JOURNAL

OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 102, NUMBER 23 NOVEMBER 5, 1980

Molecular Structure of Mercurous Halides: Hg_2F_2 and Hg_2Cl_2

Daniel A. Kleier[1a,b] and Willard R. Wadt*[1a]

Contribution from the Theoretical Division, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87545, and Thompson Chemical Laboratory, Williams College, Williamstown, Massachusetts 01267. *Received March 25, 1980*

Abstract: Ab initio generalized valence bond calculations using effective core potentials are presented for the ground state of $(HgF)_2$ and $(HgCl)_2$. Extensive calculations are also reported for HgF and compared with previous literature results for HgCl. In spite of the polar nature of the Hg–X bond in the monomer, which would favor a head-to-tail orientation of the dipoles in the dimer, a moderately strong covalent bond between the mercury atoms dictates a linear structure (X–Hg–Hg–X) for both fluoride and chloride. Comparison with solid-state data suggests that the Hg–X bonds shorten upon entering the gas phase. Stability toward disproportionation is problematical. Simple calculations predict the chloride to be about 0.6 eV more stable than Hg + $HgCl_2$, while the disporportionation of Hg_2F_2 is predicted to be nearly thermoneutral. Improved calculations shed some doubt on the stability of Hg_2Cl_2. An improved virtual orbital calculation has been performed to estimate where spectral evidence for the existence of Hg_2Cl_2 in the gas phase might be found.

I. Introduction

The goal of this paper is to answer the following question. Is the dimer of HgCl (HgF) best described by a covalent linkage between the mercury atoms of the HgCl (HgF) monomers or by a largely electrostatic interaction between HgCl (HgF) dipoles? All of the mercurous halides are known to crystallize in molecular lattices of linear X–Hg–Hg–X molecules.[2] However, these solid-state studies suffer from complications due to crystal-packing forces. Only indirect evidence is available concerning the intrinsic geometric preference of these molecules in the gas phase, and then the only question addressed is whether the molecules disproportionate. Electrostatic arguments favor a D_{2h} square geometry (i.e., Hg atoms catercorner) or a linear head-to-tail dimer (X–Hg··· X–Hg), while a strong covalent bond between the mercury atoms would favor a linear head-to-head arrangement (X–Hg–Hg–X).

In order to understand the intrinsic factors responsible for the geometry of these molecules, we have performed ab initio calculations on the mercurous fluoride and mercurous chloride dimers. The principle objective was to settle the question of the ground-state geometry, but calculations were also performed to predict the absorption spectrum of Hg_2Cl_2. It is our hope that the latter calculations will inspire spectroscopic work in this long neglected area.

II. Details of Calculation

Valence electron calculations[3,4] were performed by using double ζ plus polarization quality basis sets[5] with the halide basis sets augmented with an additional p function to describe the negative ion.[6] We used a relativistic effective core potential for Hg[7] and nonrelativistic core potentials for F and Cl.[8] Two configuration SCF calculations were carried out by using the GVBTWO program of Bobrowicz and Wadt[9] based upon the generalized valence bond procedure of Hunt, Hay, and Goddard.[10] The two-configuration wave function correctly describes the dissociation of the dimer into monomer units. We also report here for the first time electronic structure calculations on the ground state of the HgF monomer. Calculations have also been performed on the low-lying excited states of HgF, but these results are not pertinent and will be reported elsewhere.[7] The potential energy curve for the $^2\Sigma^+$ ground state of HgF was obtained by using an extensive POL-CI[11] (4910 spin eigenfunctions) based upon a set of valence orbitals which were defined by an SCF calculation on the $^2\Pi$ state.[12] Estimates of the excitation energies for the first few excited states of Hg_2Cl_2 were made from improved virtual orbital (IVO) calculations.[13]

The geometries of the square and head-to-head dimers of Hg_2F_2 and Hg_2Cl_2 were obtained by a chainwise optimization of the unique bond distances by assuming a quadratic potential. A similar scheme was used for the head-to-tail dimer of Hg_2F_2. Structures intermediate between the square and linear head-to-

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(2) (a) Grdenic, D.; Djordjevic, *J. Chem. Soc.* **1956**, 1316. (b) Havighurst, R. J. *J. Am. Chem. Soc.* **1926**, *48*, 2113. (c) Dorm, E. *Chem. Commun.* **1971**, 466.

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(5) For mercury the (3s3p4d) basis of ref 3 was contracted to [2s2p2d]. For chlorine the (3s3p) basis of ref 4 was contracted to [2s2p], and a set of 3d functions were added with an exponent of 0.5. For fluorine the (4s) basis of ref 4 was contracted to [2s], the 5p basis of ref 6 contracted to [2p] and additional 3d functions with an exponent of 0.9 were added.

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Table I. Computed Properties for $^2\Sigma^+$ Ground States of HgF and HgCl

	Hartree-Fock			POL-CI			exptl[a]		
mol	R_e, Å	ω_e, cm^{-1}	D_e, eV	R_e, Å	ω_e, cm^{-1}	D_e, eV	R_e, Å	ω_e, cm^{-1}	D_e, eV
HgF	2.02	511	0.30	2.07	351	0.99		491	(1.8)
HgCl	2.39	286	0.66	2.41	285	0.91		293	1.08

[a] Huber, K. P.; Herzberg, G. "Constants of Diatomic Molecules"; Van Nostrand-Reinhold: New York, 1979; p 314.

Table II. Relative Energies (eV) for GVB (2-Configuration) Wave Functions[a]

	F	Cl
2Hg + 2X	2.56[b]	3.10[b]
2HgX	1.96[c]	1.78[c]
X-Hg-Hg-X (lin)	0.00[a]	0.00[a]
Hg-X···Hg-X (lin)	1.37[d]	
Hg_2X_2 (square)	0.93[e]	1.12[e]
HgX_2 + Hg	−0.08[f]	0.65[f]

[a] All energies are reported relative to the GVB energy of optimized X-Hg-Hg-X. With use of effective potentials, these GVB energies are −135.3200 and −117.7071 au for Hg_2F_2 and Hg_2Cl_2, respectively. [b] Twice the single configuration SCF energy for HgX at an HgX distance of 20 au. [c] Twice the single configuration SCF energy for HgX at the Hartree-Fock optimized distance (2.02 Å for HgF and 2.39 Å for HgCl). [d] GVB energy for head-to-tail dimer. The distance between the monomers has been optimized (1.97 Å), but the Hg-F distance within the monomer was held fixed at the optimum value of 2.02 Å. [e] GVB energy for optimized square structure. The optimized HgX distances are 2.26 and 2.64 Å for square Hg_2F_2 and Hg_2Cl_2, respectively. [f] GVB energy for Hg + HgX_2. The arrangement of all four atoms was linear with the HgX distance in HgX_2 at an optimum value (1.90 Å for HgF_2 and 2.28 Å for $HgCl_2$), and the free Hg atom was 20 au removed from the closest halogen of HgX_2.

head dimer were obtained by using the linear synchronous transit method.[14]

III. Results

The ground-state properties of the monomers HgF and HgCl are summarized in Table I. Since the calculations on the dimers were performed by using GVB wave functions with a single split pair, the less accurate Hartree–Fock results must be used for consistency in calculating the relative energies of the various mercury halide moieties. The CI results for HgCl have been discussed elsewhere,[12] but those for HgF are presented here for the first time. The improvement in the POL-CI results relative to the Hartree–Fock is much more dramatic for HgF than for HgCl. This result may be traced to the very poor electron affinity calculated for fluorine at the Hartree–Fock level (1.25 eV vs. 2.61 eV for POL-CI vs. the experimental value of 3.399 eV to be compared with the Hartree–Fock, POL-CI and experimental chlorine electron affinities of 2.53, 2.96, and 3.615 eV, respectively). The small fluorine electron affinity raises the ionic $Hg^+ + F^-$ asymptote and hence leads to a weaker and shorter HgF bond. On the basis of the error in D_e for HgCl at the POL-CI level and the additional error (0.13 eV) in the fluorine electron affinity relative to chlorine, the true HgF bond energy is estimated to be ~1.3 eV.

The results of our calculations on the dimers are summarized in Table II. The dimers of both HgF and HgCl are well bound with respect to the monomers. For both of the mercurous halide dimers the linear head-to-tail structure (i.e., Hg_a–F_a–Hg_b–F_b) was found to be substantially less stable than the head-to-head dimer. However, when the Hg_a–F_a distance was optimized independently from Hg_b–F_b, the Hg_2F_2 molecule was found to have a slight tendency to disproportionate to Hg + HgF_2 at this level of approximation. While explicit computations were not performed on the head-to-tail dimer of mercurous chloride, the results of Table I together with the atomization energy calculated for $HgCl_2$ led to the prediction that Hg_2Cl_2 is stable with respect to disproportionation.

Table III. Computed and Experimentally Determined Properties of Hg_2F_2 and Hg_2Cl_2

compd	bond	calcd	exptl
	Bond Distances, Å		
Hg_2F_2	Hg-Hg	2.56	2.57[a]
	Hg-F	1.97	2.14[a]
Hg_2Cl_2	Hg-Hg	2.60	2.526[a]
	Hg-Cl	2.33	2.43[a]
	Atomic Charges on Halogen		
Hg_2F_2	−0.67	Hg_2Cl_2	−0.51

[a] Reference 2c. [b] Based on a Mulliken population analysis.

Table IV. IVO Excitation Energies for the Low-Lying States of Hg_2Cl_2 and $HgCl_2$[b]

Hg_2Cl_2		$HgCl_2$	
excitatn	ΔE, eV	excitatn	ΔE, eV
$^3(4\sigma_g \rightarrow 4\sigma_u)$	4.17	$^3(2\pi_g \rightarrow 4\sigma_g)$	5.88
$^3(4\sigma_g \rightarrow 3\pi_u)$	5.40	$^3(2\sigma_u \rightarrow 4\sigma_g)$	6.02
$^1(4\sigma_g \rightarrow 3\pi_u)$	$\underline{6.35}$	$^1(2\pi_g \rightarrow 4\sigma_g)$	6.31
$^1(4\sigma_g \rightarrow 4\sigma_u)$	$\underline{6.62}$	$^3(1\pi_u \rightarrow 4\sigma_g)$	6.46
$^3(2\pi_g \rightarrow 4\sigma_u)$	6.77	$^1(1\pi_u \rightarrow 4\sigma_g)$	$\underline{6.89}$ (5.64)[a]
$^3(2\pi_u \rightarrow 4\sigma_u)$	6.85	$^1(2\sigma_u \rightarrow 4\sigma_g)$	$\underline{8.74}$ (6.36)[a]
$^1(2\pi_g \rightarrow 4\sigma_u)$	$\underline{7.06}$	$^3(2\pi_g \rightarrow 2\pi_u)$	8.91
$^1(2\pi_u \rightarrow 4\sigma_u)$	7.13	$^1(2\pi_g \rightarrow 2\pi_u)$	$\underline{9.23}$ (6.75)[a]
$^3(2\pi_g \rightarrow 3\pi_u)$	8.32	$^3(2\sigma_u \rightarrow 2\pi_u)$	9.40
$^3(2\pi_u \rightarrow 3\pi_u)$	8.39	$^3(1\pi_u \rightarrow 2\pi_u)$	9.42
$^3(4\sigma_g \rightarrow 3\pi_g)$	8.44	$^1(2\sigma_u \rightarrow 2\pi_u)$	9.60
$^1(2\pi_g \rightarrow 3\pi_u)$	$\underline{8.47}$	$^1(1\pi_u \rightarrow 2\pi_u)$	9.77
$^1(2\pi_u \rightarrow 3\pi_u)$	8.56		
$^1(4\sigma_g \rightarrow 3\pi_g)$	8.72		

[a] Experimental values based on assignments of ref 24. [b] Excitations that give rise to dipole-allowed transitions are underlined.

In addition to the results reported in Table II, calculations were performed on three parallelogram structures along a linear synchronous transit path[14] connecting the square and linear head-to-head structures of Hg_2Cl_2. The three structures considered had path coordinates of 0.2, 0.4, and 0.9 on a coordinate axis where the linear structure was at 0.0 and the square structure at 1.0. Relative to the linear Cl–Hg–Hg–Cl structure, these three intermediate structures had energies of 1.27, 1.86, and 1.30 eV, respectively. These results indicate that a parallelogram structure is not the most favorable geometry for Hg_2Cl_2 and are consistent with a small barrier (less than 0.74 eV) separating the square structure from the linear head-to-head structure.

Table III compares the computed and experimentally[2] determined properties of the dimers. In both cases the calculated mercury halogen distance is smaller than the experimental value. Finally, improved virtual orbital calculations[13] were performed in order to obtain a rough estimate of where electronic transitions might be found for spectroscopic studies of mercurous chloride. The results of these calculations, which are based on a Hartree–Fock wave function for the ground state instead the GVB, are reported in Table IV. The excitation energies are determined simply from the difference of the occupied and IVO orbital energies (cf. Figure 1). For excitation from the $2\pi_g$ and $2\pi_u$, the IVO hamiltonian was averaged over x and y components, e.g., for triplet excitation from $2\pi_g$ the average of $[(2J_{\pi_{gy}} - K_{\pi_{gy}}) + (J_{\pi_{gx}} - K_{\pi_{gx}})]$ and $[(2J_{\pi_{gx}} - K_{\pi_{gx}}) + (J_{\pi_{gy}} - K_{\pi_{gy}})]$.

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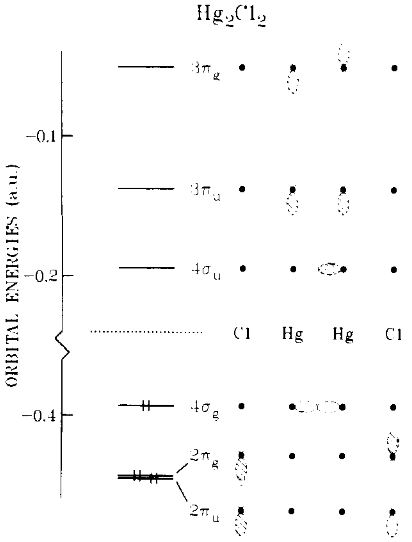


Figure 1. Orbital energy level diagram for highest occupied and lowest improved virtual orbitals of Hg_2Cl_2. The IVO energies are based on triplet excitation from $2\pi_g$ to be consistent with a similar diagram (Figure 4) for $HgCl_2$ in ref 24.

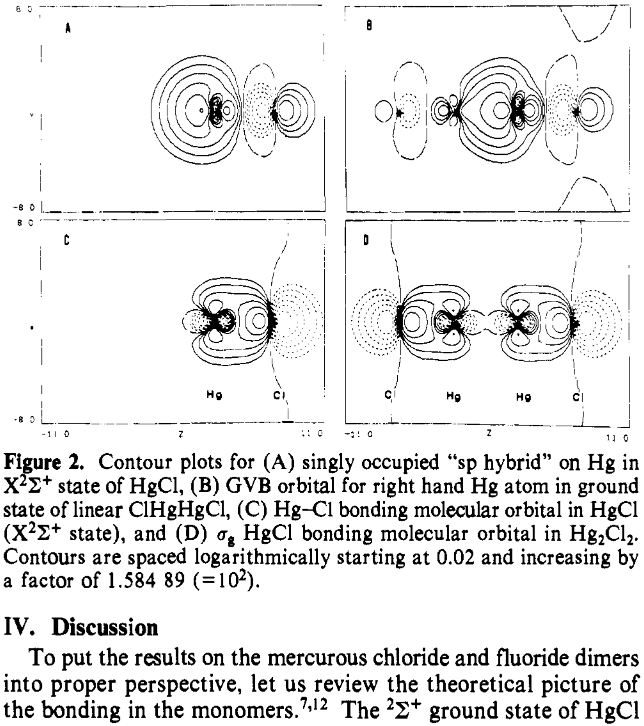


Figure 2. Contour plots for (A) singly occupied "sp hybrid" on Hg in $X^2\Sigma^+$ state of HgCl, (B) GVB orbital for right hand Hg atom in ground state of linear ClHgHgCl, (C) Hg–Cl bonding molecular orbital in HgCl ($X^2\Sigma^+$ state), and (D) σ_g HgCl bonding molecular orbital in Hg_2Cl_2. Contours are spaced logarithmically starting at 0.02 and increasing by a factor of 1.584 89 ($=10^2$).

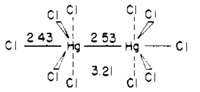
IV. Discussion

To put the results on the mercurous chloride and fluoride dimers into proper perspective, let us review the theoretical picture of the bonding in the monomers.[7,12] The $^2\Sigma^+$ ground state of HgCl and HgF is basically ionic in character at the equilibrium internuclear separation. At the Hartree–Fock level Mulliken population analyses give charges of −0.53 and −0.69 on the chlorine and fluorine, respectively, while analysis of the POL-CI wave functions indicate 78% ionic and 22% covalent character for HgCl and 85% ionic and 15% covalent for HgF. The ionic nature of the bonding is also manifest in the large dipole moment (POL-CI wave function) for the ground state, e.g., 3.28 D for HgCl.[12] Contour plots of the singly occupied 4σ and doubly occupied 3σ orbitals of HgCl are shown in Figures 2a and 2c, respectively. The 3σ orbital is primarily chlorine $3p_z$ in character, while the 4σ is primarily mercury 6s in character. Hence, an electron has been transferred from the mercury 6s, which is doubly occupied in the atomic ground state, to the chlorine $3p_z$. The 4σ orbital is hybridized away from the chlorine. However, the 6p character is quite small, being only 14% that of the 6s (18% for HgF).

Turning to the bonding in the mercurous chloride and fluoride dimers one has two countervailing forces, namely, electrostatic and covalent. Given the ionic character of the monomers, the electrostatic interaction of the two dipoles will be large and will favor head-to-tail square configurations in analogy to the alkali halides[15] or possibly head-to-tail linear configurations. On the other hand, a covalent bond can be formed between the two singly occupied 4σ orbitals, which favors a mercury-to-mercury (X–Hg–Hg–X) linear configuration. The strength of the electrostatic interaction may be crudely estimated by assuming the Hg and X atoms are point charges, $+Q$ and $-Q$. If we also assume the mercury–halogen distance (R) is the same in all configurations, then the electrostatic interaction is $-2.586Q^2/R$ for the head-to-tail square geometry, $-2.333Q^2/R$ for the head-to-tail linear geometry, and $-2Q^2/R + Q^2/[R'(1 + 3R'/2R + R'^2/2R^2)]$ for the mercury-to-mercury geometry, where R' is the Hg–Hg distance. It is obvious that the electrostatic interactions favor the square configuration. To estimate the size of the electrostatic interactions, we take Q from the monomer Mulliken population analyses and R and R' as calculated for the optimal dimer structures. For $(HgCl)_2$ and $(HgF)_2$ the electrostatic interactions stabilize the square structure relative to separate monomers by 0.58 and 1.06 eV and destabilize the mercury-to-mercury linear structure by 0.47 and 0.71 eV, respectively. Therefore, the strength of the Hg–Hg bond must be at least 1.05 eV in Hg_2Cl_2 and 1.77 eV in Hg_2F_2 for the linear covalent structure to be the equilibrium geometry.

The results presented in Table II show that the covalent Hg–Hg bond is more than strong enough to overcome the unfavorable electrostatic interactions. (Note that the Mulliken populations are basically unchanged in the dimer relative to the monomer.) The contour plots in Figure 2 demonstrate that the linear mercury-to-mercury configuration involves a simple covalent bond between the singly occupied 4σ orbitals of the monomers while the ionic HgX bonds are basically unchanged (cf. Figure 2c,d). Figure 2b shows the right GVB orbital, ϕ_R^{GVB},[16] involved in the Hg–Hg bond pair. The amount of p character in the GVB orbitals of the dimer increases significantly relative to the p character of the monomer 4σ orbital. Specifically, the p character increases to 28% of the s character in Hg_2Cl_2 and 30% in Hg_2F_2. The increased p character enhanced the directionality of the monomer 4σ orbitals and hence their overlap.

As noted above, the mercury–halogen distances computed in this work are smaller than those reported in the crystalline state. Relatively strong perturbations of the gas-phase structure might be expected in the crystal due to the rather close approach of the molecules to one another. For example, each mercury in the molecular crystal is in a distorted octahedral environment with a mercury and a chlorine along one axis at a distance of ~2.5 Å and four next nearest-neighbor chlorines at a distance of only 3.21 Å (see structure I).[2c] Conceivably, the next nearest-neighbor chlorines are close enough to transfer charge into the LUMO of the coordinated Hg_2Cl_2 molecule (Figure 1), thereby strengthening the mercury–mercury bond and weakening the mercury–chlorine bond. Furthermore, from an electrostatic point of view, "intermolecular" charge transfer from the chlorine of one molecule to the mercury of another would weaken the electrostatic attraction between $Hg^{\sigma+}$ and $Cl^{\sigma-}$, thus lengthening HgCl bonds, and also weaken the electrostatic repulsion between mercury atoms, thereby shortening the Hg–Hg bonds.



It has been suggested[17] that as the halogen in Hg_2X_2 becomes more electronegative, the hybrid orbital of Hg in the HgX bond should gain p and d character for more effective transfer of charge to the halogen. This rehybridization should then be accompanied by an increase in the s character and a shortening of the Hg–Hg

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(15) Inclusion of coulombic attraction and closed-shell repulsion terms leads to the prediction that the alkali halide dimers are slightly distorted squares. Milne, T. A.; Cubicciotti, D. *J. Chem. Phys.* **1958**, *29*, 846.

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(17) Stammreich, H.; Sans, T. *J. Mol. Struct.* **1967**, *1*, 55.

Table V. Improved Calculations of Hg-Hg Bond Strength (eV) in Hg_2Cl_2 at Optimized Geometry (R(Hg-Hg) = 2.60 Å, R(Hg-Cl) = 2.33 Å)[d]

	D_e(ClHg-HgCl)		D_e(ClHg-HgCl)
GVB(1)	1.78[a]	GVB(3/9)	2.08[b]
GVB(1/5)	2.00[a]	GVB(3/9) - CI	2.00[c]

[a] HF wave function of HgCl used as reference. [b] GVB(1) wave function of HgCl used as reference. [c] Full three-electron CI among GVB(1) and open-shell orbitals of HgCl used as reference. [d] Reference HgCl monomer geometry is R(Hg-Cl) = 2.39 Å.

bond. While a modest shortening of the Hg-Hg bond in passing from the chloride to the fluoride is revealed by our calculations (Table III), the most recent experimental work is consistent with the opposite trend. Furthermore, the percentage of p and d character in the Hg hybrid contribution to the Hg-X bond is actually slightly smaller for Hg_2F_2 than for Hg_2Cl_2. Finally, as stated previously the amount of s character in the Hg-Hg bond is slightly less for Hg_2F_2 than for Hg_2Cl_2. It thus would seem that lattice energy contributions may be important in explaining the trends in bond lengths.[18]

The present calculations predict that the mercurous chloride dimer will be stable with respect to disproportionation ($Hg_2Cl_2 \rightarrow HgCl_2 + Hg$) by 0.65 eV, which runs counter to past predictions.[19,20] Therefore, it is especially important to assess the accuracy of the theoretical calculations. The major strength of the present results is that a consistent set of wave functions was employed so that errors should tend to cancel. On the other hand, although high quality basis sets were used, the wave functions were not sophisticated and so large errors are expected for quantities such as dissociation energies, which are generally difficult to calculate. In fact, only 61% of the HgCl dissociation energy is obtained (cf. Table I) and 53% of the $HgCl_2$ atomization energy (theory = 2.45 eV; experiment = 4.66 eV[21]). The percentage errors are comparable, but the cancellation of errors is only partial as evidenced by the heat of reaction for eq 1, which is calculated

$$2HgCl(g) \rightarrow HgCl_2 + Hg(g) \qquad (1)$$

to be −1.13 eV compared to the experimental value of −2.51 eV.[21] In fact, if we use the experimental value for the heat of the monomer disproportionation reaction together with the calculated Hg-Hg bond strength, then the mercurous chloride dimer is predicted to be unstable by 0.73 eV. Nevertheless, the calculated Hg-Hg bond strength should be considerably underestimated as for the bonds in HgCl and $HgCl_2$. If we assume the error is comparable, say 57% of the true value, then the Hg-Hg bond strength is predicted to 3.12 eV and the mercurous chloride dimer is again predicted to be stable with respect to disproportionation (by 0.61 eV).

As a further check on the above line of reasoning, we consider the errors obtained by using effective core potentials, comparable basis sets and two-configuration GVB wave functions for five other diatomic molecules. Specifically, the percentage of the dissociation energy obtained was 38% for F_2, 47% for Cl_2, 79% for HF, 83% for HCl, and 77% for LiCl.[8] If the errors in the calculated Hg-Hg bond strength are as small as those for HF, HCl, and LiCl, then the mercurous chloride dimer will not be stable.

In an attempt to clarify the situation, a series of improved calculations of the Hg-Hg bond strength were performed. First we employed a separated-pair wave function, denoted GVB(1/5), in which five natural orbitals are used to describe the Hg-Hg bond pair instead of two as in GVB(1). The $4\sigma_u^2$ configuration includes

$$\mathrm{GVB}(1) = c_1 4\sigma_g^2 + c_2 4\sigma_u^2$$

$$\mathrm{GVB}(1/5) = c_1 4\sigma_g^2 + c_2 4\sigma_u^2 + c_3 3\pi_{ux}^2 + c_3 3\pi_{uy}^2 + c_4 5\sigma_g^2$$

left-right correlation, while the $3\pi_u^2$ configurations include angular correlation and the $5\sigma_g^2$ in-out correlation. The three additional correlating configurations stabilize the Hg-Hg bond by 0.22 eV (see Table V). Since the Hg-Cl bond distance changes by 0.06 Å from the monomer to the dimer, there may be nonnegligible differential correlation effects. To assess their size, a calculation was performed in which the two HgCl bond pairs were also described with GVB(1) two-term natural orbital expansions [giving a total of three split bond pairs and nine natural orbitals, denoted GVB(3/9)]. The Hg-Hg bond strength was increased by an additional 0.08 eV (cf. Table V). However, the GVB(3/9) assumes perfect-pairing spin-coupling, which may not be valid,[22] so a full six-electron CI was performed within the space of the nine natural orbitals. The Hg-Hg bond strength was reduced back to the value obtained with GVB(1/5). Therefore, there is no differential correlation effect involving the HgCl bond pairs.

The above results indicate that the mercurous chloride dimer is probably unstable with respect to disproportionation. However, we have not considered the effect of interpair correlation between the 5d electrons on Hg and the bond pair. Although each interpair correlation energy may be small, there are ten 5d pairs, so that the total correlation energy could be on the order of the 0.5 eV needed to make the dimer stable. Attempts at including similar interpair correlations in Cu_2[23] have given spuriously large bond energies because of the difficulty in separating molecular and atomic correlation. Therfore, until ways are devised to account for these interpair correlations in a reliable fashion, the most that can be said is that the present theoretical study indicates the mercurous chloride dimer may be stable in the gas phase.

The literature contains a number of statements concerning the instability of Hg_2Cl_2 in the gas phase.[19,20] Roberts[19] argues that an exceedingly strong Hg-Hg bond (≥4.45 eV) is needed to stabilize the Hg_2Cl_2 dimer. However, his arguments are based upon an erroneous estimate of −4.45 eV for reaction 1, compared to the correct value of −2.51 eV. Therefore, Roberts' statements must be dismissed. The only experimental evidence that suggests the dimer may exist in the gas phase under the proper conditions is the fact mercurous chloride can be purified by sublimation.[20]

The calculations predict that Hg_2F_2 will be slightly unstable in the gas phase. Given the poorer quality of the experimental data available for the mercury fluorides, it is difficult to assess the accuracy of the theoretical predictions. Nevertheless it is most likely that the mercurous fluoride is not stable in the gas phase.

If $(HgCl)_2$ is stable in the gas phase, then one needs to detect it to prove its existence. Since spectroscopy is the most likely means of detection, we have performed a series of IVO calculations to estimate the positions of the stronger absorption bands in Hg_2Cl_2. For a calibration of the results for Hg_2Cl_2, Table IV contains IVO calculations for $HgCl_2$, which is the species most likely to be present along with Hg_2Cl_2 and for which assignments of experimental values are available for the excitation energies.[24] The errors (1.25–2.5 eV) in the IVO excitation energies found for $HgCl_2$ are expected to carry over to Hg_2Cl_2. Consequently, the transitions to $1^1\Pi_u$ [$^1(4\sigma_g \rightarrow 3\pi_u)$] and $1^1\Sigma_u^+$ [$^1(4\sigma_g \rightarrow 4\sigma_u)$] in Hg_2Cl_2 are expected to occur at wavelengths (≥200 nm) longer than the longest wavelength transition (to $1^1\Pi_u$) in $HgCl_2$. The transition to $1^1\Sigma_u^+$ in Hg_2Cl_2 is expected to be especially strong in analogy to the transition to $1^1\Sigma_u^+$ [$^1(2\sigma_u \rightarrow 4\sigma_g)$] in $HgCl_2$.[24] As to the nature of the two lowest absorption features in Hg_2Cl_2, the $1^1\Pi_u$ is expected to be broad and featureless as it is dissociative. The $1^1\Pi_u$ state correlates with HgCl ($X^2\Sigma^+$) + HgCl ($A^2\Pi$), i.e., HgCl ($X^2\Sigma^+$) + Hg (^1S) + Cl (^2P) since the A state is itself dissociative, and the energy of this asymptote is D_e(ClHg-HgCl) + D_e(HgCl) ≳ 2.51 + 1.08 ≳ 3.6 eV. Therefore, the $1^1\Pi_u$ state will have sufficient energy to dissociate. On the other hand, the $1^1\Sigma_u^+$ state correlates with HgCl ($X^2\Sigma^+$) + HgCl ($B^2\Sigma^+$), the energy of which is given by D_e(ClHg-HgCl) + T_e[HgCl ($B^2\Sigma^+$)]

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$\gtrsim 2.51 + 2.90 \gtrsim 5.4$ eV. The resulting asymptotic energy is close to the expected excitation energy so that either there will be discrete structure (nondissociative) in absorption or (dissociative) emission will be observed from the B state of HgCl. In either case, the Hg_2Cl_2 absorption spectrum and resulting emissions should be very different from $HgCl_2$.[24] Therefore, examination of the 200–250-nm region in gas mixtures produced by subliming mercurous chloride may reveal spectroscopic features that can be assigned definitively to Hg_2Cl_2; i.e., it should be possible to discriminate between Hg_2Cl_2 and $HgCl_2$.

V. Conclusion

Two-configuration GVB calculations on the mercurous chloride and fluoride dimers show that both species will have linear mercury-to-mercury geometries (X–Hg–Hg–X). The geometry of the dimer is dictated by a strong covalent Hg–Hg bond, which prevails over the electrostatic interactions of the ionic monomers that favor head-to-tail square geometries. The calculations indicate that Hg_2Cl_2 may be stable in the gas phase. IVO calculations indicate that if Hg_2Cl_2 does exist in the gas phase, it should have distinctive spectroscopic features in the 200–250-nm region that can be used to discriminate between $HgCl_2$ and Hg_2Cl_2.

Acknowledgment. This work was performed under the auspices of the U.S. Department of Energy.

Note Added in Proof: Our preliminary spectroscopic studies of vapor phase Hg_2Cl_2 indicate a broad unstructured band centered at approximately 250 nm and a structured band at about 192 nm. The former band may be due to a transition to the dissociative $1\,^1\Pi_u$ state and could possibly include a superimposed transition to the $1\,^1\Sigma_u{}^+$ state. Much work remains to be done to confirm these tentative assignments. We also note that the mercury 254-nm line is quite prominent suggesting that some disproportionation has occurred.

Intramolecular Proton Tunnelling in the Ground and Lowest Excited Singlet States of 9-Hydroxyphenalenone

R. Rossetti, R. C. Haddon, and L. E. Brus*

Contribution from Bell Laboratories, Murray Hill, New Jersey 07974.
Received April 28, 1980

Abstract: Vibronically resolved fluorescence and fluorescence excitation spectra have been observed for 9-hydroxyphenalenone in solid Ar and Ne. There are strong spectral changes when the phenolic proton is deuterated, implying that the proton motion is coupled to a C_s–C_{2v} rearrangement of the oxygen–carbon molecular framework. In the deuterated compound, a ground-state tunnelling splitting $\Delta = 9 \pm 1$ cm^{-1} is observed. This value increases to 170 cm^{-1} in the excited electronic state. This value, along with other spectral and X-ray structural data, allows us to calculate double-minimum potential energy curve shapes for both ground and excited electronic states by using an approximate theoretical model. The hydride has calculated tunnelling splittings of 127 ± 10 and 617 ± 50 cm^{-1} in ground and excited electronic states, respectively. The calculated ground-state proton-tunnelling times are ~0.13 and ~1.7 ps for the hydride and deuteride, respectively.

Introduction

One interesting question in chemical dynamics involves the interconversion kinetics of molecules that are stable in several equivalent conformations. 9-Hydroxyphenalenone (hereafter 9-HPO), for example, could be postulated to undergo an intramolecular proton transfer between two equivalent cannonical structures as shown in Figure 1.[1] The transformation as drawn principally involves proton motion as the "reaction coordinate", coupled with rearrangement of carbon–oxygen framework bond lengths and angles as the π electrons adjust to the moving proton. A theory of the influence of the π-electron component on potentially symmetrical hydrogen bonds in molecules such as 9-HPO has been recently presented.[2]

9-HPO could be characterized by a double minimum potential as shown in Figure 1 or by a symmetric C_{2v} location for the proton as shown in the lower left corner of the figure. A variety of experiments have provided information about the structure. 9-HPO has a very strong hydrogen bond,[2,3] and the crystalline X-ray structure shows an unusually short O···O distance (2.486 Å).[1] These observations suggest either a C_{2v} structure or "fast" equilibration between two local minima.[1] Deuteron quadrupole studies also support fast exchange between equivalent minima.[4] Gas-phase ESCA spectra show two inequivalent O atoms on the $\sim 10^{-15}$-s time scale.[5] This last experiment shows that the acidic proton remains localized on one O atom for at least several O–H vibrational periods.

The classic experimental method for the analysis of potential energy curve shapes is vibronically resolved electronic spectroscopy. In a molecule as large as 9-HPO, hot bands and rotational structure would normally obscure vibronic structure. Therefore we have investigated the sharp, laser-excited fluorescence and fluorescence excitation spectra of 9-HPO isolated in rare-gas matrices at 4.2 K. This method has been previously applied to other problems of internal structure in large organic species,[6–9] including a study of proton transfer in an excited state of methyl salicylate.[9]

Internal proton-transfer processes may be spectrally resolved when the corresponding rates are too fast to be time resolved with present picosecond laser technology. As illustrated in Figure 1, the vibrationally relaxed "$v = 0$" level of the ground electronic state is doubly degenerate if there are two local minima. Proton tunnelling will split the "$v = 0$" level into two components O^+ and

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