Hg–Hg bond also weakly. The Hg–Hg bond length in Hg_2Cl_2–$(ClHg)_8$–MMP is equal to that in Hg_2Cl_2–MMP. The Hg–Cl bond is contracted by 0.08 Å by the MP. We find that the Hg–Cl bond length calculated in Hg_2Cl_2–$(ClHg)_8$–MMP is considerably longer (by 0.13 Å) than the experimental crystalline value. We admit that our model, to account for the short-range interaction, is not perfect. The eight (XHg) groups do not form close surrounding. That is, the properties of isolated HgX can be different from the properties of HgX in Hg_2X_2. Therefore, the effect of the short-range interaction on the Hg–Cl bond length may be overestimated. A suitable number of nearest neighbors is given by eight (Hg_2X_2) molecules. Because of computational limitations, we have not calculated $(Hg_2X_2)_{10}$.

Summarizing, in both Hg_2F_2 and Hg_2Cl_2 crystals, there exists a great short-range interaction between the Hg_2X_2 molecule and the neighboring (XHg) entities. The Hg–X bond expansion is mainly caused by the short-range interaction. In the Hg_2F_2 crystal, the short-range interaction could also strongly expand the Hg–Hg bond, but the long-range MP has a large contraction effect so that the bond expansion is largely restrained. In Hg_2Cl_2, the short-range interaction and the long-range MP have only small effects on the Hg–Hg bond length and two effects on the Hg–Hg bond length cancel out. Even though we have included the (XHg) neighbors in the calculation, a quantitative agreement between the theoretical and observed Hg–Hg bond lengths cannot be achieved. The calculated R_{HgHg} values are still $\sim$0.07 Å longer than the experimental crystalline data.

Kaupp and von Schnering (23) have performed a quasi-relativistic periodic Hartree–Fock calculation on bulk Hg_2F_2. Their optimized Hg–Hg and Hg–F bond lengths are 2.57 and 2.19 Å, respectively, which are apparently close to our results on Hg_2F_2–$(FHg)_8$–MMP. We note that our density-functional calculations as well as the periodic Hartree–Fock calculation did not include dispersion, which may partially account for the longer theoretical Hg–Hg bond length.

CONCLUSIONS

In the crystal Hg_2F_2, the constituent atoms are so near that a Hg_2F_2 molecule in an electrostatic field based on a purely ionic picture ($q = \pm 1$) does not form a reliable model for the solid. The calculated Hg–Hg bond length is sensitive to the point-charge values used for the neighbors. So one has to use the calculated (Mulliken) atomic charges, which are significantly smaller than the formal oxidation states. With the spherical expansion for the point charges, we can obtain the Hg–Hg bond energy which is in good agreement with the thermodynamic data. The reasonable agreements of the calculated various properties with experimental crystalline data indicate that the improved point-charge model is effective for the crystal Hg_2F_2. This model is also applicable to Hg_2Cl_2. The Hg–Hg bond expansion of 0.02 Å in going from Hg_2F_2 to Hg_2Cl_2 is correctly reproduced by the calculations.

The calculations cannot reproduce the rather short Hg–Hg bond lengths. The most reliable experimental determinations of the Hg–Hg bond length by single-crystal X-ray diffraction are those of Dorm (11) and Schrötter and Müller (13). They are about 2.51 Å. From the calculated Hg–Hg frequencies (which are smaller than experimental data) and the two sets of calculations, we have the indications that theoretical Hg–Hg bond lengths from relativistic X_α calculations may be 0.07 Å too long. The difference between the calculated and observed Hg–Hg bond lengths is not due to the deficiencies in the crystal-field model.

ACKNOWLEDGMENT

This work was supported by the Natural Science Foundation of Fujian Province, People's Republic of China.

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