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Ab initio spectroscopic properties for $HgTl^+$

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Abstract

Relativistic coupled cluster calculations are presented, which describe the potential energy curve of the yet unknown molecule $HgTl^+$, and predict its spectroscopic properties. Correlation consistent pseudopotential valence basis sets were used in order to minimize the basis set superposition error for the weakly interacting atoms. The vibrational–rotational constants were obtained as $R_e = 334.2$ pm, $D_0 = 2272$ cm^{-1}, $\omega_e = 46$ cm^{-1}, $\omega_e x_e = 0.17$ cm^{-1}, and $B_e = 0.0147$ cm^{-1} at the CCSD(T) level. The bonding in $HgTl^+$ can be described mainly as a charge induced dipole interaction, thus explaining why this species is stronger bound than isoelectronic Hg_2, which can mainly be described by dispersion forces ($R_e = 363 \pm 4$ pm, $D_0 = 380 \pm 15$ cm^{-1}, $\omega_e = 19$ cm^{-1}). (Int J Mass Spectrom 201 (2000) 17–21) © 2000 Elsevier Science B.V.

Keywords: Van der Waals; *Ab initio* calculations; Spectroscopic constants

1. Introduction

The accurate description of weakly interacting atoms or molecules, often denoted as Van der Waals complexes, remains a challenge for computational chemistry [1]. Such compounds most frequently involve interactions between two closed shell systems, as in the mercury atom dimer [2], or closed–open shell interactions such as HgTl [3], TlAr [4, 5] etc. Open–open shell weak interactions are rare and mostly found in heavy elements like Tl_2 (in this case the weak interaction is caused by spin–orbit coupling) [6] or when the singly occupied molecular orbital is delocalized over a large number of atoms. In the last decade great effort has been spent to determine accurate spectroscopic properties for the ground electronic state of Hg_2 [6–8], where the interaction between two mercury atoms can best be described by dispersion forces [9]. We mention in particular the work by Dolg and Flad [7] who achieved excellent results for Hg_2 by using energy consistent spin–orbit coupled relativistic pseudopotentials in combination with very large valence basis sets including *g* functions in order to suppress what is known as the basis set superposition error (BSSE) [10]. The BSSE can often increase the dissociation energy of weakly bound systems by more than 50% at the correlated level when standard Hartree–Fock (HF) optimized basis sets are used even if they are of HF limit quality [9].

The cationic molecule $HgTl^+$ is isoelectronic to Hg_2 and to our knowledge has not yet been studied by theoretical or experimental means. The positive charge of $HgTl^+$ would not only allow for a mass

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Table 1
Relativistic ccv-MP2 valence basis sets for Hg and Tl

Hg	s	21.808620	11.643380	6.352293	2.579950	1.618329
		0.741351	0.263827	0.109004	0.046954	0.02
		0.005				
	p	9.605107	7.331637	3.574473	2.069620	1.251303
		0.662142	0.306699	0.134152	0.056913	0.015
	d	4.715790	3.111544	1.320395	0.581027	0.241737
		0.094501	0.04	0.015	0.005	
	f	3.6	1.848018	0.624074	0.25	
Tl	s	17.170890	12.670850	6.859759	2.745601	1.672097
		0.780851	0.373853	0.159493	0.065712	0.02
		0.005				
	p	9.032815	7.322255	4.050419	2.071695	1.265296
		0.658453	0.280717	0.110834	0.039746	0.015
	d	4.432548	3.366243	1.386112	0.638469	0.276661
		0.106445	0.04	0.015	0.005	
	f	2.750690	1.842186	0.7946722	0.3171252	

spectroscopic investigation but should also enhance the bond strength as compared to neutral Hg_2. The charge induced dipole (CID) interaction of the Tl^+ ion with the Hg atom is inversely proportional to the fourth power of their internuclear distance R^{-4} whereas dispersion forces (DF) are proportional to R^{-6}. Therefore, CID interactions are expected to dominate the bonding situation in $HgTl^+$. We note that the neutral species HgTl, which has been investigated as a possible candidate for excimer laser activity, exhibits a dissociation energy of 800 cm^{-1} [3], and is thus stronger bound than Hg_2 (380 cm^{-1}) [11]. It is therefore likely that the closed shell interaction between Hg and Tl^+ is sufficiently strong to be identified or even to determine its dissociation energy by mass spectrometric methods [12].

It is well known that for a theoretical investigation of heavy elements such as Hg or Tl relativistic effects are of crucial importance. For weakly interacting systems electron correlation effects are important to describe the contribution of dispersion type forces. In our investigation of $HgTl^+$ we account for both effects by employing scalar relativistic pseudopotential coupled cluster calculations. Small-core relativistic pseudopotentials for Hg and Tl are used in order to obtain results of comparable accuracy to all-electron methods. Special care is taken to avoid the BSSE at the correlated level by using correlation consistent valence basis sets for Hg and Tl. The bonding between Hg and Tl^+ is analyzed in terms of contributions of electrostatic and dispersive interactions.

2. Computational details

The energy-consistent scalar relativistic pseudopotentials of the Stuttgart group were used for Hg [13] and Tl [4]. These are small-core pseudopotentials with a $[Kr4d^{10}4f^{14}]$ definition of the core (core charges $Q_{\mathrm{Hg}} = 20$ and $Q_{\mathrm{T}} = 21$). Twenty-three single points were calculated to obtain the Born–Oppenheimer (BO) potential energy curve $V(R)$ for the $Tl^+ + Hg$ system at the coupled cluster level [CCSD(T)] [14] and corrected for the BSSE using the counterpoise correction by Boys and Bernardi [10]. Virtual orbitals greater than 100 atomic units (a.u.) were omitted from the correlation treatment. Large uncontracted (11s10p9d4f) Gaussian type (GTO) valence basis sets were used. These basis sets were derived by numerically optimizing a (9s9p6d) set at the second-order Møller–Plesset level (MP2) of theory [15] and extending it by an additional set of diffuse and MP2-optimized polarization functions. These correlation consistent valence MP2 basis sets (ccv-MP2) should be able to suppress the BSSE at smaller bond distances and are listed in Table 1.

The rovibrational spectroscopic constants were derived from a numerical Numerov–Cooley proce-

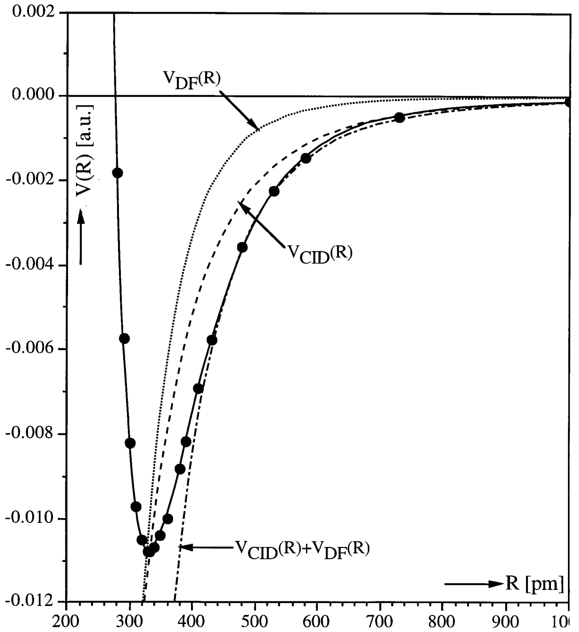

Fig. 1. Potential energy curve of $HgTl^+$. The dots indicate the calculated CCSD(T) points; the solid line represents the extended Morse potential of Eq. (1). The dotted curve corresponds to the dispersion interaction $V_{DF}(R)$. The dashed curves show the ion-induced dipole interaction $V_{CID}(R)$, and the sum of both interactions, respectively.

dure [16, 17]. It turned out that for weakly interacting systems the Numerov–Cooley procedure implemented in MOLCAS3 [17] may become numerically unstable. This problem can be circumvented by multiplying each potential energy value by a factor of $f = 10.0$ before deriving the vibrational–rotational constants that are accordingly too large by this factor. Scaling of the vibrational–rotational Hamiltonian and dividing the reduced mass by f yields the correct values.

3. Results and discussion

The calculated BSSE corrected CCSD(T) diatomic potential curve $V(R)$ for $HgTl^+$ is shown in Fig. 1. As shown before [18], the original Morse potential [19] can be extended as follows,

$$V(R) = \sum_{i=1}^{n} A_i e^{-\alpha_i(R-R_e)}$$

using the boundary condition

$$D_e = -\sum_{i=1}^{n} A_i \tag{1}$$

where A_i and α_i are fit parameters. The original Morse potential is a special case of this equation with $n = 2$, $A_1 = D_e$ and $\alpha_2 = 2\alpha_1$. This comparably simple extension leads to very accurate and smooth potential curves that, in our experience, is superior to most other standard approximations, and is as accurate as, for example, the extended Rydberg potential [20]. An excellent least squares fit is obtained by the choice of $n = 4$ and the following parameters (atomic units are used throughout): $A_1 = 0.003013$, $A_2 = -0.01050$, $A_3 = 0.01690$, $A_4 = 0.001346$, $\alpha_1 = 1.4437$, $\alpha_2 = 1.4405$, $\alpha_3 = 0.6231$, $\alpha_4 = 0.1951$ with a standard deviation of only 4.8×10^{-6} a.u. This approximation is shown in Fig. 1 as well.

The spectroscopic constants derived from the potential curve are listed in Table 2 and will facilitate the future identification of this gas phase species using spectroscopic methods. At all levels of theory $HgTl^+$ is significantly stronger bound than isoelectronic Hg_2 ($R_e = 363 \pm 4$ pm, $D_0 = 380 \pm 15$ cm^{-1}, $\omega_e = 19$ cm^{-1}) as anticipated from the additional charge [21]. Accordingly, the $HgTl^+$ CCSD(T) potential energy curve can accommodate more vibrational energy levels compared to Hg_2 [9]. As expected from a CID interaction $HgTl^+$ is—even at the HF level—a stable molecule with a D_0 of 1753 cm^{-1}, in contrast to Hg_2 where the HF potential curve is repulsive [9]. Despite the dominant role of charge induced interaction in $HgTl^+$, electron correlation is important to describe the bonding situation. Upon inclusion of correlation at the CCSD[T] level the bond distance is shortened by 24 pm and the dissociation energy increased by 30% (523 cm^{-1}). Obviously, MP2 leads to overbinding in $HgTl^+$—a common tendency of this method.

A comparison of the uncorrected data with the BSSE corrected data in Table 2 shows that the

Table 2
Spectroscopic constants for $HgTl^{+a}$

	HF	MP2	CCSD	CCSD(T)
BSSE corrected				
R_e	357.9	322.4	338.8	334.2
D_e	1772	2801	2116	2295
D_0	1753	2774	2094	2272
ω_e	37.5	53.5	44.0	46.3
$\omega_e x_e$	0.24	0.23	0.19	0.17
B_e	0.0128	0.0158	0.0143	0.0147
CD_e	1.68	2.47	3.29	3.55
α_e	8.25	8.53	8.60	8.44
Uncorrected				
R_e	357.8	320.7	337.5	332.9
D_e	1807	2921	2191	2385
D_0	1789	2894	2169	2362
ω_e	37.9	54.7	45.1	47.6
$\omega_e x_e$	0.23	0.25	0.24	0.24
B_e	0.0128	0.0160	0.0144	0.0148
CD_e	1.74	1.77	2.01	1.75
α_e	8.28	8.68	8.77	8.69

[a] Hartree–Fock, HF; second-order many-body perturbation theory, MP2; and coupled cluster singles-doubles, CCSD; with noniterative triples, CCSD(T). Bond distances R_e in pm, bond dissociation energies, D_e and D_0 (the latter corrected for vibrational contributions) in cm^{-1}, harmonic frequencies ω_e in cm^{-1}, anharmonicity constant $\omega_e x_e$ in cm^{-1}, rotational constant B_e in cm^{-1}, centrifugal distortion constant CD_e in 10^{-7} cm^{-1}, vibration–rotational coupling constant α_e in 10^{-5} cm^{-1}. The sign convention of Huber and Herzberg is used [6].

ccv-MP2 basis sets perform excellently. At the HF level the dissociation energy decreases by only 36 cm^{-1} or 2.1% of the total D_0 including counterpoise correction. This effect would most likely be smaller for basis sets optimized at the HF level. However, at the MP2 level the BSSE error in the dissociation energy amounts to 120 cm^{-1} or 4.3% of the corrected D_0 and lies with 90 cm^{-1} or 4.0% of the corrected D_0, slightly lower at the CCSD(T) level. Because the BSSE itself depends on the distance of the interacting fragments this difference between the methods can be ascribed to the smaller MP2 bond distance rather than to a better performance of the basis set at the coupled cluster level. Indeed, the BSSE at MP2 is only 3.9% for the $R = 334$ pm, which is the equilibrium distance at the CCSD(T) level. In summary, our results suggest that MP2 optimized basis sets can be safely applied at the coupled cluster level in order to suppress the BSSE. We note that this method of generating a correlation consistent basis set is less computer time intensive than a CISD optimization as carried out by Dunning and co-workers [22].

A CID interaction [23] is represented by

$$V_{\mathrm{CID}}(R) = -\frac{q^2}{2}\,\alpha_{\mathrm{D}}^{\mathrm{Hg}} R^{-4} \tag{2}$$

where q is the charge of the cation ($q = 1$ for Tl^+), $\alpha_{\mathrm{D}}^{\mathrm{Hg}}$ is the static dipole polarizability of Hg (34 a.u.) [24], and R is the internuclear bond distance. The resulting curve for $V_{\mathrm{CID}}(R)$ is shown in Fig. 1 in comparison with the fitted potential energy curve $V(R)$. The reasonable agreement of curves down to the experimental bond distance shows that the Hg–Tl^+ bond can be described mainly by a CID interaction. Yet the CID model slightly underestimates the bonding of $HgTl^+$ for longer distances and dispersion forces have to be included. In order to discuss dispersion forces we calculated the static dipole polarizability of Tl^+ because experimental values are not available. Using a finite field model as outlined in [25], we obtain $\alpha_{\mathrm{D}}^{\mathrm{Tl^+}} = 23.8$ a.u. at the HF level, 17.6 a.u. at the MP2 level, and 20.0 a.u. at the CCSD and CCSD(T) level. As expected we have $\alpha_{\mathrm{D}}^{\mathrm{Tl^+}} < \alpha_{\mathrm{D}}^{\mathrm{Hg}}$. Using the general form of a London equation [26], a reasonable fit for the dispersion interaction can be generated if

$$V_{\mathrm{DF}}(R) = -A\alpha_{\mathrm{D}}^{\mathrm{Hg}}\alpha_{\mathrm{D}}^{\mathrm{Tl^+}} R^{-6} \tag{3}$$

is adjusted to the difference between the CCSD(T) potential curve and the CID interaction at longer bond distances, which yields $A = 0.85$ a.u. The curve obtained for $V_{\mathrm{DF}}(R)$ is also shown in Fig. 1. The coefficient A obtained by this simple fit procedure is not unreasonable as a comparison, as the explicit London equation shows [26]

$$V_{\mathrm{DF}}(R) = -\frac{3}{2}\,\frac{\alpha_{\mathrm{D}}^{\mathrm{Hg}}\alpha_{\mathrm{D}}^{\mathrm{Tl}}}{R^6}\,\frac{I_{\mathrm{Hg}} I_{\mathrm{Tl^+}}}{I_{\mathrm{Hg}} + I_{\mathrm{Tl^+}}} \tag{4}$$

If we use the experimental ionization potentials $I_{\mathrm{Hg}} = 0.3836$ a.u. and $I_{\mathrm{Tl^+}} = 0.7507$ a.u. [6], a value of $A = 0.38$ a.u. is obtained. This difference is not unexpected and is partly attributed to the fact that in the above treatment higher order terms in the weak electrostatic perturbation are neglected but are implicitly accounted for in the *ab intio* potential curve. Moreover, ionization potentials have been used in Eq. (4) instead of average excitation energies originally proposed by London [26]. Note that the Slater–Kirkwood formula [27] would predict even a smaller value of $A = 0.21$ a.u. The sum of both interactions, $V_{DF}(R) + V_{CID}(R)$, gives an excellent fit of the CCSD(T) potential for distances $R > 450$ pm where repulsive forces can be neglected. In summary, the CID interaction is the dominant contribution to the bonding in $HgTl^+$ and explains the large difference from its isoelectronic Hg_2.

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