Improved Pseudopotential Calculations of the Adiabatic Potentials and Oscillator Strengths of Tl-Heavy Noble Gas Systems*

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The thallium-heavy noble gas potentials and absorption oscillator strengths as a function of internuclear separation have been recalculated using a somewhat modified Baylis' model for the electronic interaction between the atoms. The calculated potentials associated with the $6^2P_{1/2}$, $6^2P_{3/2}$ and $7^2S_{1/2}$ thallium states are compared to the potentials determined by Cheron et al. from the measurement of continuum emission intensities on the extreme wings of the Tl resonance lines due to noble gas perturbers. The shift and broadening coefficients for the 3776 and 5350 Å lines of thallium perturbed by noble gases have also been estimated from the present potentials. The agreement with the experiment is quite good. Moreover, the very strong emission TlXe band centered at approximately 6000, 4300 and 3650 Å, as observed experimentally, can be predicted by the calculated potentials as well.

1. Introduction

Interatomic potentials are required for understanding various physical processes that occur when two atomic particles collide. These are, for example, excitation transfer, quenching of excited states, pressure broadening of spectral lines, depolarization, etc. These processes have been most widely investigated, both experimentally and theoretically, on the alkali-rare gas (RG) atom systems. Relatively little work has, however, been done on the Group III element-RG pairs. Most works of this kind concerned thallium-RG systems. Cheron et al. [1] have reported on an analysis of the far wing emission intensities of the 5350 and 3776 Å resonance lines of thallium perturbed by noble gases. From the observed spectra they have deduced the potential energy curves for all Tl-RG pairs with the thallium atom being in $6^2P_{1/2}$, $6^2P_{3/2}$ and $7^2S_{1/2}$ electronic states. Potentials originating from higher excited states of Tl have not yet been determined. Cheron et al. have also identified the two continuum bands centered at approximately 4300 and 6000 Å that lie to the red of thallium atomic lines at 3776 and 5350 Å, respectively. These bands were also observed by Schlie et al. [2] for TlXe. Moreover, they observed a very strong emission band on the red side of the thallium 3519/29 Å line. This emission band is centered at approximately 3650 Å. Cheron et al. [3] have also measured the shift and broadening coefficients of the resonance lines of thallium perturbed by noble gases. Both the observed emission bands and the measured shift and broadening coefficients are related directly to the thallium-RG perturber interatomic potentials associated with the states between which the transitions occur. However, the potentils themselves are still little known.

So far the only Tl-RG potentials cited in the literature are those published by Cheron et al. [1]. One of us (E. C.) has published the theoretical potentials for Tl-RG pairs (Czuchaj [4]) but, because of a large discrepancy with the "measured" ones, they seem to lie far beyond the experimental error. The large disagreement between the calculated and "measured" potentials indicates that the model potential used in the previous calculations was insufficient. In this context it was desirable to refine the model and to repeat the calculations. Such improved calculations have been carried out and the new potentials obtained match the existing experimental data fairly well.

In addition, the molecular electronic wavefunctions obtained as a result of the diagonalization of the diatomic Hamiltonian have been exploited for calculating the absorption oscillator strengths of the Tl-RG pairs as a function of internuclear separa-

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tion. These have been calculated for the transitions from the molecular states associated with the $6^2P_{1/2}$, $6^2P_{3/2}$ and $7^2S_{1/2}$ states of thallium to all remaining excited states of the diatomic involved in the calculations.

The Baylis method along with the modifications made in the present calculations is outlined in the following section. The details of the calculations are described in Section 3. Section 4 is devoted to the oscillator strengths. The results obtained are discussed in Sect. 5, while the conclusions are given in the last section.

2. Method of Calculations

Great advantages in calculating the potential energy curves of diatomic systems were achieved by using model potentials for the electronic interaction. A basic disadvantage is, however, that the error in such calculations is always difficult to be estimated. In the previous calculations and the present ones the model potential proposed by Baylis (Baylis [5]) is used to calculate interatomic potentials for the thallium-RG pairs. In this model the electronic interaction between the thallium atom and a RG-atom is represented by three terms

$$V(\boldsymbol{r}, \boldsymbol{R}) = W(R) + G(\boldsymbol{r}, \boldsymbol{R}) + F(\boldsymbol{r}, \boldsymbol{R}) , \tag{1}$$

where $\boldsymbol{r}$ and $\boldsymbol{R}$ are, respectively, the position vectors of the Tl-valence electron and of the rare gas atom nucleus relative to the thallium nucleus. $W(R)$ is here the pseudointeraction of the thallium core with the rare gas atom, which in an electron gas treatment of the atoms can be put in the form

$$W(R) = \frac{3\hbar^2}{10 m_e} (3\pi^2)^{2/3} \int \mathrm{d}\boldsymbol{r} \{[\varrho_T(r) + \varrho_B(r')]^{5/3} - \varrho_T^{5/3}(r) - \varrho_B^{5/3}(r')\} , \tag{2}$$

where $\varrho_T(r)$ and $\varrho_B(r')$ are the radial electronic charge densities of the thallium core and the rare gas atom, respectively, $r' = |\boldsymbol{R} - \boldsymbol{r}|$ and m_e is the electronic mass. Similarly, the term $G(\boldsymbol{r}, \boldsymbol{R})$ which represents the pseudointeraction ("Pauli repulsion") of the thallium valence electron with the rare gas atom can be expressed in terms of the radial electronic charge density of the rare gas atom $\varrho_B(r')$ as follows

$$G(\boldsymbol{r}, \boldsymbol{R}) = \frac{\hbar^2}{2 m_e} [3\pi^2 \varrho_B(r')]^{2/3} . \tag{3}$$

The third term in (1), i.e. $F(\boldsymbol{r}, \boldsymbol{R})$, is the electrostatic interaction between the atoms which is taken to be simply that of a polarizable dipole (the rare gas atom) in the field of the thallium valence electron plus the thallium core. In the original formulation of the method $F(\boldsymbol{r}, \boldsymbol{R})$ was assumed to be

$$F(\boldsymbol{r}, \boldsymbol{R}) = -\frac{1}{2} \alpha_B e^2 \left[\frac{\boldsymbol{R}}{R^3} - \frac{\boldsymbol{r}'}{r'^3} \right]^2 \tag{4}$$

for $r' \geqq r_0$ and

$$F(\boldsymbol{r}, \boldsymbol{R}) = -\tfrac{1}{2} \alpha_B e^2 [R^{-4} + r_0^{-4}] \tag{5}$$

for $r' < r_0$. Here α_B is the polarizability of the rare gas and r_0 is an adjustable parameter ("radius" of the rare gas atom) which has to be determined for each atomic pair separately. Setting so the interaction between the atoms and defining the zero energy of the system when the two atoms are in the ground states and isolated, the Hamiltonian of the system can be written in the form

$$H_e(\boldsymbol{r}, \boldsymbol{R}) = H_0(\boldsymbol{r}) + V(\boldsymbol{r}, \boldsymbol{R}) , \tag{6}$$

where $H_0(\boldsymbol{r})$ is the valence electron Hamiltonian of the free thallium atom. In order to obtain the interatomic potentials of the thallium-RG system the Hamiltonian [6] is diagonalized in the basis of the Tl-valence electron wavefunctions. The basis functions are taken in the $|(nls)jm_j\rangle$-representation, where the thallium wavefunction is a product of a radial part multiplied by a spin-orbit coupling function. The central problem of the calculations is to calculate the matrix elements of the model potential in the basis functions. This procedure is described in detail by Baylis [5] and by Pascale and Vandeplanque [6] and will not be repeated here.

In general, the potential $V(\boldsymbol{r}, \boldsymbol{R})$ is expanded in terms of Legendre polynomials

$$V(\boldsymbol{r}, \boldsymbol{R}) = \sum_{L=0}^{\infty} V^{(L)} P_L(\cos \vartheta) , \tag{7}$$

where ϑ is the angle between the vectors $\boldsymbol{r}$ and $\boldsymbol{R}$ and $V^{(L)}(r, R)$ are the moments of the multipole expansion. The corresponding angular integrals can be expressed by Clebsch-Gordan coefficients, but the radial matrix elements

$$V^{(L)}_{nl, n'l'} = \langle nl \mid V^{(L)}(r, R) \mid n'l' \rangle \tag{8}$$

should be integrated numerically. Here the $|nl\rangle$'s stand for the radial wavefunctions of the thallium

atom taken in the present calculations to be the Simons functions (Simons [7]). The Simons functions behave asymptotically like the Bates-Damgaard functions but at the origin they are finite. These radial orbitals are characterized by the quantum numbers n and l and by the quantum defect δ of the thallium atom. They are normalized but not orthogonal. Finally, the matrix element of the Hamiltonian (6) can be expressed as $H_{ik} = E_i S_{ik} + V_{ik}$, where E_i is the energy of the thallium atom in the $|(n\,l\,s)\,j\,m_j\rangle$-state

$$(E_i \equiv E_{nlj}) \quad \text{and} \quad S_{ik} \equiv \langle (n\,l\,s)\,j\,m_j | (n'\,l'\,s)\,j'\,m_j' \rangle = S_{nl,\,n'l}\,\delta_{ll'}\,\delta_{jj'}\,\delta_{m_j m_j'}$$

is the small overlap matrix which has to be taken into account in the calculations. Since the matrix S_{ik} is regular, the problem reduces to solving the secular equation

$$\det |[E_i - \varepsilon_\alpha(R)]\,\delta_{ik} + (S^{-1}\,V)_{ik}| = 0 \tag{9}$$

for the adiabatic energies $\varepsilon_\alpha(R)$.

Many improvements of the original Baylis method when applied to the alkali-RG systems were made by various authors (Pascale and Vandeplanque [6], Czuchaj and Sienkiewicz [8], Düren and Moritz [9], Düren et al. [10]). Although some of these improvements were implemented in previous calculations of the adiabatic potentials of the thallium-RG pairs, the results obtained then proved to be far unsatisfactory. A large discrepancy between the calculated and "measured" potentials seemed to indicate that the used model potential was insufficient.

First of all the potentials calculated previously were very strongly repulsive as compared to the ones determined by Cheron et al. [1]. Two terms of the model potential are responsible for repulsion between the atoms, namely G and W. The matrix elements of the pseudopotential G are mainly determined by the shape of the Tl-wavefunctions, while W depends strongly on the radial charge density distribution of the Tl-core electrons. The thallium atom is like an inverted alkali in that it has a split ground state ($6\,^2P_{1/2}$ and $6\,^2P_{3/2}$) with a separation of 0.98 eV, whereas its first excited state ($7\,^2S_{1/2}$) is at 3.28 eV. Moreover, unlike the alkalis the thallium atom possesses the outer closed subshell $6s^2$. Its contribution to the interaction between the atoms seems to be of significant importance. In previous calculations the electronic density distribution for the thallium core was taken from Gombas and Szondy [11]. However, there are some indications suggesting that the Gombas densities are of little accuracy. For example, better agreement with the experiment was obtained when the adiabatic potentials for the alkali-RG pairs were calculated with the Gombas [12] electronic density distributions for the rare gases than with those taken from Gombas and Szondy [11] (comp. Pascale and Vandeplanque [6]). Therefore, contrary to the previous calculations we have not taken the Gombas-Szondy distribution for the $6s^2$ electrons. Instead, we have derived a new distribution which has been obtained with the Simon's orbitals for the 6s state of the thallium ion TlIII and via the variational principle for the ground-state energy of TlII (two-electron model). The variational procedure allowed us to obtain an effective charge seen by TlII 6s electrons. In this way the corresponding Simon's orbitals have been corrected by introducing $Z_{\text{eff}} = 2.636$ instead of $Z_{\text{net}} = 3$.

Finally, the required distribution takes the form

$$\varrho(r) = 0.76852946\, r^{4.052104} \exp\{-2.602106\, r\} \tag{10}$$

with the distribution maximum at $r = 1.557\, a_0$, whereas the corresponding Gombas-Szondy distribution is given by the expression

$$\varrho_G(r) = 0.00910663\, r^7 \exp\{-2.03\, r\} \tag{11}$$

with the distribution maximum at $r = 3.448\, a_0$. Both the distributions satisfy the normalization condition

$$\int_0^\infty \varrho(r)\,\mathrm{d}r = 2\,.$$

The use of the new electronic density distribution for the Tl $6s^2$ subshell allowed us to obtain the interatomic potentials which are in reasonable agreement with the available experimental data. The remaining electronic charge density distributions concerning the Tl atom and the rare gases have not been changed as compared to the previous calculations. On account of their compactness slight changes of respective distributions do not affect the model potential at intermediate and large internuclear separations. In order to show how the interaction between the atoms depends on the electronic density distribution of the Tl $6s^2$ electrons we demonstrate in Fig. 1 the pseudointeraction $W(R)$

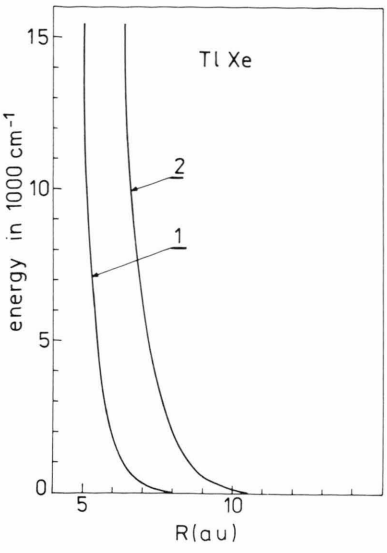

Fig. 1. Pseudointeraction $W(R)$ between the Tl-core and the Xe atom: 1) calculated with the $6s^2$ electronic density distribution of thallium given by (10), 2) calculated with the Gombas-Szondy distribution for the $6s^2$ electrons given by (11).

calculated for TlXe with both the Gombas-Szondy distribution (11) and the new one given by (10).

Another improvement of the calculations, as compared to the previous ones, is the use of a larger number of basis functions. Previously, the basis included the Tl-states from the ground state to the $7\,^2D_{5/2}$ one, while now it contains all the Tl-states from the ground state $6\,^2P_{1/2}$ up to the $8\,^2D_{5/2}$ state. However, the larger number of the basis states is of minor importance in obtaining the present potentials. It assures only higher stability of the molecular terms.

3. Adiabatic potentials

The adiabatic potentials of a thallium-RG pair are obtained by solving the secular equation (9). The matrix $E_i\delta_{ik} + (S^{-1}V)_{ik}$ is non-symmetric. Its off-diagonal elements are by three or more orders of magnitude smaller than the diagonal ones. Moreover, elements $(S^{-1}V)_{ik}$ and $(S^{-1}V)_{ki}$ do not differ considerably from each other. This urged us to replace the matrix $E_i\delta_{ik} + (S^{-1}V)_{ik}$ by a symmetric one, the off-diagonal elements of which have simply been taken as $[(S^{-1}V)_{ik} + (S^{-1}V)_{ki}]/2$. In view of the present semiempirical calculations such an approximation seems quite justified. As the result we could use the Jacobi procedure to diagonalize the molecular matrix and, in consequence, to obtain the adiabatic potentials of the systems under consideration. The matrix elements V_{ik} have been calculated using the Simons wavefunctions for the thallium atom. These are defined by the atomic energies of thallium which we have taken from the tables of Moore [13]. The other parameters necessary in the calculations are the polarizabilities of the rare gases, taken here from Dalgarno and Kingston [14] and the coefficients defining the electronic charge density distributions of the atoms. These are taken from Gombas [12] for the rare gases and from Gombas and Szondy [11] for the thallium atom except for the $6s^2$ subshell. The pseudointeraction term G has been calculated exactly as in the original work of Baylis, whereas the pseudopotential $W(R)$ has been computed according to (2) including all the closed shells of the atoms. The radial integrals involved in the matrix elements $\langle nl \mid F^{(L)}(r, R) \mid n'l' \rangle$ were computed in the whole range of variation of the variable r.

The adjustable parameter r_0 defining the "radius" of a rare gas atom (as required by the original Baylis' method) could not, however, be determined in the manner as it was done for the alkali-RG pairs. For an alkali-RG system r_0 was determined by fitting the well-depth of the calculated ground-state potential of the diatomic to that known from the scattering experiment. Unfortunately, there are no scattering data or other theoretical potentials for the Tl-RG systems which could be used for this purpose. What seems to be the most reliable for the Tl-RG diatomics is the well-depth of the $B^2\Sigma_{1/2}$ potential, originating in the Tl $(7\,^2S_{1/2})$ state, as determined by Cheron et al. [1] from continuum emission intensities on the extreme wings of the Tl resonance lines in the presence of noble gas perturbers. By fitting the calculated well-depth of the $(1/2)7\,^2S_{1/2}$ potential to that of the Cheron et al. potential we could determine the values of r_0 for the TlAr, TlKr and TlXe pairs which are compiled in Table 1. Unfortunately, this procedure fails completely for TlHe and TlNe, as it did already in the case of the alkali atoms (comp. Düren and Moritz [9]). This fact confirms once more the weakness of the model for these particular systems.

Table 1. Polarizabilities α_B and "radii" r_0 of the noble gases.

Noble gas	$\alpha_B\,[a_0^3]$	$r_0\,[a_0]$
Argon	11.080	0.810
Krypton	16.734	0.863
Xenon	27.292	1.029

4. Oscillator strengths

The electronic absorption oscillator strength at the internuclear separation R for a transition in a thallium-rare gas system from a lower molecular state described by the wavefunction $\Psi_{\Gamma M}(\boldsymbol{r}, R)$ to an upper molecular state described by the wavefunction $\Psi_{\Gamma' M'}(\boldsymbol{r}, R)$ is defined by

$$f_{\Gamma\Omega,\Gamma'\Omega'}(R) = \frac{2m_e(\varepsilon_{\Gamma'\Omega'}(R) - \varepsilon_{\Gamma\Omega}(R))}{3\hbar^2 e^2 g_l} \cdot \sum_{MM'\mu} |\langle \Gamma M | D_\mu | \Gamma' M' \rangle| , \tag{12}$$

where

$$\langle \Gamma M | D_\mu | \Gamma' M' \rangle = \int \Psi^*_{\Gamma M}(\boldsymbol{r}, R)\, D_\mu \Psi_{\Gamma' M'}(\boldsymbol{r}, R)\, \mathrm{d}\boldsymbol{r} \tag{13}$$

is the μ-spherical component of the transition dipole moment of the system, $\varepsilon_{\Gamma\Omega}(R)$ and $\varepsilon_{\Gamma'\Omega'}(R)$ are the adiabatic potential energies of the two states; M is the value of the projection of the total angular momentum of the system onto the internuclear axis taken as the quantization axis; Γ is the set of thallium quantum numbers which along with M specify the molecular state of the diatomic in the separated atom limit; g_l is the statistical weight factor for the lower molecular state and $\Omega = |M|$. The other symbols have their usual meaning. The dipole moment induced in the rare gas atom by the valence electron and by the core of the thallium atom has been included in the present pseudopotential model for the calculations of the adiabatic potentials and molecular electronic wavefunctions. Due to that the potentials behave correctly as R^{-6} at large internuclear distances. However, both these local field corrections and the effect of core polarization have not been included in the dipole transition moment itself. In view of limited accuracy of the present model potential calculations we thought the above corrections to the Tl-RG dipole moment as of minor importance.

Finally, we take the dipole moment of the diatomic system simply as

$$\boldsymbol{D} = -e\boldsymbol{r} . \tag{14}$$

Its μ-spherical component $D_\mu = -e r_\mu$, where r_μ is defined as goes:

$$r_\mu = \begin{cases} \dfrac{-x - iy}{\sqrt{2}}, & \mu = 1 , \\ z , & \mu = 0 , \\ \dfrac{x - iy}{\sqrt{2}}, & \mu = -1 . \end{cases}$$

Here x, y and z are the components of the vector $\boldsymbol{r}$ with z taken along the internuclear axis. The molecular electronic wavefunctions of the diatomic are expressed as a linear combination of the basis functions $\varphi_{\gamma M}(\boldsymbol{r})$.

$$\Psi_{\Gamma M}(\boldsymbol{r}, R) = \sum_{\gamma} C^{\Gamma M}_{\gamma M}(R)\, \varphi_{\gamma M}(\boldsymbol{r}) , \tag{15}$$

where $\gamma = \{nlsj\}$ and M specify the $|\gamma M\rangle$ basis state. The expansion coefficients tend asymptotically to the Kronecker delta $C^{\Gamma M}_{\gamma M}\ (R \to \infty) = \delta(\Gamma, \gamma)$. From (13) and (15) it follows that the molecular electric dipole moment can be expressed in terms of the atomic dipole moments

$$d^{\mu}_{\gamma M, \gamma' M'} = -e \int \varphi^*_{\gamma M}(\boldsymbol{r})\, r_\mu\, \varphi_{\gamma' M'}(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r} \tag{16}$$

which, in turn, can easily be calculated with the Simons' radial wavefunctions. For the atomic dipole moments the well-known selection rules hold. For transitions between states of the diatomic system, the only selection rule which still holds is $\Delta M = 0, \pm 1$.

In the present calculations the transitions from the molecular states associated with the $6^2P_{1/2}$, $6^2P_{3/2}$ and $7^2S_{1/2}$ atomic states of thallium to all the upper molecular states are considered. That means that the oscillator strengths have been calculated for the molecular transitions which are associated with both the allowed (S–P, P–D) and forbidden (P–P, S–S, S–D) atomic transitions in the thallium atom.

5. Results and Discussion

The present calculations in their final stage required only the diagonalization of the effective molecular Hamiltonian as described in Section 3. The diagonalization has been performed on the ICL S4-70 computer at ZIPO in Gdansk. For

obvious reasons it is impossible to present here all the results obtained. They will be published as preprint of our Institute and will be available upon request [15]. In this paper only some of the results are demonstrated and commented on. The interatomic potentials have been calculated for internuclear distances varying from 4 au up to 50 au with diffeent step sizes. The four lowest potentials for TlAr, TlKr and TlXe are shown in Figs. 2–4, respectively. They are also compared to the corresponding potentials determined by Cheron et al. [1]. All the potential energy curves tend asymptotically to the corresponding Tl terms which are marked on the right-hand side of each figure. With decreasing internuclear separation the potentials exhibit some minima. The minima of the ground-state potentials for TlXe and TlKr nearly cover the minima of the Cheron's potentials although, in order to determine the value of the parameter r_0 we fitted only the well-depths of the potentials associated with the $7\,^2S_{1/2}$ thallium state. As is seen, the minima of the latter potentials are only shifted from each other by about $0.5\,a_0$. In general, the calculated potentials are less repulsive than the "measured" ones. The worst agreement is obtained for TlAr in accord with the finding that the Baylis model applies better to heavier atoms. Our potentials prove also to be much more attractive than the "measured" potentials at larger internuclear separations. The largest discrepancy between the calculated and "measured" potentials is found for that associated with the $6\,^2P_{3/2}$ thallium term.

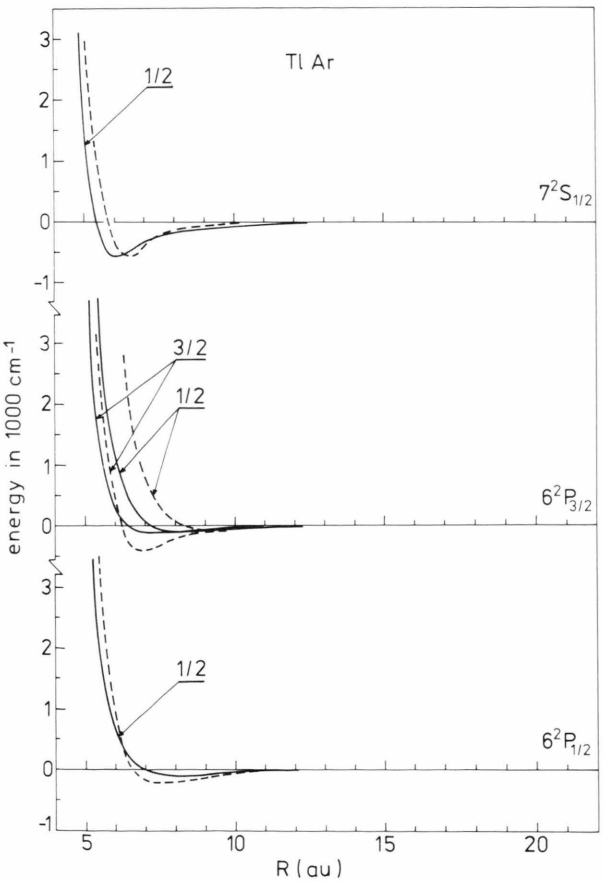

Fig. 2. Potential energy curves for thallium interacting with argon: full lines (———) – present calculations, broken lines (------) – deduced by Cheron et al. [1]. The potentials are specified by the quantum number Ω and the parent atomic term marked on the right-hand side of the picture. In the text all potentials are denoted by Ω in parenthesis followed by the parent atomic term.

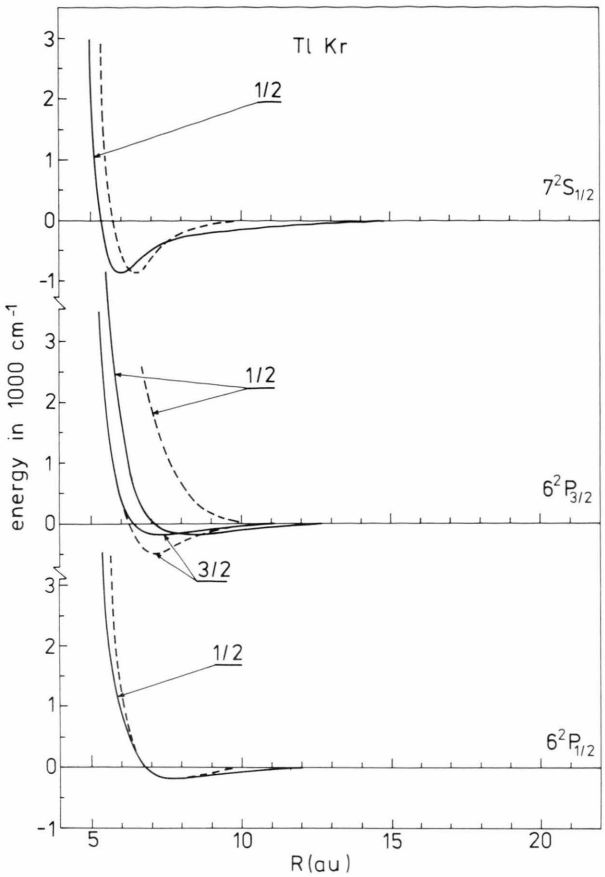

Fig. 3. Same as in Fig. 2 for TlKr.

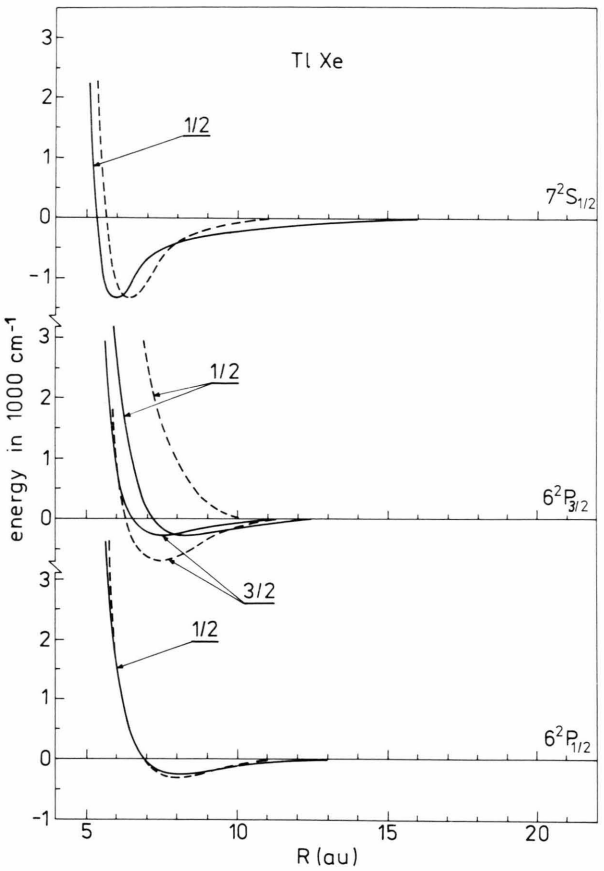

Fig. 4. Same as in Fig. 2 for TlXe.

Whereas the "measured" $(1/2)6\,^2P_{3/2}$ potential is the most repulsive and the $(3/2)6\,^2P_{3/2}$ one is the most attractive, the proper calculated potentials exhibit nearly the same shape. Their minima are only shifted from each other by about $1\,a_0$. Thus the potential $(1/2)6\,^2P_{3/2}$ becomes more repulsive than the $(3/2)6\,^2P_{3/2}$ one, although the difference between them is not so distinct as for the "measured" potentials.

From a more detailed analysis of the calculations it results that the molecular terms $(3/2)6\,^2P_{3/2}$ and $(1/2)6\,^2P_{3/2}$ differ from each other chiefly by a contribution arising from the diagonal matrix element $\langle 61\,(j=3/2)\,|\,(G^{(2)}+F^{(2)})\,|\,61\,(j=3/2)\rangle$ (comp. also (1) and (7)), which adds to the $(3/2)6\,^2P_{3/2}$ potential with a factor of $-1/5$ and to the potential $(1/2)6\,^2P_{3/2}$ with a factor of 1/5. The matrix element itself depends rather strongly on R. In the intermediate range of internuclear separations it is negative, whereas at small values of R it becomes positive. In consequence the potential $(3/2)6\,^2P_{3/2}$ lies considerably below the potential $(1/2)6\,^2P_{3/2}$ at small values of R, but with increasing internuclear separation the difference between the potentials decreases and at still larger values of R changes sign. This is seen in Figures 2–4.

Figure 5 displays the potential curves for TlXe which are associated with upper thallium terms. As is seen, the potential $(1/2)7\,^2P_{1/2}$ exhibits extremely large bonding with a well-depth of $3573\,\mathrm{cm}^{-1}$ at $R_m = 6.25\,a_0$. All the remaining potentials are considerably shallower, some of them exhibit also structure. The proper potentials for TlKr and TlAr have a similar character to that of TlXe and they are not presented in this paper. In Table 2 we have compiled the potential well parameters ε_m and R_m

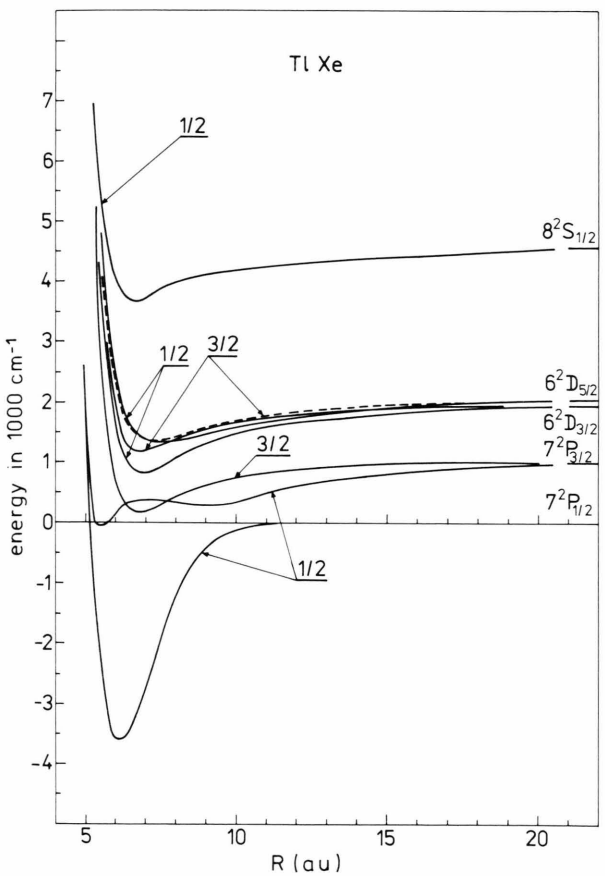

Fig. 5. Potential energy curves calculated for TlXe and associated with some upper Tl terms.

for the ground- and first three excited states of thallium-heavy noble gas pairs. From the behaviour of the calculated potentials at large internuclear separations, where the van der Waals attraction predominates, we have also estimated the van der Waals C_6 constants. These are compiled in Table 3.

Table 2. Potential well parameters ε_m (cm^{-1}) and R_m (a_0) of the ground state and the first three excited states of thallium-noble gas systems.

Noble gas	Ground state		$(1/2)6^2P_{3/2}$		$(3/2)6^2P_{3/2}$		$(1/2)7^2S_{1/2}$	
	ε_m	R_m	ε_m	R_m	ε_m	R_m	ε_m	R_m
Argon	91	8.0	99	8.35	107	7.25	540[a]	6.0
Krypton	152	7.85	173	8.25	166	7.25	850[a]	6.0
Xenon	236	8.0	267	8.25	247	7.35	1320[a]	6.0

[a] The well-depth of the $(1/2)7^2S_{1/2}$ state has been deduced from the potential curve determined by Cheron et al. [1].

Table 3. The van der Waals constants $C_6(10^7\,cm^{-1}\,a_0^6)$ estimated from the present calculations for Tl-rare gas pairs.

Perturber	State	C_6
Argon	$(1/2)6^2P_{1/2}$	4.6
	$(1/2)7^2S_{1/2}$	23.8
	$(1/2)6^2P_{3/2}$	7.5
	$(3/2)6^2P_{3/2}$	4.1
Krypton	$(1/2)6^2P_{1/2}$	7.0
	$(1/2)7^2S_{1/2}$	38.4
	$(1/2)6^2P_{3/2}$	11.0
	$(3/2)6^2P_{3/2}$	5.4
Xenon	$(1/2)6^2P_{1/2}$	11.1
	$(1/2)7^2S_{1/2}$	57.0
	$(1/2)6^2P_{3/2}$	17.0
	$(3/2)6^2P_{3/2}$	10.2

Subsequently, we used these C_6-constants to estimate the broadening γ and shift Δ coefficients for the resonance lines of Tl perturbed by rare gases. These spectroscopic parameters have been calculated according to the approximate formulae for the full width γ of the atomic line

$$\gamma/N = 8.16\, C_6^{2/5}\, v^{3/5}$$

and the red-shift/width ratio

$$|\Delta/\gamma| = 0.36\,, \tag{17}$$

where v is the mean relative velocity of the atoms (comp. Sobelman [16]). The calculated γ and Δ coefficients are compiled in Table 4, where they are also compared to the ones determined from the experiment by Cheron et al. [3]. As is seen the agreement is fairly good.

For the TlXe mixture both Cheron et al. [1] and Schlie et al. [2] have observed very strong emission bands centered at approximately 4300 and 6000 Å situated on the red side of the thallium atomic lines at 3776 Å ($7^2S_{1/2}-6^2P_{1/2}$) and 5350 Å ($7^2S_{1/2}-6^2P_{3/2}$), respectively. These two bands are interpreted as appearing due to the molecular transitions from the $(1/2)7^2S_{1/2}$ state of TlXe to the two molecular terms $(1/2)6^2P_{1/2}$ and $(3/2)6^2P_{3/2}$, respectively. Our calculations confirm such an interpretation. Indeed, the transition from the minimum of the $(1/2)7^2S_{1/2}$ potential at $R = 6\,a_0$ to the ground state $(1/2)6^2P_{1/2}$ results in the radiation at 4244 Å, whereas transitions from the vicinity of the potential minimum give rise to an emission band extended from 4088 Å (at $R = 6.25\,a_0$) to 4466 Å (at $R = 5.75\,a_0$). The observed emission band at 4300 Å lies completely in this range. Similarly, the transition from the poten-

Table 4. Comparison of the full width γ/N (cm^{-1}/r.d.)[a] and shift Δ/N (cm^{-1}/r.d.)[a] of the Tl resonance lines in the presence of noble gases.

Line	Perturber	Present calculations		Experiment[b]	
		γ/N	Δ/N	γ/N	Δ/N
3776 Å	Argon	0.84	−0.30	1.01 (±0.06)	−0.27 (±0.04)
($7^2S_{1/2}-6^2P_{1/2}$)	Krypton	0.87	−0.31	0.91 (±0.7)	−0.23 (±0.05)
	Xenon	0.93	−0.33	0.98 (±0.10)	−0.27 (±0.05)
5350 Å	Argon	0.81	−0.29	0.84 (±0.06)	−0.27 (±0.02)
($7^2S_{1/2}-6^2P_{3/2}$)	Krypton	0.85	−0.30	0.72 (±0.04)	−0.25 (±0.02)
	Xenon	0.90	−0.32	0.72 (±0.02)	−0.28 (±0.02)

[a] 1 r.d. = 2.69×10^{19} atoms/cm^3 is the density of an ideal gas at standard temperature and pressure.
[b] Experimental values are taken from Cheron et al. [3]. γ and Δ of the 5350 Å line have been calculated at the average value of two C_6 constants for the $6^2P_{3/2}$ Tl state.

tial minimum of the same excited state to the $(3/2)6\,^2P_{3/2}$ state entails the radiation at 6060 Å, while transitions from the near surroundings of the minimum result in emission of a wide band from 5807 Å (at $R = 6.25\,a_0$) to 6436 Å (at $R = 5.75\,a_0$). Again the observed band at 6000 A falls entirely within this range. Moreover, Schlie et al. [2] have also observed a very intense emission band at approximately 3650 Å, i.e. to the red of the thallium 3519/29 Å line ($6\,^2D_{3/2,5/2} - 6\,^2P_{3/2}$). This band has been attributed to the TlXe excited excimer state associated with the Tl $6\,^2D_{3/2,5/2}$ term. The present calculations verify this supposition too. The molecular transition from the minimum of the $(1/2)6\,^2D_{3/2}$ potential (at $R = 7.0\,a_0$) to the $(1/2)6\,^2P_{3/2}$ molecular term results in radiation at 3692 Å, whereas transitions from the vicinity of the minimum give an emission band which extends from 3640 Å (at $R = 7.5\,a_0$) to 3733 Å (at $R = 6.75\,a_0$). The observed band at 3650 Å lies completely in this range.

Concerning the oscillator strengths we demonstrate some of them on a semilogarithmic scale in

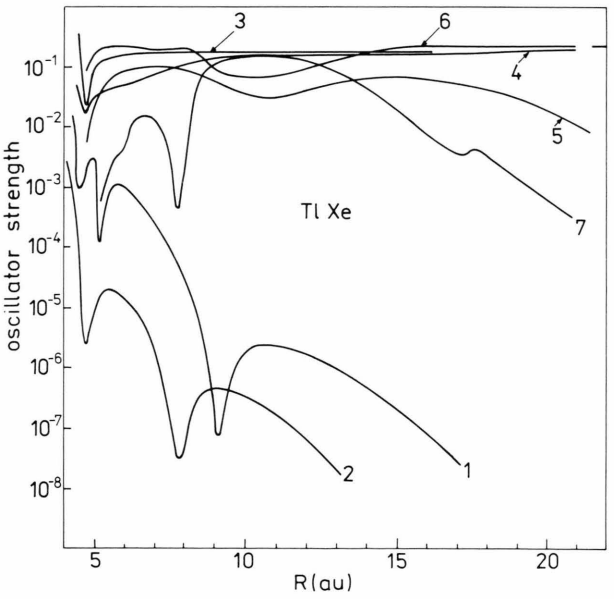

Fig. 6. Absorption oscillator strengths as a function of internuclear separation calculated for TlXe:

1) $(1/2)6\,P_{1/2} - (1/2)6\,P_{3/2}$-transition,
2) $(1/2)6\,P_{1/2} - (3/2)6\,P_{3/2}$-transition,
3) $(1/2)6\,P_{1/2} - (1/2)7\,S_{1/2}$-transition,
4) $(1/2)6\,P_{1/2} - (1/2)6\,D_{3/2}$-transition,
5) $(1/2)6\,P_{1/2} - (1/2)6\,D_{5/2}$-transition,
6) $(1/2)6\,P_{1/2} - (3/2)6\,D_{3/2}$-transition,
7) $(1/2)6\,P_{1/2} - (3/2)6\,D_{5/2}$-transition.

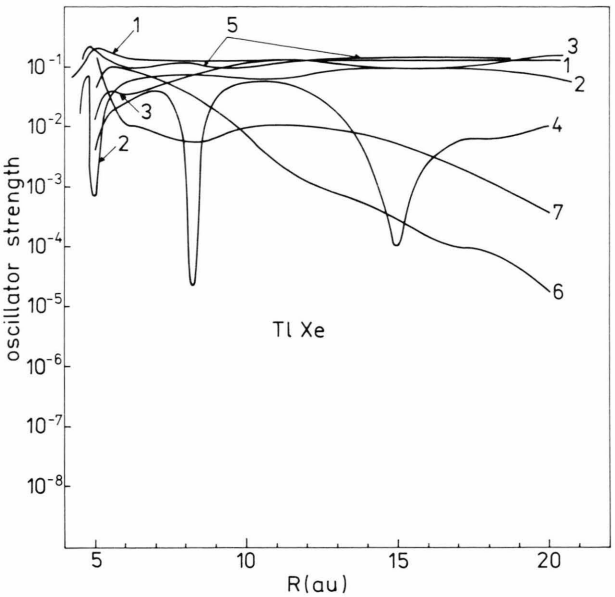

Fig. 7. Same as in Fig. 6 for the transitions:

1) $(1/2)6\,P_{3/2} - (1/2)7\,S_{1/2}$, 5) $(1/2)6\,P_{3/2} - (3/2)6\,D_{5/2}$,
2) $(1/2)6\,P_{3/2} - (1/2)6\,D_{3/2}$, 6) $(1/2)6\,P_{3/2} - (1/2)7\,P_{1/2}$,
3) $(1/2)6\,P_{3/2} - (1/2)6\,D_{5/2}$, 7) $(1/2)6\,P_{3/2} - (1/2)7\,P_{3/2}$.
4) $(1/2)6\,P_{3/2} - (3/2)6\,D_{3/2}$.

Figures 6–8. These concern only the molecular transitions originating in the parent states $6\,^2P_{1/2}$ and $6\,^2P_{3/2}$ of the thallium atom. For the molecular oscillator strengths the material for any comparison is rather poor. We only find that the oscillator strengths for the molecular transitions associated with allowed atomic transitions tend asymptotically to finite values, while at small and intermediate internuclear distances they weakly depend on R. Their asymptotic values roughly approximate the corresponding atomic oscillator strengths of the thallium atom, although some of them are in very good agreement with the experimental values (see Table 5). This confirms also the validity of the use of the Simons functions as the basis functions in the present calculations. The Simons functions enable one to allow for the contribution to the transition dipole moment from small distances of the Tl valence electron which, in turn, is entirely neglected in the Coulomb appoximation (see also Bardsley and Norcross [17]). As to the oscillator strengths for molecular transitions associated with the forbidden atomic transitions in thallium we find that they asymptotically tend to zero as it should be.

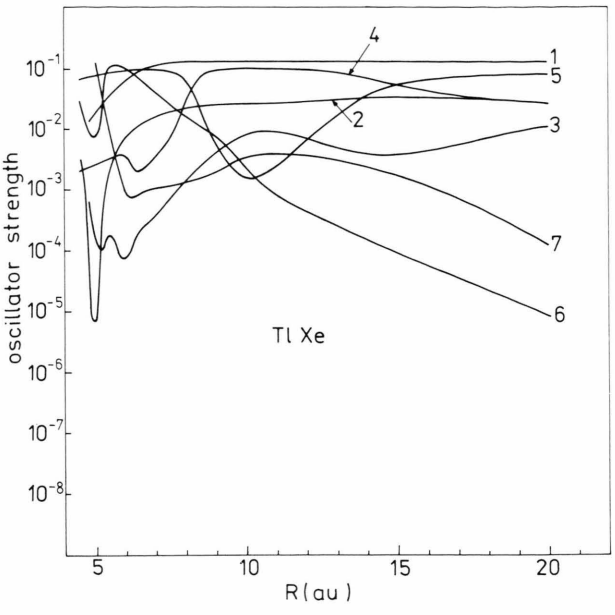

Fig. 8. Same as in Fig. 6 for the transitions:
1) $(3/2)6P_{3/2}-(1/2)7S_{1/2}$, 5) $(3/2)6P_{3/2}-(3/2)6D_{5/2}$,
2) $(3/2)6P_{3/2}-(1/2)6D_{3/2}$, 6) $(3/2)6P_{3/2}-(1/2)7P_{1/2}$,
3) $(3/2)6P_{3/2}-(1/2)6D_{5/2}$, 7) $(3/2)6P_{3/2}-(1/2)7P_{3/2}$.
4) $(3/2)6P_{3/2}-(3/2)6D_{3/2}$,

However, as R decreases, different basis states contribute to the molecular state. This mixing of the basis states becomes more important at small and intermediate internuclear distances. Due to the mixing of the basis states with various values of the orbital angular momentum of the thallium atom forbidden atomic transitions become "allowed" molecular transitions and the corresponding oscillator strengths reach quite large values. We also notice that several of the oscillator strengths exhibit sharp minima at some values of R. These are associated with an oscillatory character of the expansion coefficients $C(R)$. They are simply connected with the nodes in the expansion coefficients which most contribute to the molecular states involved in the transition.

6. Conclusions

Baylis' model potential method has been adapted to calculate the adiabatic potentials and oscillator strengths as a function of internuclear separation for the thallium-heavy RG systems. The calculated potentials have been compared with the potentials

Table 5. Absorption oscillator strengths for some transitions of thallium.

Transition	Present calculation	Relativistic calculation [17]	Coulomb approximation [19]	Experimental value [19]
$6^2P_{1/2}-7^2S_{1/2}$	0.1850	0.1350 (0.138)	0.0700	0.1330 (± 0.007)
$-8^2S_{1/2}$	0.0184	0.0188 (0.0194)	0.0170	0.0176 (± 0.0016)
$-9^2S_{1/2}$	0.0061	0.0067 (0.0069)	0.0072	0.0062 (± 0.0008)
$6^2P_{3/2}-7^2S_{1/2}$	0.1300	0.1630 (0.1790)	0.1000	0.1510 (± 0.007)
$-8^2S_{1/2}$	0.0147	0.0156 (0.0185)	0.0170	0.0136 (± 0.0014)
$-9^2S_{1/2}$	0.0050	0.0052 (0.0063)	0.0056	0.0048 (± 0.0005)
$6^2P_{1/2}-6^2D_{3/2}$	0.4400	0.2780 (0.4020)	0.2200	0.2900 (± 0.0220)
$-7^2D_{3/2}$	0.1268	0.0742 (0.1200)	0.0640	0.0740 (± 0.0090)
$-8^2D_{3/2}$	0.0543	0.0031 (0.0528)	0.0310	0.0280 (± 0.0040)
$6^2P_{3/2}-6^2D_{3/2}$	0.0345	0.0392 (0.0533)	0.0350	0.0400 (± 0.0040)
$-7^2D_{3/2}$	0.0104	0.0087 (0.0135)	0.0085	0.0091 (± 0.0009)
$-8^2D_{3/2}$	0.0060	0.0034 (0.0056)	0.0031	0.0040 (± 0.0004)
$6^2P_{3/2}-6^2D_{5/2}$	0.2080	0.3460 (0.4660)	0.3200	0.3460 (± 0.0350)
$-7^2D_{5/2}$	0.0619	0.0790 (0.1210)	0.0810	0.0810 (± 0.0090)
$-8^2D_{5/2}$	0.0240	0.0308 (0.0501)	0.0280	0.0280 (± 0.003)
$7^2S_{1/2}-7^2P_{1/2}$	0.3320 (0.315) [a]	0.4160 (0.4520)		
$-8^2P_{1/2}$	0.0252	0.0094 (0.0137)		
$-9^2P_{1/2}$	0.0080	0.0018 (0.0032)		
$7^2S_{1/2}-7^2P_{3/2}$	0.7500	0.8470 (0.9070)		
$-8^2P_{3/2}$	0.0516	0.0454 (0.0559)		
$-9^2P_{3/2}$	0.0156	0.0120 (0.0161)		

Values in parentheses are calculated by Bardsley and Norcross neglecting the core polarization term in the transition matrix element.

[a] Result obtained by Neuffer and Commins [18].

deduced from the experiment by Cheron et al. Agreement between the theoretical and experimental potentials seems to be fairly good, especially for TlXe and TlKr. Some of the observed effects attributed to the Tl-RG excimers can be interpreted on the basis of the obtained potentials. By the modification of the model potential introduced in the present calculations the large discrepancy between the "measured" potentials and the ones calculated previously has been removed. The calculations show that the Baylis' model allows one to calculate adiabatic potentials also for systems other than alkali-rare gas, provided that suitable modifications of the model are made.

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