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Electronic Structure and Dissociation Curves for the Ground States
of Tl_2 and Tl_2^+ from Relativistic Effective Potential Calculations

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Abstract

The dissociation curves for the ground states of Tl_2 and Tl_2^+ were computed using a generalization of the molecular relativistic ω - ω coupling formalism of Lee, Ermler and Pitzer. Relativistic effects, as represented by the Dirac equation, were introduced using effective potentials generated from atomic Dirac-Fock wavefunctions using a generalization of the improved effective potential formulation of Christiansen, Lee and Pitzer. Our calculations show that the ground state of Tl_2^+ is $1/2_g$ with computed D_e and R_e values of 0.58 eV and 3.84 Å. For Tl_2 we find that the ground state is 0_u^- but the 0_g^+ and the 1_u states are only slightly higher in energy; the potential curves for these states are repulsive to about 3.5 Å and then essentially flat beyond that radius. While corrections for correlation will increase D_e somewhat, Tl_2 is only weakly bound in any of these states which dissociate to normal atoms. The cause is undoubtedly related to the large spin-orbit splitting between the $6p_{1/2}$ and $6p_{3/2}$ thallium spinors.

Introduction

Although dissociation energies and other spectroscopic parameters for the ground states of most of the group III homonuclear diatomic molecules have been determined experimentally,¹ to our knowledge this is not the case for Tl_2 . Drowart and Honig,² suggest an upper limit to the bond energy of Tl_2 of 0.9 eV. This is based on the failure to observe any Tl_2 signal in Tl vapor at approximately 900°K,³ and therefore implies no lower limit. Considering this upper limit and the bond energies of Hg_2 and Pb_2 they estimated the Tl_2 bond energy to be about 0.6 eV. This value has been reported in some subsequent reviews as if it were an experimental result. The only positive experimental data concerning Tl_2 appear to be the spectra of Ginter *et al.*,⁴ which include emission bands in the range 15,300 to 16,000 cm^{-1} and adsorption bands in the range 23,000 to 23,500 cm^{-1} for Tl vapor at about 1600°K. Unfortunately a detailed interpretation of the spectra appears unfeasible for the present; indeed, it is not absolutely certain that these bands arise from Tl_2 . There is considerable interest in the properties of Tl_2 in relation to recent experiments on parity nonconservation in transitions in atomic thallium.⁵ In an effort to explore this situation we have computed dissociation curves for the three states, 0_g^+ , 0_u^- and 1_u , of Tl_2 which dissociate to neutral atoms in their ground states. In addition we have computed dissociation curves for the lowest $1/2_g$ and $1/2_u$ states of Tl_2^+ . Although this ion has been detected experimentally,⁶ its molecular parameters have not been reported.

Since for many purposes it can be considered to have only a single valence electron (due to the relativistic contraction, the 6s shell is substantially lower in energy), and because of the large spin-orbit splitting, almost 1 eV between the $6p_{1/2}$ and $6p_{3/2}$ spinors, Tl is a

particularly interesting subject for heavy element bonding studies. Unlike light atom bonding which is usually described in terms of sigma, pi, etc. spin-orbitals, bonding between heavy atoms⁷ must be described in terms of spinors which are usually combinations of spin-orbitals of differing angular symmetry. This mixing of sigma, pi, etc. spin-orbitals is the result of the spin-orbit coupling as given by the Dirac equation. The $6p_{1/2}$ spinor is composed essentially of 6p sigma and pi type spin-orbitals with coefficients of $\sqrt{1/3}$ and $\sqrt{2/3}$ respectively. Therefore a bonding spinor formed as a sum or difference of two such atomic spinors on different centers, retaining the overall g or u symmetry, must be either sigma-bonding and pi-antibonding or else sigma-antibonding and pi-bonding. For this reason one would not expect the $p_{1/2}$ spinors, alone, to form substantial molecular bonds in Tl_2 . In our previous TlH calculations⁸ we found that the bonding spinor, though predominantly $p_{1/2}$ near the thallium nucleus, became progressively sigma-like towards the hydrogen, forming a reasonably strong sigma bond with the hydrogen 1s orbital. For Tl_2 one would expect the pi-antibonding component to play a more important role. Furthermore, in contrast to simple molecular orbital theory, this mixture of bonding and antibonding character in our molecular spinor model for $p_{1/2}$ bonds makes a prediction of the relative stabilities of the bonds in the corresponding ions difficult. Thus it is not obvious whether Tl_2^+ should be more or less strongly bonded than Tl_2 .

Method

All of our present molecular calculations were done using the same molecular spinor formalism as was used for TlH.⁸ In this formalism the molecular calculations are carried out in terms of ω - ω coupling, the

spin-orbit effects being included explicitly in the SCF optimizations. The important relativistic effects (those implied by the Dirac equation), were introduced using effective potentials (EP) derived from full Dirac-Fock atomic wavefunctions. The important differences between our present calculations and those of Lee *et al.*⁹ include the redefinition of the EPs, using the formulation of Christiansen *et al.*,¹⁰ which greatly improves the accuracy relative to all-electron calculations, and the inclusion of correlating configurations⁸ which allows us to obtain a reasonable representation of molecular dissociation curves. Since the important mathematical details were given in references 8, 9 and 10, they will not be repeated here.

As in our previous calculations on TlH, we treat explicitly only the outer 13 electrons of atomic thallium (the ten 5d electrons, two 6s electrons and the single $6p_{1/2}$ electron. The atomic spinors from which we derived our pseudospinors and EP were obtained from atomic calculations using a version of the numerical Dirac-Fock program written by Desclaux.¹¹ The double-zeta Tl basis set employed in these calculations is identical to that used in our calculations on TlH.⁸ The exponents were optimized for the ground state atom after averaging the spin-orbit effects out of the relativistic EP. The excess d and s basis functions will allow some polarization for the $p_{1/2}$ bonding spinor. Also, as for TlH, the maximum n quantum number allowed by our molecular integral program was four. Because of this, and because the p and d basis functions were optimized for spin-orbitals rather than for spinors, we expect that the overall quality of the basis is somewhat less than double-zeta.

Calculations and Results

Using the above relativistic EPs and basis set, potential energy curves were computed for the lowest 0_g^+ , 0_u^- and 1_u states of Tl_2 which

dissociate to ground state atoms. For the 0_u^- and 1_u states these were single configuration calculations. For the 0_g^+ state this requires two configurations, the difference being a double excitation from a $1/2_g$ to a $1/2_u$ spinor. For this case the coupling is the same as in reference 8, $K_{gu}^+ + K_{gu}^-$, where the K^+ and K^- refer to the exchange of electrons with angular momentum of the same and opposite signs, respectively. Plots of the dissociation curves for these three states are shown in Figure 1. As can be seen these curves show very little bonding character, and in fact the 1_u curve shows no minimum in this approximation.

Though there is no clear experimental evidence that the Tl_2 ground state is substantially bound, there is evidence that Tl_2^+ is stable.⁶ For further comparison we have computed curves for the lowest $1/2_g$ and $1/2_u$ states of Tl_2^+ using single configuration wavefunctions. It should be noted that, although the single configuration functions dissociate to neutral and positively charged atoms, the core spinors on both are forced to be equivalent. However, calculations on Ar_2^+ where this problem should be more severe¹² suggest that the resulting error is probably very small. Also, since no electron pairs are formed during bonding, we expect that correlation corrections will be relatively small. Plots of these two curves are given in Figure 2. The D_e and R_e values are 0.58 eV and 3.84 Å for $1/2_g$ and 0.06 eV and 3.50 Å for $1/2_u$, respectively. In Table I we list the energies at various distances for the 0_g^+ , 0_u^- and 1_u states of Tl_2 as well as for the $1/2_g$ and $1/2_u$ states of Tl_2^+ .

Discussion

Although further correlation corrections will certainly increase the well depths for the 0_g^+ , 0_u^- , and 1_u states of Tl_2 , because of the relatively large bond lengths, and because the molecular spinors are

distorted only slightly from primitive combinations of atomic spinors, we expect the corrections will be fairly small. (Indeed, further calculations on the O_g^+ state using an eight configuration MCSCF wavefunction lowered the potential minimum by only about .01 eV.) Nevertheless, the shallowness of the wells and the minimal separation between the three curves make detailed conclusions regarding the dissociation energies, the locations of the minima and even the relative order of these three states impossible for the present. But we can conclude that the bonding in Tl_2 is very weak.

This conclusion that the bond in Tl_2 is weak comes as no surprise considering our earlier discussion of bonding between $p_{1/2}$ spinors. The underlying cause is illustrated in figure 3 where we have plotted the potential curves for O_g^+ , O_u^- and 1_u states of Tl_2 along with curves for the corresponding $1\Sigma_g^+$, $3\Sigma_g^-$ and $3\Pi_u$ terms without spin-orbit coupling. These latter curves were computed using the same EPs as before but with the individual $p_{1/2}$ and $p_{3/2}$, etc. components averaged to eliminate the spin-orbit effect; thus other relativistic effects were retained. The $1\Sigma_g^+$, $3\Sigma_g^-$ and $3\Pi_u$ curves dissociate to spin-averaged 2P atoms. They have been placed at the proper energies with reference to the true $^2P_{1/2}$ and $^2P_{3/2}$ atoms and our calculated curves for the O_u^- , O_g^+ and 1_u molecular states. It is evident that in the absence of the spin-orbit effect, Tl_2 is a well-bound molecule in any of the $1\Sigma_g^+$, $3\Sigma_g^-$ or $3\Pi_u$ states. However the potential minima for these states are well above the energy for a pair of $^2P_{1/2}$ atoms. Hence the absence of strong bonding in Tl_2 appears to arise from the spin-orbit term and is a purely relativistic effect. Although the inclusion of the spin-orbit term also lowers the energy of the Tl_2 molecule, this is the result of the transition from molecular

spin-orbitals with considerable bonding nature to molecular spinors which closely approximate simple combinations of atomic $p_{1/2}$ spinors.

In the $^1\Sigma_g^+$ state the two valence electrons are sigma bonding, in the $^3\Sigma_g^-$ term both are pi bonding, while in the $^3\Pi_u$ term one is sigma and the other pi bonding. Correction for electron correlation will probably lower the singlet state more than the triplets; hence sigma and pi bonding strengths appear to be about equal for the two-electron system. For Tl_2^+ , however, sigma bonding is stronger as indicated by the lower energy of the $1/2_g$ state as compared to $1/2_u$. With the introduction of the spin-orbit term, both the $^3\Sigma_g^-$ and $^1\Sigma_g^+$ terms yield 0_g^+ states. The actual (lowest) 0_g^+ state shows very little departure from the $p_{1/2}$ atomic spinors. The $^3\Sigma_g^-$ term also includes a 1_g state which dissociates to one $^2P_{1/2}$ and one $^2P_{3/2}$ atom. We did not calculate a full potential curve for the 1_g state but a few single-configuration calculations at bonding distances indicated that its energy was well above that for 0_g^+ . Similarly the $^3\Pi_u$ term includes 0_u^+ and 2_u states (dissociating to one $^2P_{1/2}$ and one $^2P_{3/2}$ atom) as well as the 0_u^- and 1_u states. Exploratory calculations indicated that the 0_u^+ and 2_u states also had energies substantially above those for the 0_u^- and 1_u states. In view of the higher energies for their dissociated atoms, the 1_g , 0_u^+ and 2_u states may be more strongly bound with smaller R_e and larger D_e and ω_e values than for the lower energy states. The tentative R_e values are 3.02, 3.26, and 3.30 Å for the 1_g , 0_u^+ , and 2_u states, respectively.

It is known that for the alkali metals the M_2^+ ions are more strongly bound than the neutral M_2 molecules. Thus it is not too surprising that Tl_2^+ is more strongly bonded than Tl_2 . This phenomenon has not been fully explained for the alkali metals, to the best of our knowledge, and the situation is more complex for thallium. We are investigating further

this and other aspects of these states of Tl_2 and Tl_2^+ ; also we hope to treat various excited states of Tl_2 .

While we see possible assignments and therefore no conflict with the experimental spectra attributed to Tl_2 , it is not worthwhile to suggest definite assignments until our calculations for excited states are completed. At that time we expect to discuss both the spectral interpretation and various aspects of the bonding in these species.

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Table I. Dissociation Curves for the Lowest 0_g^+ , 0_u^- and 1_u States of Tl_2 and for the $1/2_g$ and $1/2_u$ States of Tl_2^+ ^a

R(bohr)	Tl_2			Tl_2^+	
	0_g^+	0_u^-	1_u	$1/2_g$	$1/2_u$
5.0	.0349	.0405	.0478	.2576	.2420
5.5	.0162	.0132	.0196	.2186	.2186
6.0	.0081	.0028	.0079	.2002	.2102
6.5	.0036	.0007	.0031	.1921	.2080
7.0	.0012	-.0015	.0011	.1892	.2083
7.5	.0001	-.0014	.0004	.1892	.2095
8.0	-.0003	-.0011	.0002	.1907	.2106
8.5	-.0004	-.0007	.0000	.1928	.2116
10.0	-.0001	-.0001	.0001	.2000	.2126
15.0	(0.0) ^a	0.0000	0.0000	.2097	.2109

^a All energies are in atomic units relative to the 0_g^+ energy at $R = 15.0$.

Figure Captions:

Figure 1: Dissociation curves for the 0_g^+ , 0_u^- and 1_u states of Tl_2 which dissociate to ground-state atoms.

Figure 2: Dissociation curves for the lowest $1/2_g$ and $1/2_u$ states of Tl_2^+ .

Figure 3: Potential curves for the 0_g^+ , 0_u^- and 1_u states of Tl_2 with $3\Sigma_g^-$, $3\Pi_u$ and $1\Sigma_g^+$ curves (computed without spin-orbit coupling), for comparison.

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