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A theoretical study of gas-phase and solid-state $Hg(CF_3)_2$

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Abstract

Gas-phase and solid-state $Hg(CF_3)_2$ have been studied using a relativistic density-functional method. The crystalline environment was simulated by a cut-off-type Madelung potential. Bond lengths, dissociation energies, force constants, and enthalpy of sublimation are calculated. The influence of the crystal field (CF) on the molecular properties is well reproduced by the CF model. The intermolecular bonding in the crystal structure is examined and is revealed to be dominated by electrostatic effects. The relatively high enthalpy of sublimation evaluated for the crystal compound ($\Delta H_{sub} = 18.7$ kcal) accounts for its relatively high melting points. A hypothetical crystal $Hg(CH_3)_2$ is shown to have a small ΔH_{sub} (3 kcal mol^{-1}), which explains why no solid-state $Hg(CH_3)_2$ exists. Ionization potentials for all the valence MOs of the gas-phase $Hg(CF_3)_2$ are predicted. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: $Hg(CF_3)_2$ compound; Density-functional calculations; Crystal field effects; Ionization potentials

1. Introduction

$Hg(CF_3)_2$ is an attractive species for structural and spectroscopic studies because of its molecular simplicity and its utility in chemical syntheses. In contrast to $Hg(CH_3)_2$, there are relatively few theoretical studies of $Hg(CF_3)_2$ [1]; experimental studies are also rare [2,3]. Molecular geometry for the gas-phase species has been measured experimentally [2]. Vibrational spectra were recorded only in solution [3]. No experimental measurements on the ionization potentials (IPs) have been reported. One purpose of this study is to predict some unknown molecular properties of $Hg(CF_3)_2$. The existence of crystalline $Hg(CF_3)_2$ has also stimulated our interest in this compound. No solid-state $Hg(CH_3)_2$ has been found. This causes some conjecture on this unique property of $Hg(CF_3)_2$. It was suggested [3] that there exists relatively strong intermolecular bonding in the crystal $Hg(CF_3)_2$; the bonding occurs via interaction between Hg and six F atoms of the neighboring molecules. Because the intermolecular Hg···F distances are rather long (3.18 Å, which is larger than the sum of van der Waals radii [4], $R_{Hg}^{vdW} + R_{F}^{vdW} = 1.55 + 1.47 = 3.02$ Å), the extent of the interaction is questionable. It is also reasonable to ask why no solid-state $Hg(CH_3)_2$ exists. These are interesting points that we wish to investigate. On the other hand, the gas-phase $Hg(CH_3)_2$ has slightly shorter Hg–C and C–F bonds than has the crystal compound. It is also of interest to examine whether the differences between the gas-phase and solid-state bond lengths could be reproduced by calculation. Another interesting aspect is the variation of the Hg–C bonding on the CH_3/CF_3 substitution. Experimentally, the Hg–C bond length in $Hg(CF_3)_2$ is slightly longer than that in $Hg(CH_3)_2$. According to group electronegativities [5] and the Schomaker–Stevenson rule [6], a change in the Hg–C bond length is then predicted which is opposite to that of the experimental results. Because of our interest in the comparison of bonding behaviors between $Hg(CF_3)_2$ and $Hg(CH_3)_2$, the latter molecule has been included in our calculations. There have been a number of theoretical calculations on $Hg(CH_3)_2$ [7–10].

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2. Computational method

The calculations were carried out using the Amsterdam density-functional (ADF) program developed by Baerends and co-workers [11] and its quasi-relativistic extension of Ziegler et al. [12] The STO basis used is of triple-zeta quality. For Hg, the 5d and 6s shells were considered as valence shells; two 6p and one 5f polarization functions were added ($\zeta_{6p} = 2.60$, $\zeta'_{6p} = 1.35$, $\zeta_{5f} = 2.70$). For C and F, 2s and 2p were considered as valence shells and one 3d polarization function was added ($\zeta^{C}_{3d} = 2.2$, $\zeta^{F}_{3d} = 2.0$). The other shells of lower energy, i.e. [Xe4f^{14}] for Hg and [He] for C/F, were described as core and were treated by the frozen-core approximation [11a]. Among the various exchange–correlation potentials implemented, 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. Thus far, a universally 'best' functional for the accurate prediction of geometries and energies of a variety of systems has still not been found. Using their 'Gaussian-2' theoretical procedure, Pople and co-workers [13] have carried out an extensive and systematic test of different DF formalisms on 32 light neutral molecules. It was shown that the VWN-B-P functional (see Section 4.1) can give accurate binding energies for those molecules. However, we found that for the present heavy systems, the VWN-B-P functional greatly overestimates the Hg–C bond length and underestimates the binding energy. In order to obtain accurate results, there is a need to test the performance of the different functionals and we have tested the VWN-B-P, VWN-S, and X_α functionals for the present gas-phase systems. Finally, the simple X_α functional was adopted in the solid-state calculations as it best reproduces the experimental data (see Table 2).

3. Crystal structure and crystal field modeling

The crystal structure of $Hg(CF_3)_2$ was determined by Brauer et al. [3]. The unit cell is shown in Fig. 1. It belongs to a cubic crystal system with space group $Pa3$ and with lattice constants $a = b = c = 8.127$ Å; one unit cell contains four $Hg(CF_3)_2$ molecules. The positional parameters for the atoms (Hg, C, F) are given in Table 1. A structural feature of the compound is that $Hg(CF_3)_2$ 'molecules' are isolated. The shortest intermolecular F···F distance is 3.145 Å, which is twice as large as the van der Waals radius of F ($2R_F^{vdW} = 2.94$ Å) [4]. In order to investigate the stability of $Hg(CH_3)_2$ in the solid state, its crystal structure is needed. We assumed the crystal structure of $Hg(CF_3)_2$ for $Hg(CH_3)_2$. Because the C–H bond length is significantly shorter than the C–F one, the lattice constant (a) as well as the positional parameters (x, y, z) for $Hg(CH_3)_2$ were scaled appropriately according to the relationship among the R (bond lengths), a, and xyz, where the experimental Hg–C and C–H bond lengths in the gas phase were used to approximate the bond lengths in the solid state (in fact the bond lengths in the gas phase and solid state are very similar). The obtained a and xyz values for the hypothetical $Hg(CH_3)_2$ are shown in Table 1.

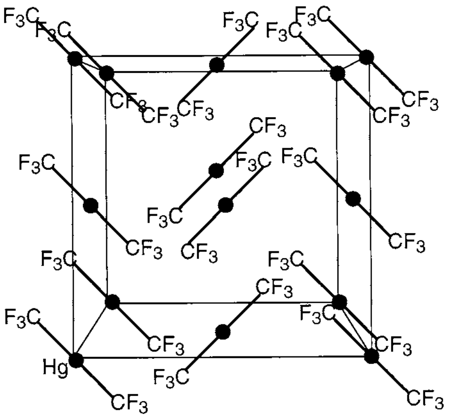

Fig. 1. Unit cell of crystal $Hg(CF_3)_2$.

Because the adjacent molecules are considerably separated, there are no significant short intermolecular interactions in the crystal structure. In this case, we may assume that the predominant effect on the molecular properties can be attributed to the electrostatic interaction from the surrounding atoms. As a simple model, the surrounding atoms are treated as a set of

Table 1
Positional parameters (x, y, z) and lattice constant $a(=b=c)$ for $Hg(CF_3)_2$ [a] and hypothetical $Hg(CH_3)_2$

		x	y	z	$a(=b=c)$ (Å)	Bond lengths used for $Hg(CH_3)_2$ (Å)
$Hg(CF_3)_2$	Hg	0.0	0.0	0.0	8.127	
	C	0.15	0.15	0.15		
	F	0.0818	0.2951	0.1766		
$Hg(CH_3)_2$ (hypothethical)	Hg	0.0	0.0	0.0	6.627	Hg–C = 2.10, C–H = 1.10
	C	0.183	0.183	0.183		
	H	0.1148	0.3281	0.2096		

[a] From Ref. [3].

Table 2
Calculated properties [a] for $Hg(CF_3)_2$ and $Hg(CH_3)_2$ (FM, MCF, X = F, H)

			$R_{Hg–C}$	D_e	$k^s_{Hg–C}$	$k^{as}_{Hg–C}$	$R_{C–X}$	$\angle_{HgCX}$	$k^s_{C–X}$	$k^a_{C–X}$
$Hg(CF_3)_2$	FM	VWN-B-P	2.205	2.15	1.62					
		X_α	2.158	2.73	1.88	1.89	1.345	111.9	7.35	6.98
		Experimental [b]	2.101		2.18	1.98	1.345	112.0	5.15	4.33
	MCF	X_α	2.160	3.54	1.89	1.83	1.350	112.8	7.10	7.14
		Experimental [c]	2.118				1.349	111.7		
$Hg(CH_3)_2$	FM	VWN-B-P	2.160	2.26	1.96					
		VWN-S	2.127	3.47	2.21					
		X_α	2.127	2.99	2.18	1.98	1.103	110.2	4.95	
		Experimental [d]	2.083	2.52	2.38	2.35	1.106		4.739	
	MCF	X_α	2.122	3.12	2.22					

[a] Bond lengths R in Å, dissociation energies D_e in eV, symmetric and antisymmetric force constants k^s and k^{as} in N cm^{-1}, bond angles in degrees; available experimental data are given for comparison.

[b] Experimental bond lengths and bond angles from Ref. [2]; experimental force constants (obtained in solution) from Ref. [3].

[c] Ref. [3].

[d] Experimental bond lengths from Ref. [25]; experimental force constants from Ref. [26]; experimental dissociation energies from Ref. [27].

infinite point charges that create a Madelung potential in which the molecule is immersed. Numerous successful calculations have shown that the so-called point-charge model allows efficient and accurate studies of molecular solid compounds [14–18].

The Madelung potential in the spatial region of the molecule is calculated following the Ewald method [19]. A description of the method can also be found in Ref. [14]. In a practical calculation, one defines a radius parameter for each atom of the central molecule under consideration. Inside the superposition of these spheres, the Madelung potential is evaluated on a point grid, and is then simulated by fitted charges at a finite number of surrounding points of the real crystal lattice. In calculating the Madelung potential, the point-charge values were obtained first from a Mulliken population analysis of the free molecule (FM). The resulting new charge from the ADF calculation on the molecule in the crystal field (MCF) is then fed back into the Madelung potential calculation. The process was repeated with the corrected field until convergence was reached. For the present crystal system, 138 point-charges at the (nearest) lattice sites have been used to build up the crystalline environment. The error of the fitted potentials is less than 0.001 eV.

Because the simple point-charge model neglects the short-range overlap from the nearest neighbors, a slight modification of the Madelung potential, $V_{Madelung}$, has been made by using a Coulomb cut-off type pseudopotential:

$$V_{eff}(r) = \mathrm{Max}(V_{Madelung}(r), C) \tag{1}$$

Here Max means to give the maximum value of the arguments. Eq. (1) accounts for the fact that the valence electrons of the molecule 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 [20] to balance the nuclear attraction.

The bond energy in the crystal field (CF) is defined as: AB(in CF) → A(free) + B(free). It now consists of two parts:

$$E^{total}_{bond} = \frac{1}{2} E_{latt} + E^{internal}_{bond} \tag{2}$$

where $E^{internal}_{bond}$ is the bond energy of the molecule, as calculated in the CF. E_{latt} is the electrostatic interaction between the atoms (or fragments) and the lattice. The factor 1/2 is necessary in order not to count this interaction twice in the whole crystal:

$$E_{latt} = \sum_A \left[\int \rho\hat{A}(\vec{r})\cdot V_{eff}(\vec{r})\cdot d\vec{r} + Z_A \cdot V_{eff}(R_A) \right] \tag{3}$$

where ρ_A is the electronic density of atom A, Z_A the nuclear charge of A, and R_A the position vector of A.

4. Results and discussion

The results (bond lengths, bond angles, dissociation energies, symmetric and antisymmetric force constants), for both FM and MCF, are collected in Table 2. The symmetry of FM is taken to be D_{3d}. MCF has symmetry of S_6. The bond lengths and force constants were determined from a fifth-degree polynomial fit to nine energy points around the equilibrium. The dissociation energy D_e is defined as:

$$Hg(CX_3)_2 \ (FM/MCF) \rightarrow Hg \ (free) + 2CX_3 \ (free) \tag{4}$$

Table 3
Gross Mulliken populations on the AOs of Hg and charge distributions on Hg and CX_3 (FM, MCF, X = F, H)

		Hg-5d	Hg-6s	Hg-6p	Hg-5f	Q_{Hg}	$Q_{\mathrm{CX_3}}$
$Hg(CF_3)_2$	FM	9.86	0.81	0.27	0.03	1.04	−0.52
	MCF	9.84	0.62	0.10	0.02	1.42	−0.71
$Hg(CH_3)_2$	FM	9.85	0.85	0.22	0.03	1.06	−0.53
	MCF	9.83	0.75	0.14	0.03	1.25	−0.63

4.1. Free $Hg(CH_3)_2$ and $Hg(CH_3)_2$

For free $Hg(CH_3)_2$, three kinds of DF approximations were used: the simple X_α potential, Vosko–Wilk–Nusair local spin-density potential [21] plus Becke's gradient correction for exchange [22] and Perdew's gradient correction for correlation [23] (labeled as VWN-B-P), and VWN potential plus Stoll's self-interaction correction for correlation [24] (labeled as VWN-S). There are experimental data [25,26] which can serve as a means of testing the different DF potentials. For free $Hg(CF_3)_2$, the X_α and VWN-B-P potentials were used.

The Hg–C bond lengths calculated with the simple X_α and with the correlated VWN-S potentials are identical; they are ca. 0.04 Å longer than the experimental value. The X_α and VWN-S calculated Hg–C force constants are also very similar and agree well with experiment. However, the VWN-S potential considerably overestimates the dissociation energy, by nearly 1 eV, whereas the X_α potential gives a result closer to experiment, the deviation $D_e^{\mathrm{calc}} - D_e^{\mathrm{exptl}}$ being about 0.5 eV. The VWN-B-P calculated D_e is lower than the experimental value by 0.3 eV. However, the VWN-B-P bond length $R_{\mathrm{Hg–C}}$ is 0.08–0.1 Å too long and the corresponding force constant $k_{\mathrm{Hg–C}}$ is 0.4–0.7 N cm^{-1} too small. Among the three DF potentials, the X_α potential is able to yield good results for all the cases (for R, D, k). Therefore, we decided to adopt the simple X_α potential for the calculations here.

At the X_α level, the calculated symmetric Hg–C and C–F force constants ($k^{\mathrm{s}}_{\mathrm{Hg–C}}$, $k^{\mathrm{s}}_{\mathrm{C–F}}$) in $Hg(CF_3)_2$ are 1.88 and 7.35 N cm^{-1}, respectively. According to the calculated results for $Hg(CH_3)_2$, the X_α method probably underestimates the Hg–C force constant by 0.2–0.3 N cm^{-1}. The experimental data for the Hg–C and C–F force constants were obtained only in solution (benzene), where $k^{\mathrm{s}}_{\mathrm{Hg–C}}$ and $k^{\mathrm{s}}_{\mathrm{C–F}}$ are 2.18 and 5.15 N cm^{-1}, respectively. Therefore, the experimental data of $k_{\mathrm{Hg–C}}$ in solution may stand for experimental data in the gas phase. However, we find that the experimental C–F force constants are considerably smaller than the calculated ones. The very large discrepancy between the calculation and experiment is somewhat surprising because the calculated and experimental C–F bond lengths are identical. To check the calculational accuracy, we also calculated the C–H force constant in $Hg(CH_3)_2$, where experimental $k_{\mathrm{C–H}}$ in the gas phase is available. We find that the X_α value of $k_{\mathrm{C–H}}$ shows good agreement with the experimental one. An experimental measurement for $k_{\mathrm{C–F}}$ in the gas-phase $Hg(CF_3)_2$ is desirable to verify the calculated value. The calculation shows that $k^{\mathrm{s}}_{\mathrm{C–F}}$ is significantly larger than the antisymmetric force constant $k^{\mathrm{as}}_{\mathrm{C–F}}$ .The trend is consistent with the measured values in solution.

The Hg–C bond length is calculated to be slightly longer in $Hg(CF_3)_2$ than in $Hg(CH_3)_2$ (by 0.03 Å). This is in good agreement with experiment (by 0.02 Å). Correspondingly, the Hg–C force constant is 0.2–0.3 N cm^{-1} smaller in $Hg(CF_3)_2$ than in $Hg(CH_3)_2$, again in agreement with experiment. No experimental data for Hg–CF_3 bond strengths are available. The calculation predicts that the dissociation energy for $Hg(CF_3)_2$ is 0.25 eV smaller than that for $Hg(CH_3)_2$. Although the group electronegativity (EN) of CF_3 (EN = 3.32) is thought to be larger than that of CH_3 (EN = 2.30) [5], the Hg–C bond in $Hg(CF_3)_2$ is in fact weaker than that in $Hg(CH_3)_2$. This is opposite from what one would predict on the basis of ligand EN.

Table 3 gives the gross Mulliken populations on Hg atomic orbitals (AOs) and charge distributions (Q) on Hg and CF_3/CH_3. There is a large Hg-6p contribution to the Hg–C bonding; the Hg-5f contribution is very small. The electron number on Hg-6p also reflects the degree of sp hybridization around Hg. Hg in free $Hg(CF_3)_2$ bears a positive charge of ca. 1.0 ($\ll 2$), indicating that the bond between Hg and CF_3 is significantly covalent. Q_{Hg} in $Hg(CH_3)_2$ is comparable with that in $Hg(CF_3)_2$. The charge distributions do not agree with common opinion that the CF_3 group is more

Table 4
Relativistic effects [a] on the calculated Hg–C bond length $R_{\mathrm{Hg–C}}$ (Å), dissociation energy D_e (eV), and Hg–C force constant $k^{\mathrm{s}}_{\mathrm{Hg–C}}$ (N cm^{-1}) (FM, MCF)

		$\Delta^{\mathrm{rel}}R_{\mathrm{Hg–C}}$	$\Delta^{\mathrm{rel}}D_e$	$\Delta^{\mathrm{rel}}k^{\mathrm{s}}_{\mathrm{Hg–C}}$
$Hg(CF_3)_2$	FM	−0.12	−0.38	0.40
	MCF	−0.14	−0.40	0.42
$Hg(CH_3)_2$	FM	−0.11	−0.24	0.48

[a] $\Delta^{\mathrm{rel}}A = A^{\mathrm{rel}} - A^{\mathrm{nrel}}$.

Table 5
Calculated dissociation energies (ΔE in eV) for the first dissociation step of $Hg(CF_3)_2$ and $Hg(CH_3)_2$

	ΔE^{calc}	ΔE^{exp}
$Hg(CF_3)_2 \rightarrow HgCF_3 + CF_3$	2.48	
$Hg(CF_3)_2 \rightarrow HgCH_3 + CH_3$	2.77	2.49 [a]

[a] Ref. [27].

Table 6
Calculated ionization potentials (IPs in eV) obtained using the transition-state method [a]

MO	IP	Percent character [b]	
		Hg	CF_3
$1a_{1g}$, $1a_{2u}$	35.69		100 $1a_1$
$2a_{1g}$	20.15		88 $2a_1$
$3a_{1g}$	17.90	25 5d	10 $2a_1$, 54 $3a_1$
$4a_{1g}$	15.03	56 5d	34 $3a_1$
$5a_{1g}$	11.65	30 6s	43 $4a_1$
$1a_{2g}$, $1a_{1u}$	12.45		100 $1a_2$
$1e_{1g}$, $1e_{1u}$	33.19		100 $1e_1$
$2e_{1g}$, $2e_{1u}$	17.39		100 $2e_1$
$3e_{1g}$	17.26	88 5d	
$4e_{1g}$	16.44	96 5d	
$5e_{1g}$	13.86		95 $3e_1$
$6e_{1g}$	12.88		96 $4e_1$
$2a_{2u}$	19.90		100 $2a_1$
$3a_{2u}$	16.33		95 $3a_1$
$4a_{2u}$	9.66	10 6p	86 $4a_1$
$3e_{1u}$	13.94		100 $3e_1$
$4e_{1u}$	13.02		100 $4e_1$

[a] The major fragment orbital contributions to the MOs are given.
[b] From Mulliken population analysis.

electron-withdrawing than the CH_3 group. Table 4 shows the relativistic effects on the Hg–C bond properties. Relativity leads to significant Hg–C bond contraction. The relativistic increase in k_{Hg-C} is consistent with the relativistic bond contraction. However, there is a large relativistic destabilization for the Hg–C bond. We have also evaluated the energy required to remove the first CX_3 ligand from $Hg(CX_3)_2$ (X = F, H). The values (ΔE) are given in Table 5. An experimental ΔE value is known for $Hg(CH_3)$ [27]; the agreement between the calculation and experiment is good. In Table 6 we present the calculated IPs for all occupied molecular orbitals (MOs) of $Hg(CF_3)_2$. These predicted IPs may be useful for future work on photoelectron spectra. The major fragment orbital contribution to each MO are given in Table 6. The valence MO energy diagram is shown in Fig. 2. The HOMO $4a_{2u}$ shows 10% Hg-6p participation. The lower lying $5a_{1g}$ shows large mixture of Hg-6s and CF_3-$4a_1$.

4.2. $Hg(CF_3)_2$ and $Hg(CH_3)_2$ in the solid state

We now examine the influence of the CF on the molecular properties. The Hg–C bond in $Hg(CF_3)_2$ lengthens by 0.002 Å upon going from FM to MCF. The Hg–C force constants for FM and MCF are also nearly identical. Experimentally, the Hg–C bond lengthening seems to be more pronounced (by 0.02 Å). The FM has 0.005 Å shorter C–F bond than MCF has. This calculated bond length shift is consistent with the experimental finding (0.004 Å). Corresponding to the C–F bond expansion in the CF, there is a decrease of 0.25 N cm^{-1} in the force constant k^{s}_{C-F}. In the CF, the calculated symmetric and antisymmetric force constants are nearly the same. This is in contrast to the FM case. The ionicity of the Hg–C bond in the solid is enhanced by the CF, the Q_{Hg} for MCF being 1.42.

By comparison of the calculated energies between FM and MCF, we can determine the enthalpy of the sublimation of the solid compound, viz. $\Delta H_{sub} = D_e(MCF) - D_e(FM)$. The enthalpy of sublimation represents the CF stabilization energy on the molecule. Because the calculated ΔH_{sub} is the difference between D_e(MCF) and D_e(FM), the possible errors brought about by the DF used will cancel. It has been shown that ΔH_{sub} can be evaluated accurately by the point-charge model [18]. The obtained ΔH_{sub} for $Hg(CF_3)_2$ is 0.81 eV (18.7 kcal mol^{-1}). This is a relatively large value which may account for the relatively high melting point (163°C) for this compound [3]. For the hypothetical solid-state $Hg(CH_3)_2$, the ΔH_{sub} was found to be

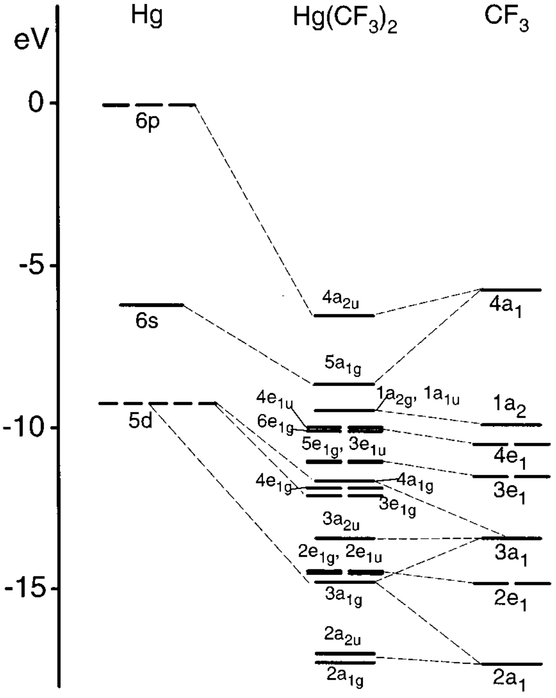

Fig. 2. Orbital energy diagram of Hg, CF_3 and $Hg(CF_3)_2$ free.

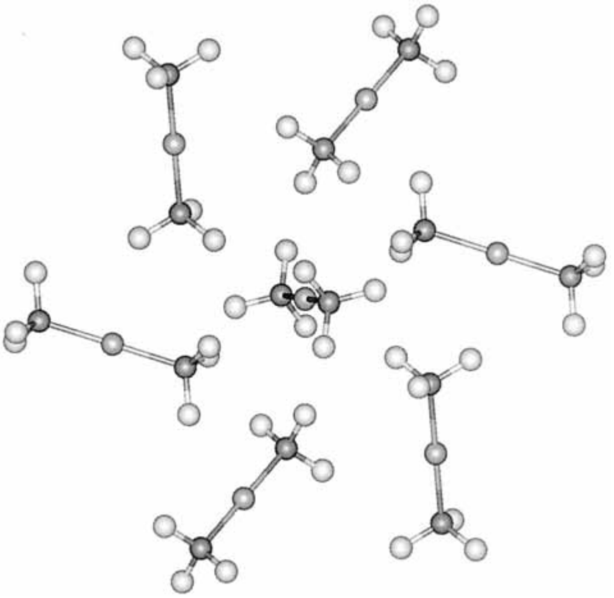

Fig. 3. One central $Hg(CF_3)_2$ molecule and its six neighbors in the crystal $Hg(CF_3)_2$ structure.

Table 7
Interaction energy (E_{int} in eV) between a central $Hg(CF_3)_2$ molecule and its six neighbors in the crystal structure [a]

	E_{int}	ΔH_{sub}
$Hg(CF_3)_2$–CF (MCF → FM)		0.81
$[Hg(CF_3)_2]^{central}$–$[Hg(CF_3)_2]_6^{neighbor}$(A) [b]	0.68	0.34[d]
$[Hg(CF_3)_2]^{central}$–$[Hg(CF_3)_2]_6^{neighbor}$(B) [c]	0.61	0.31[d]
$Hg(CF_3)_2$–[point-charges]$_6$ (MCF → FM)		0.32

[a] The calculated enthalpy of sublimation (ΔH_{sub} in eV) and the contribution of E_{int} to ΔH_{sub} are given.

[b] (A): with 6p polarization functions on the central Hg.

[c] (B): excluding 6p polarization functions on the central Hg.

[d] The value ($= E_{int}/2$) represents a contribution of the interaction energy to ΔH_{sub}.

0.13 eV (3 kcal mol^{-1}). The very small CF stabilization energy implies that a solid-state $Hg(CH_3)_2$ could easily sublimate. This explains why no solid-state $Hg(CH_3)_2$ exists.

The existence of solid $Hg(CF_3)_2$ has caused some conjecture about the bonding in this compound. It was suggested [3] that there may exist significant intermolecular bonding which occurs via the six 3.18 F···Hg interactions per Hg atom, namely, via interactions between nonbonding F-2p orbitals and unfilled Hg-6p orbitals. It was also suggested that Coulombic attraction between the oppositely charged F and Hg atoms may be significant. In order to obtain a quantitative estimate of the intermolecular interaction between a central $Hg(CF_3)_2$ and its six nearest neighbors F, we have calculated a large cluster $[Hg(CF_3)_2]_7$ cut from the crystal structure. The arrangement of the seven $Hg(CF_3)_2$ molecules in the structure is shown in Fig. 3, where one central $Hg(CF_3)_2$ is surrounded by six neighboring $Hg(CF_3)_2$ molecules. The whole system involves 63 atoms. The interaction energy is defined as

$$[Hg(CF_3)_2]_7(\text{cluster}) \rightarrow Hg(CF_3)_2(\text{central}) + [Hg(CF_3)_2]_6(\text{neighbors}) \quad (5)$$

$$E_{int} = E(\text{central}) + E(\text{neighbors}) - E(\text{cluster}) \quad (6)$$

where the three systems were calculated at their fixed positions in the structure.

Table 7 shows the E_{int} values. The $[Hg(CF_3)_2]$–$[Hg(CF_3)_2]_6$ interaction energy is calculated to be 0.68 eV. The contribution of this energy to the enthalpy of sublimation is given by $E_{int}/2$. Thus, the E_{int} contributes 0.34 eV to the ΔH_{sub}. This is about 40% of the calculated ΔH_{sub}. In order to assess the effect of Hg-6p polarization orbitals on the intermolecular bonding, we performed another set of calculations by removing 6p basis sets on Hg in the central $Hg(CF_3)_2$. The calculated E_{int} is reduced by only 0.07 eV. Therefore, there is little participation by Hg-6p orbitals in the intermolecular bonding. After obtaining the quantitative $[Hg(CF_3)_2]$–$[Hg(CF_3)_2]_6$ interaction energy, it would be of interest to examine if the intermolecular interactions can be treated solely electrostatically. Therefore, we replaced the $[Hg(CF_3)_2]_6$ with 54 point-charges (labeled as [point-charges]$_6$) and calculated a $[Hg(CF_3)_2]$–[point-charges]$_6$ system. The values of the point-charges are those obtained from Mulliken population analysis ($Q_{Hg} = 1.42$, $Q_C = 1.26$, $Q_F = -0.66$). In such a CF generated by only [point-charges]$_6$, the enthalpy of sublimation is evaluated to be 0.32 eV. This value is very close to the contribution of E_{int} to ΔH_{sub}. Therefore, the intermolecular bonding in the structure is dominated by electrostatic effects and the crystal environment can be represented by point-charges. The result also indicates that the electric field generated by only the neighboring ions is not sufficient to describe the influence of the whole lattice.

5. Conclusions

We arrive at the following main conclusions from the results:

1. The present point-charge model is quite suitable for the study of the crystal $Hg(CF_3)_2$. The calculated difference in bond lengths between FM and MCF is consistent with the experimental data on the gas-phase molecule and solid-state compound.
2. The calculations clearly show that the Hg–C bond is weaker in $Hg(CF_3)_2$ than in $Hg(CH_3)_2$. This is in agreement with experimental evidence. The dissociation energy of $Hg(CF_3)_2$ [$Hg(CF_3)_2 \rightarrow Hg + 2CF_3$] is about 0.25 eV smaller than that of $Hg(CH_3)_2$.

3. The solid-state $Hg(CF_3)_2$ has relatively high enthalpy of sublimation (18.7 kcal mol^{-1}), which accounts for its relatively high melting point. The intermolecular interactions in crystal structure are mainly electrostatic. A calculation on a hypothetical crystal $Hg(CH_3)_2$ compound shows that it has only small enthalpy of sublimation (3 kcal mol^{-1}). This is the reason why no solid-state $Hg(CH_3)_2$ exists.
4. IPs for all the valence MOs of the gas-phase $Hg(CF_3)_2$ are predicted, which may be useful for future work on photoelectron spectra.

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