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Citation: *The Journal of Chemical Physics* **82**, 3741 (1985); doi: 10.1063/1.448910

View online: <http://dx.doi.org/10.1063/1.448910>

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Relativistic configuration interaction calculations of the low-lying states of TlF

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(Received 31 July 1984; accepted 6 October 1984)

Relativistic configuration interaction calculations (including spin-orbit interaction) are carried out for the nine low-lying ω - ω states arising from the $^1\Sigma^+$, $^3\Pi$, $^1\Pi$, $^3\Sigma^-$, $^3\Sigma^+$, and $^3\Delta$ Λ - S states of TlF. Our calculations confirm the earlier assignment of experimentally observed spectra to some of these states. We have calculated the spectroscopic properties of both experimentally observed states ($^1\Sigma_0^+$, $^3\Pi_{0+}$, $^3\Pi_1$, $^1\Pi_1$) and $^3\Pi_{0-}$, $^3\Pi_2$, $0^-(\Pi)$, $2(\Pi)$, and $0^+(\text{III})$ states. The calculated spectroscopic properties are in good agreement with experimental values. The potential energy curves of the excited states of TlF [$^3\Pi_{0+}$, $^3\Pi_1$, $^3\Pi_2$, $^3\Pi_{0-}$, $0^-(\Pi)$, $0^+(\text{III})$, and $2(\Pi)$] contain maxima thus confirming the recent experimental observations which predict potential barriers in the excited Π states. Vibrational bands higher than $v' = 3$ for $^3\Pi_{0+}$ and $v' = 8$ for $^3\Pi_1$ could be observed. The present calculations explain this based on the crossing of repulsive $0^-(\text{I})$ state with $^3\Pi_{0+}$ and $^3\Pi$, thus leading to predissociation.

I. INTRODUCTION

The photoionization of vapors of nonvolatile materials such as thallous halides has been performed successfully several years ago by Trenin and co-workers.¹⁻² Berkowitz and Chupka³ have reexamined the ion-pair processes observed by Trenin for TlI and also observed the high energy processes which ionize the molecule. The vaporization reactions of thallous halide have also been studied quite extensively by Cubicciotti and co-workers.⁴ The vapor pressure and mass spectrometric studies of the vapors indicate the existence of dimers as well as small amounts of trimers and tetrameric species.⁴⁻⁶ Murad, Hildenbrand, and Main⁷ have calculated the dissociation energies of group (III) A monohalides using high temperature mass spectrometric techniques which employ a mass spectrometer equipped with a Knudsen cell. These authors also predicted the possibility of maxima in the potential energy curves of the excited Π states. This prediction is based on the fact that the spectroscopically derived dissociation energies are higher than the thermochromic values suggesting the existence of maxima in the potential energy curves of these states. Berkowitz and Walker⁸ have studied the vapors of TlF, TlCl, and TlBr by photoionization mass spectrometry. In this technique the thresholds for the formation of Tl^+ is used to calculate the dissociation energies of these molecules. The calculated values for dissociation energies confirm the existence of barriers in the excited $^3\Pi_{0+}$ and $^3\Pi_1$ states.

As mentioned by Barrow and co-workers⁹ the first spectra of thallous fluoride was observed by Boizova and Butkow¹⁰ and was studied further by Howell.¹¹ Howell studied both the absorption and emission spectra of TlF

quite extensively. The systems he observed were assigned to $^3\Pi_{0+} \rightleftharpoons ^1\Sigma_0^+$, $^3\Pi_1 \rightleftharpoons ^1\Sigma_0^+$, and $^1\Sigma^+ \rightarrow ^1\Pi_1$. Howell also calculated the spectroscopic properties of these states based on these experimental observations. Barrow and co-workers⁹ carried out the rotational analysis of the bands of the $A\ ^3\Pi_{0+}$, $B\ ^3\Pi_1-X\ ^1\Sigma^+$ systems.

Brom and Fransen⁵ have investigated the infrared spectra and structure of matrix-isolated thallium halide clusters. In addition to the spectra of monomers the spectra of Tl_2F_2 and Tl_2Cl_2 dimers have also been observed and a linear $(\text{X}-\text{Tl}-\text{Tl}-\text{X})$ structure was proposed by these authors.

The microwave spectra,¹² the Stark-Zeeman spectra,¹³ and the rotational spectra of TlF by the molecular beam electric resonance method have also been recorded. This molecule has been a subject of a number of investigations.¹⁻¹⁴ Thus, there seems to be significant experimental interest on TlF to make it an interesting candidate for theoretical calculations.

Relativistic quantum calculations of molecules containing very heavy atoms as well as corresponding comparative nonrelativistic calculations are topics of recent activity.¹⁵⁻²⁹ Some of the recent developments in this area have been reviewed by Pitzer^{19,20} and Pyykkö.^{21,31} These calculations have been extremely successful in predicting spectroscopic properties of molecules containing very heavy atoms such as TIH , Pb_2 , Sn_2 , etc.¹⁵⁻¹⁸ Thus in the light of extensive experimental and theoretical interest in TlF, it was decided to carry out relativistic quantum calculations of the low-lying states of TlF.

In Sec. II, the methodology of this investigation is described. Section III discusses the results and compares calculated results with available experimental values. In Sec. IV, the properties of the potential energy curves and the nature of the relativistic CI wave function are discussed.

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II. METHODOLOGY OF CALCULATIONS

The method of relativistic configuration interaction that we use here was developed by Christiansen, Balasubramanian, and Pitzer.¹⁵ The details of this method are described in that paper. In summary, we employ relativistic effective core potentials for the heavy atoms in the molecules. These potentials are averaged with respect to spin at the SCF stage and differenced for the spin-orbit operator. This method of averaging with respect to spin reduces a spinor calculation (or a MCSCF spinor calculation) into a spin-orbital calculation and can thus be incorporated into a nonrelativistic SCF program. Further, we transform complex Slater basis sets into real Cartesian functions, since our SCF and CI codes were developed primarily for polyatomics. The spin-orbit integrals obtained using the spin-orbit operator mentioned above are introduced as one-electron integrals at the configuration interaction stage.

The TlF molecule has a closed shell ground state arising from $\sigma_p^2\pi_p^4$ (only p valence electrons on Tl and F are shown). Table I shows a few low-lying states resulting from single and double excitations from the σ_p and π_p orbitals to the lowest unoccupied σ^* and π^* orbitals. In Table I, we show states arising from these configurations in both Λ - S and ω - ω coupling schemes. The σ^* orbital is antibonding while the π^* orbital is dominantly on Tl and is only slightly antibonding. Thus the π^* orbital is lower in energy than the σ^* orbital. Hence, the states arising from $\sigma\pi^4\pi^*$, i.e., $^3\Pi_{0+}$, $^3\Pi_{0-}$, $^3\Pi_1$, $^3\Pi_2$, and $^1\Pi_1$ are the most low-lying states. The dissociation relationships of some of the low-lying molecular states into atomic states are shown in Table II. As one can see from Table II, since the spin-orbit splitting of F, ($^2P_{3/2} - ^2P_{1/2} = 404 \text{ cm}^{-1}$) is quite small, several molecular states dissociate into Tl $^2P_{1/2} + \text{F } ^2P_{3/2}$ and Tl $^2P_{1/2} + \text{F } ^2P_{1/2}$ which are not very far apart. However, the $^2P_{1/2} - ^2P_{3/2}$ splitting of the Tl atom is quite large. This splitting was calculated by Christiansen, Balasubramanian, and Pitzer¹⁵ and was found to be 0.92 eV or 7440 cm^{-1} . The corresponding experimental value is 7793 cm^{-1} . Thus the states dissociating into Tl($^2P_{3/2}$) + F($^2P_{1/2}$, $^2P_{3/2}$) are well separated from the states dissociating into Tl($^2P_{1/2}$) + F($^2P_{1/2}$, $^2P_{3/2}$) in the near dissociation limits.

TABLE I. A few low-lying states of TlF.

Configuration	Λ - S states	ω - ω states
$\sigma^2\pi^4$	$^1\Sigma^+$	0^+
$\sigma\pi^4\pi^*$	$^3\Pi$ $^1\Pi$	$0^-, 0^+, 1, 2$ 1
$\sigma^2\pi^3\pi^*$	$^1\Sigma^+$ $^1\Sigma^-$ $^1\Delta$ $^3\Sigma^+$ $^3\Sigma^-$ $^3\Delta$	0^+ 0^- 2 $0^-, 1$ $0^+, 1$ 3, 2, 1
$\sigma^2\sigma^*\pi^3$	$^3\Pi$ $^1\Pi$	$0^-, 0^+, 1, 2$ 1

TABLE II. Dissociation relationship of low-lying molecular states of TlF to atomic states.

Molecular states	Dissociation limit	
	Tl	F
$0^+, 1, 1(\text{II}), 2, 0^-$	$^2P_{1/2}$	$^2P_{3/2}$
$1(\text{III}), 0^+(\text{II}), 0^-(\text{II})$	$^2P_{1/2}$	$^2P_{1/2}$
$3, 2(\text{II}), 2(\text{III}), 1(\text{IV}), 1(\text{V}), 1(\text{VI}),$ $0^+(\text{III}), 0^+(\text{IV}), 0^-(\text{III}), 0^-(\text{IV})$	$^2P_{3/2}$	$^2P_{3/2}$
$0^+(\text{V}), 1(\text{VII}), 2(\text{IV}), 0^-(\text{V}), 1(\text{VIII})$	$^2P_{3/2}$	$^2P_{1/2}$

Next, we consider the choice of configurations in the relativistic configuration interaction calculation. In our calculations, we include spin-orbit interaction as one electron integrals at the CI stage. The inclusion of spin-orbit interaction at the CI stage mixes Λ - S states of different Λ - S symmetry but the same ω - ω symmetry. For example, the $^1\Sigma_0^+$ would mix with the $^3\Pi_{0+}$ as well as $^3\Sigma_0^+$, etc. The amount of mixing (that is, the coefficient in the CI wave function) is determined variationally in these CI calculations. As one can see in Table I, there are quite a few low-lying Λ - S states which give rise to 0^+ states. Many of these low-lying states must be included to adequately calculate correlation and spin-orbit mixing effects.

The CI code that we use is for configurations expressed in terms of real functions. Thus, we need to expand configurations involving complex orbitals into configurations involving real orbitals. To illustrate the $^3\Pi_{0+}$ state arising from $\sigma\pi^4\pi^*$ can be written in terms of complex orbitals as $\pi^4\sigma\alpha\pi^*\alpha$ and $\pi^4\sigma\beta\pi^*\beta$. These configurations upon expansion over real functions yield $\pi^4\sigma\alpha\pi_x\alpha$, $-i\pi^4\sigma\alpha\pi_y\alpha$, $\pi^4\sigma\beta\pi_x\beta$, and $+i\pi^4\sigma\beta\pi_y\beta$. Thus, some of the configurations would have imaginary coefficients. Of course, there is no difference in energies in either complex or real representations. Since the CI code is designed for polyatomics we use configurations involving real orbitals.

The details of the list of various reference configurations included in our CI calculations of the various states are shown in Table III. For the $0^+(\text{I})$ state extensive

TABLE III. Reference configurations and total number of configurations included in CI calculations.

State	RC ^a	Total no. of configurations
$0^+(\text{I})$	$\sigma^2\pi^4(1), \sigma\pi^4\pi^*(4), \sigma^2\pi^3\pi^*(8),$ $\sigma\sigma^*\pi^4(2), \sigma^*\pi^2\pi^*(1), \sigma^2\pi^2\pi^*(16)$	5895
$0^-(\text{I})$	$\sigma\pi^4\pi^*(4), \sigma^2\pi^3\pi^*(8), \sigma\sigma^*\pi^4(2)$	1950
$1(\text{I})$	$\sigma\pi^4\pi^*(4), ^3\Pi_1, ^1\Pi_1, \pi^4\pi^*(^3\Sigma_1^-, 1)$ $\sigma^2\pi^3\pi^*(8), \sigma\sigma^*\pi^4(1),$ $\sigma^2\pi^2\pi^*(15)$	2040
$2(\text{I})$	$\sigma\pi^4\pi^*(^3\Pi_2, 2), \pi^4\pi^*(^2\Delta, 2),$ $\sigma^2\pi^3\pi^*(8), \sigma^2\pi^2\pi^*(2)$	1183

^a RC: Reference configurations. Numbers in parentheses are the number of real reference configurations.

single and double excitations were allowed from the first five reference configurations and limited single and double excitations from the rest of the reference configurations. Excitations from σ_d orbital of Tl and F_{2s} orbital were also allowed from the $\sigma^2\pi^4$ reference configuration.

In the $0^+(\text{II})$ state, there was practically no mixing of $\sigma^2\pi^3\pi^*$ configurations. Also, our trial calculations of the $0^+(\text{III})$ state arising from $\sigma^2\pi^3\pi^*$ configurations indicated there is no appreciable contribution from the $\sigma\pi^4\pi^*$ configurations. Thus, in our $0^+(\text{III})$ calculations we included all the reference configurations in $0^+(\text{I})$ and $0^+(\text{II})$ states (described before) except the configurations from $^3\Pi_{0+}(\sigma\pi^4\pi^*)$. Thus, our $0^+(\text{III})$ calculations cannot be regarded as very accurate.

The SCF calculations were carried out using relativistic effective potentials for Tl with $d^{10}s^2p^1$ as the valence electrons of the Tl atom. We included all the electrons of F atom in our SCF calculations. At the CI level the $1s$ orbital on F, δ_d and π_d orbitals on Tl were frozen. The excitations from the σ_d orbitals of Tl were allowed for the $0^+(\text{I})$ state.

The basis sets we used for Tl and F are double zeta Slater type functions. The exponents of the basis sets were optimized for the 2P states of Tl and F. The optimized exponents are shown in Table IV.

II. RESULTS AND DISCUSSIONS

The energies of nine low-lying states of TlF [$0^+(\text{I})$, $0^+(\text{II})$, 1 , 0^- , 2 , $1(\text{II})$, $0^-(\text{II})$, $0^+(\text{III})$, and $1(\text{II})$] were calculated as a function of internuclear distances. The spectroscopic properties of bound states are listed in Table V. In that table, we also indicate the available experimental values of some of these states. Table VI shows the actual energies of all nine states with respect to the dissociation limit [$\text{Tl}(^2P_{1/2}) + \text{F}(^2P_{3/2})$]. The potential energy curves for those states are shown in Figs. 1 and 2.

As one can see from Table V, the calculated and the available experimental values for R_e and ω_e are in very good agreement. However, the T_e values are only in reasonable agreement. The reason for the higher calculated T_e values for the excited states is that our $0^+(\text{I})$ state calculations included excitations from σ_d and F_{2s} orbitals from the $\sigma^2\pi^4$ reference configuration. These excitations were necessary to obtain reasonable D_e values for the $0^+(\text{I})$ state. However, we could not include these excitations

TABLE V. Calculated spectroscopic properties of low-lying bound states of TlF and available experimental values.

State	R_e (Å)		T_e (cm $^{-1}$)		ω_e (cm $^{-1}$)	
	Theory	Expt.	Theory	Expt.	Theory	Expt.
$0^+(\text{I})$	2.04	2.08	0	0	592	477
$0^+(\text{II})$	2.12	2.05	40 462	35 186	462	436
$0^-(\text{I})$	2.10	...	40 891	...	345	...
$1(\text{I})$	2.12	2.08	42 612	36 863	326	366
$1(\text{II})$	2.69	...	45 164	45 546	396	346
$2(\text{I})$	2.10	...	46 245	...	340	...
$2(\text{II})$	2.92	...	49 700	...	264	...
$0^-(\text{II})$	2.90	...	50 053	...	279	...

in other excited reference configurations such as $\sigma\pi^4\pi^*$ (four such real configurations), etc., since inclusion of these excitations in excited configurations generate a large number of configurations that go beyond the capabilities of our computer code. Thus, the $0^+(\text{I})$ state is somewhat more correlated in comparison to the excited states. Nevertheless, we could unambiguously assign the experimentally observed transitions.

As one can see in Table V, our calculations confirm the earlier assignment of the X , A , and B states of TlF to 0^+ , $0^+(\text{II})$ (dominantly $^3\Pi_{0+}$), and $1(^3\Pi_1)$ states, respectively. We also show in that table properties of $0^-(\text{I})$, $2(\text{I})$, $2(\text{II})$, and $0^-(\text{II})$ states for which experimental values have not yet been calculated. The $1(\text{II})$ state is attributable to the [$C \rightarrow X(0^+)$] emission system.

Absorption continua in the region of 45 400 cm $^{-1}$ and above 50 000 cm $^{-1}$ have also been observed. However, none of the systems has been assigned presumably because of the continuous nature of these bands. Our calculations indicate several states with T_e values in this region. They are $2(\text{I})$, $2(\text{II})$, and $0^-(\text{II})$. Our calculations of the $0^+(\text{III})$ indicate a significant mixing of $^3\Sigma_{0+}^-$ arising from $\sigma^2\pi^3\pi^*$, with the $^1\Sigma_{0+}^+$ arising from $\sigma^2\pi^3\pi^*$ (with dominant contribution being from $^3\Sigma_{0+}^-$). This suggests the existence of an $0^+(\text{IV})$ state close to the $0^+(\text{III})$ state which would have T_e value greater than 50 000 cm $^{-1}$. Thus, these continua of bands can be attributed to $0^+(\text{IV})$ [dominantly $^1\Sigma^+(\text{II})_{0+}$ arising from $\sigma^2\pi^3\pi^*$ with significant mixing with $\sigma^2\pi^3\pi^*(^3\Sigma_{0+}^-)$]. Also, as one can see in Table I, there are several 1 states arising from $\sigma^2\pi^3\pi^*$ configurations. These states could also be attributed to those continua of bands in the region above 50 000 cm $^{-1}$.

Howell points out that no bands involving levels higher than $\nu' = 3$ for $^3\Pi_{0+}[0^+(\text{II})]$ were observed. He has postulated the existence of a repulsive state which crosses with $^3\Pi_{0+}$ and $^3\Pi_1$ so as to produce predissociation in both $^3\Pi_{0+}$ and $^3\Pi_1$ explaining the fact that higher vibrational bands of $^3\Pi_1$ and $^3\Pi_{0+}$ could not be observed. Howell could not unambiguously assign this repulsive state. As one can see from Fig. 1 the $^3\Pi_{0-}$ [i.e., $0^-(\text{I})$] crosses with $0^+(\text{II})$ as well as 1 although the crossing with $0^+(\text{II})$ is at a relatively shorter distance in comparison to the crossing with the 1 state. This clearly explains why only up to $\nu' = 3$ bands were observed for $^3\Pi_{0+}$ while up to eight bands could be observed for $^3\Pi_1$. Thus this repulsive state is $0^-(\text{I})$. The transition $0^+(\text{I}) \rightarrow 0^-(\text{I})$ is

TABLE IV. The optimized exponents for the Slater type basis sets of Tl and F atoms. Numbers in parentheses are the principal quantum numbers.

	Tl	F
s	3.2154 (6)	9.9906 (1)
	1.8982 (6)	7.3006 (1)
		3.4475 (2)
p		2.1406 (2)
	2.565 (6)	4.563 (2)
	1.3627 (6)	1.9611 (2)
d	4.8018 (4)	1.0 (3)
	2.619 (4)	

TABLE VI. Potential energies of some low-lying states of TlF.

R	$0^+(I)$	$0^+(II)$	$0^-(I)$	1	2	1(II)	$0^+(III)$	$0^-(II)$	2(II)
3.0	0.0581	0.2383	...	0.2328	0.2455	0.2917	0.4725
3.4	-0.1052	0.0786	...	0.0874	0.1016	0.0	0.2995	0.2878	0.2841
3.6	-0.1324	...	0.0539	0.0630	...	0.1127
3.8	-0.1417	0.0445	0.0442	0.0528	0.0685	0.0988	0.1909	0.1876	0.1857
4.0	-0.1402	0.0409	0.0429	0.0507	0.0673	0.0895	0.1639	0.1597	0.1579
4.2	-0.1328	0.0430	0.0443	0.0515	0.0687	0.0819	0.1435	0.1397	0.1380
4.5	-0.1166	0.0477	0.0456	0.0505	0.0702	0.0770	0.1201	0.1176	0.1161
5.0	-0.0878	0.0478	0.0444	...	0.0094	0.0710
5.2	-0.0756	0.0435	...	0.0677	0.0884	0.0912	0.0899
6.0	-0.0360	0.0882	0.0955	0.0924
∞	0.0	0.0015	0.0	0.0	0.0	0.0	0.0339	0.0015	0.0339

symmetry forbidden and thus one would expect the predissociated continuum of $^3\Pi_{0+}$ and $^3\Pi_1$ bands to be of somewhat less intensity in comparison to the band systems. This is compatible with Howell's observed spectra which shows the continuum to be of lower intensity in comparison to bands in these systems. The $C(1)$ state is also

predissociated. As one can see in Fig. 1 the 1(II) state is only slightly bound and it has a barrier near the minimum which could lead to predissociation.

Rao and Rao³⁰ report band spectra of TlF in the region of 28 500–29 500 cm^{-1} . These bands are abruptly cut off. Only seven bands could be observed. The vibra-

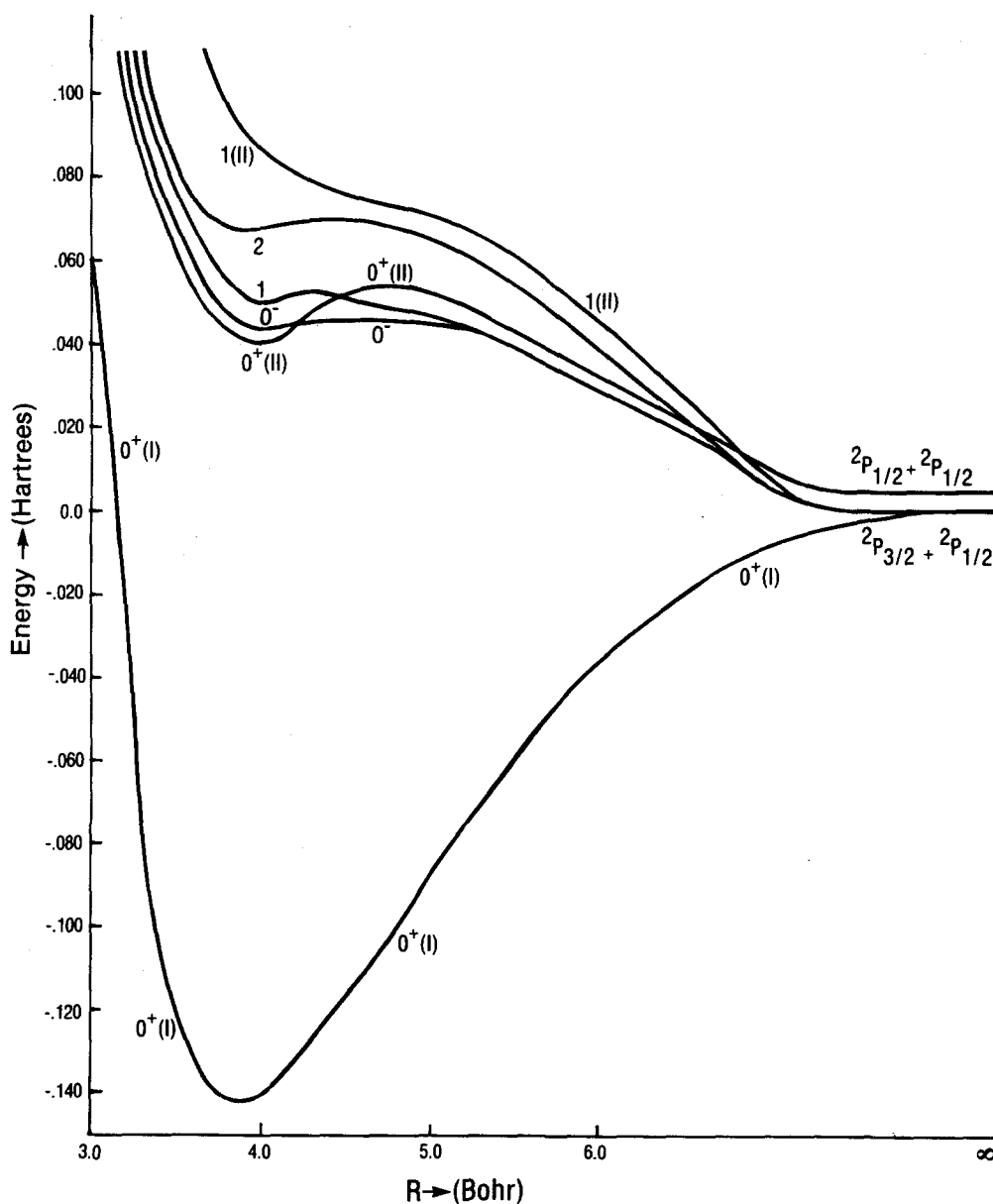


FIG. 1. Potential energy curves of some low-lying states of TlF.

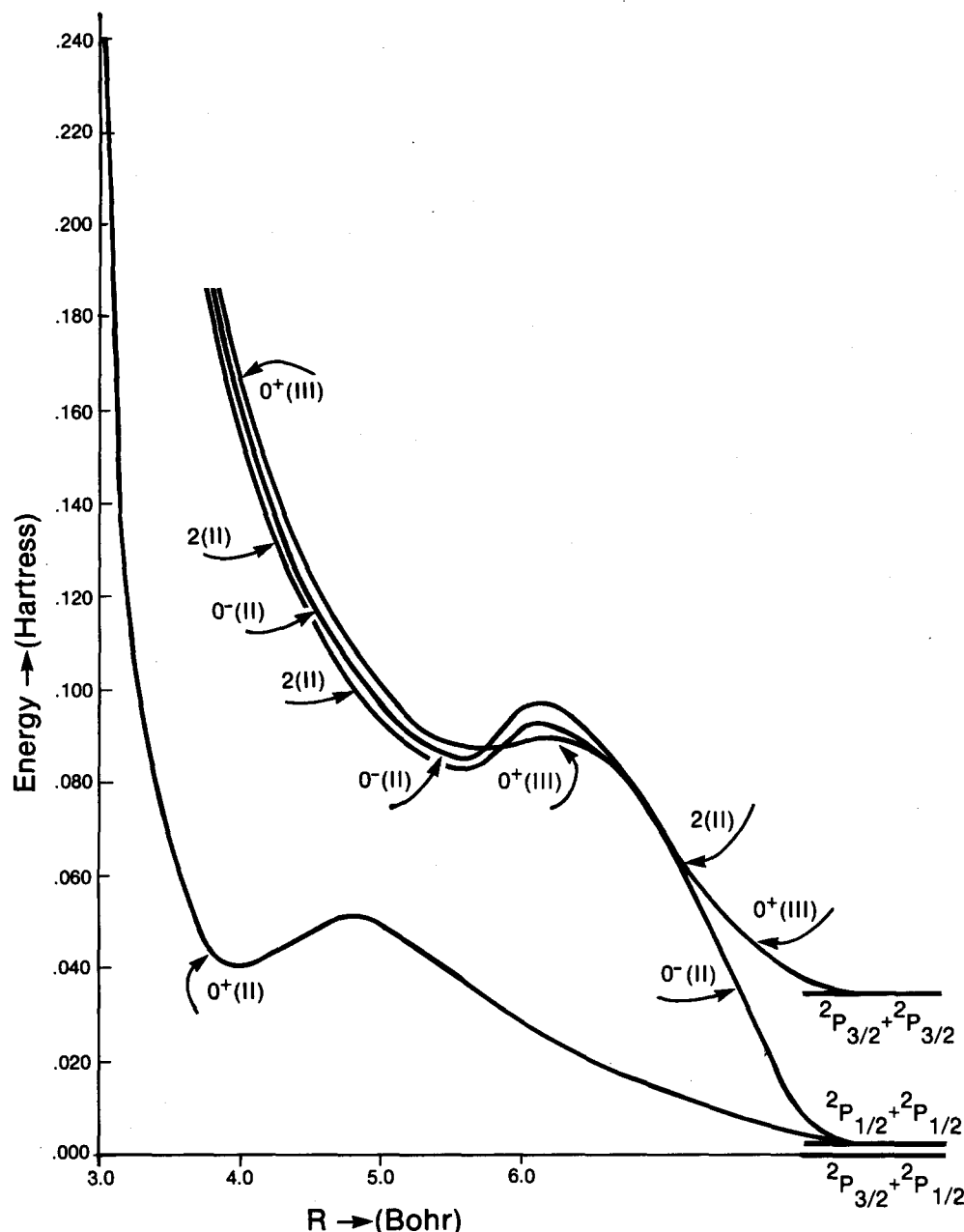


FIG. 2. Potential energy curves of some low-lying states of TlF.

tional frequency of the upper state calculated by these authors is about 194 cm^{-1} suggesting that this is attributable to a state with a shallow minimum. Our calculations indicate that there are no bound excited states near equilibrium geometries in this region. However, at long distances it is possible for one of the excited states to have such a shallow minimum. This would, of course, explain the fact that only seven vibrational bands could be seen. In fact, such minima were calculated by Christiansen, Balasubramanian, and Pitzer for TlH. From the T_e value of this state ($29\,08\text{ cm}^{-1}$) one can infer that it has to be one of the states dissociating into $^2P_{1/2} + ^2P_{1/2}$ or $^2P_{1/2} + ^2P_{3/2}$ (Tl + F). Since our calculations were more accurate at near equilibrium geometries than at long distances we did not attempt calculations in this region. Thus, this state cannot be assigned unambiguously.

Murad, Hildenbrand, and Main⁷ as well as Berkowitz and Walter⁸ have predicted the existence of maxima in

the potential energy curves of excited II states of TlF. This prediction was based on the higher spectroscopic dissociation energy obtained from Birge-Sponer extrapolation of the excited II states. The spectroscopic dissociation energies for these molecules were thus higher than the thermochemical values. As seen in Figs. 1 and 2, the excited II states, $0^+(\text{II})$, 0^- , 1, 2, and $1(\text{II})$, as well as $0^-(\text{II})$, $0^+(\text{III})$, and $2(\text{II})$ states have maxima in their potential curves. This is also compatible with the fact that many of these states are bound but their dissociation limits are way down and thus they have to go through maxima.

While Howell assigned the *A* and *B* states to $^3\Pi_{0+}$ and $^3\Pi_1$ states correctly, however, presumably, because of lack of any theoretical calculations on these systems he has incorrectly assigned these to $^3\Pi_{0+}$ and $^3\Pi_1$, arising from $\sigma^2\pi^3\sigma^*$ configuration. Our SCF calculations indicate clearly that the σ^* orbital is very highly antibonding while

the π^* orbital is only very slightly antibonding and it is dominantly thallium p orbital. At 4.0 bohr the energy of the σ^* orbital is 0.1238 hartree a.u. while the energy of the π^* orbital is 0.039 hartrees. Our CI calculations also confirm that the $^3\Pi$ arising from $\sigma^2\pi^3\sigma^*$ is much higher in energy in comparison to $^3\Pi$ arising from $\sigma\pi^4\pi^*$ configuration. Thus the $A0^+$ and $B1$ states are dominantly $^3\Pi_{0+}$ and $^3\Pi_1$, arising from $\sigma\pi^4\pi^*$ configuration. Based on the electronic properties of isoelectronic BF and AlF molecules Murad, Hildebrand, and Main,⁷ correctly conclude that the lowest-lying $^3\Pi$ and $^1\Pi$ states arise from $\sigma\pi^4\pi^*$ configuration. Thus it appears that recent investigators seem to recognize this.

Our calculated dissociation energy for the $0^+(I)$ state is 3.86 eV. This value is in reasonable agreement with the photoionization mass spectrometric value of Berkowitz and Walter (4.57 eV).⁸ The difference is attributable to the fact that although our CI for the $0^+(I)$ state is quite extensive, it is not complete.

IV. THE NATURE OF BONDING AND CI WAVE FUNCTIONS OF TlF

First we start discussing the nature of the molecular orbitals of TlF near equilibrium geometries. The highest occupied orbital is quite bonding in nature. It is a mixture of Tl 6s, Tl 6p, and F 2p. The highest occupied π orbital is, however, a completely localized p orbital on F. Thus, the occupied π orbital is like a lone pair. The lowest unoccupied π orbital is mainly Tl 6p with a small mixing of F 2p and slightly antibonding. The lowest unoccupied σ orbital is also dominantly on Tl but is more antibonding than the π^* orbital.

At near equilibrium geometries the CI wave function of the $0^+(I)$ state is dominantly $\sigma^2\pi^4(^1\Sigma_0^+)$ (93%) with only 0.15% contribution from the $^3\Pi_{0+}(\sigma\pi^4\pi^*)$ configurations indicating that correlation from the $\sigma^2\pi^4$ reference configuration is much more important than spin-orbit interaction for the $0^+(I)$ state at near equilibrium geometries. At large distances and near dissociation limits the configurations such as $\sigma\pi^4\pi^*$, $\sigma\sigma^*\pi^4$, $\sigma^2\pi^3\pi^*$, etc., become more important so that this state would dissociate into the neutral atoms [$^2P_{1/2}(\text{Tl}) + ^2P_{3/2}(\text{F})$].

The $1(I)$ state is (92%) $^3\Pi_1$ and (8%) $^1\Pi_1$ at 4.0 bohr. [The corresponding percentage is approximately switched in the $1(II)$ state.] At longer distances the $^1\Pi_1$ and $^3\Pi_1$ states heavily mix. At very short distances the $0^-(I)$ state is dominantly $^3\Pi_{0-}$ (91%) with the rest of the population attributable to single and double excitations from $^3\Pi_{0-}$ reference configurations. The $2(I)$ state also behaves alike at near equilibrium geometries. The $0^+(II)$ state is dominantly $^3\Pi_{0+}$ (87%) but had some mixing with $\sigma^2\pi^4(^1\Sigma^+)$ (3%) state.

The $0^+(III)$ state had a very interesting behavior. The set of states arising from $\sigma^2\pi^3\pi^*$ were the ones

immediately above $\sigma\pi^4\pi^*$ as one would expect from the nature of σ , π , and π^* orbitals. There are two 0^+ states arising from $\sigma^2\pi^3\pi^*$ configurations, namely, $^3\Sigma_0^+$ and $^1\Sigma_0^+$. Thus one would expect the $0^+(III)$ state to be a mixture of $^3\Sigma_0^+$ and $^1\Sigma_0^+$ arising from the $\sigma\pi^3\pi^*$ configurations. At 3.8–6.0 bohr the $0^+(III)$ CI wave-function contained coefficients from both $^3\Sigma_0^+$ configurations (imaginary coefficients) and $^1\Sigma_0^+$ configurations (real coefficients). As the distance was increased the contribution from $^1\Sigma_0^+$ configurations increased. At 4.0 bohr, the $0^+(III)$ state was 62% $^3\Sigma_0^+$ and 17.5% $^1\Sigma_0^+$. The $\sigma\sigma^*\pi^4(^1\Sigma_0^+)$ also makes significant contribution (8%) to the $0^+(III)$ state. The rest of the contribution is due to excitations from these reference configurations. At very short distances (3.0–3.4 bohr) there is an avoided crossing arising from $\pi^4\pi^*\pi^2$ configuration. At 3.0 bohr, the $0^+(III)$ is 77% $^3\Sigma_0^+$ arising from $\pi^4\pi^*\pi^2$, 8% $^3\Sigma_0^+(\sigma^2\pi^3\pi^*)$, and 3% $^1\Sigma_0^+(\pi^4\pi^*\pi^2)$.

ACKNOWLEDGMENT

The author would like to thank a referee for his invaluable comments.

- ¹ A. Trenin, Phys. Rev. **36**, 147 (1930).
- ² A. Trenin and B. Popov, Z. Phys. **75**, 338 (1932).
- ³ J. Berkowitz and W. A. Chupka, J. Chem. Phys. **45**, 1287 (1966).
- ⁴ D. Cubicciotti, J. Phys. Chem. **68**, 1528 (1964); **68**, 3834 (1964); **69**, 1410 (1965); F. J. Keneshea and D. Cubicciotti, *ibid.* **71**, 1958 (1967), and the back references given therein.
- ⁵ J. M. Brom, Jr. and H. F. Fransen, J. Chem. Phys. **54**, 2874 (1971).
- ⁶ D. Cubicciotti, High Temp. Sci. **2**, 65 (1970).
- ⁷ E. Murad, D. L. Hildenbrand, and R. P. Main, J. Chem. Phys. **45**, 263 (1966).
- ⁸ J. Berkowitz and T. A. Walter, J. Chem. Phys. **49**, 1184 (1968).
- ⁹ R. F. Barrow, H. F. K. Cheall, P. M. Thomas, and P. B. Zeeman, Proc. Phys. Soc. **71**, 128 (1958).
- ¹⁰ Z. V. Boizova and K. V. Butkov, Phys. Z. Sowjetunion. **5**, 705 (1936); as referred in Ref. 9.
- ¹¹ H. G. Howell, Proc. R. Soc. London, Ser. A **160**, 242 (1937).
- ¹² M. Mendel and A. H. Bartlett, Phys. Rev. **98**, 1159 (1955).
- ¹³ W. Drechsler and G. Graff, Z. Phys. **163**, 165 (1961).
- ¹⁴ R. K. Ritchie and H. Lew, Can. J. Phys. **43**, 1701 (1965).
- ¹⁵ P. A. Christiansen, K. Balasubramanian, and K. S. Pitzer, J. Chem. Phys. **76**, 5087 (1982).
- ¹⁶ K. Balasubramanian and K. S. Pitzer, Chem. Phys. Lett. **100**, 273 (1983).
- ¹⁷ K. Balasubramanian and K. S. Pitzer, J. Chem. Phys. **78**, 321 (1982).
- ¹⁸ K. S. Pitzer and K. Balasubramanian, J. Phys. Chem. **86**, 3068 (1982).
- ¹⁹ K. S. Pitzer, Acc. Chem. Res. **12**, 271 (1979).
- ²⁰ K. S. Pitzer, Int. J. Quantum Chem. **25**, 131 (1984).
- ²¹ P. Pykkö, Adv. Quantum Chem. **11**, 35 (1978).
- ²² J. S. Cohen, W. R. Wadt, and P. J. Hay, J. Chem. Phys. **71**, 2955 (1979).
- ²³ W. R. Wadt and P. J. Hay, J. Am. Chem. Soc. **101**, 5198 (1979).
- ²⁴ Y. S. Lee and A. D. McLean, J. Chem. Phys. **76**, 735 (1982).
- ²⁵ A. D. McLean, J. Chem. Phys. **79**, 3392 (1983).
- ²⁶ L. Kahn, Int. J. Quantum Chem. **25**, 149 (1984).
- ²⁷ P. J. Hay, J. Am. Chem. Soc. **103**, 1390 (1981).
- ²⁸ S. W. Wang and K. S. Pitzer, J. Chem. Phys. **79**, 3851 (1983).
- ²⁹ K. Balasubramanian, J. Phys. Chem. (in press).
- ³⁰ J. V. R. Rao and P. T. Rao, Indian J. Phys. **29**, 20 (1955).
- ³¹ P. Pykkö, Int. J. Quantum Chem. **25**, 1 (1984).