Adiabatic Potentials and Oscillator Strengths of Thallium-Noble Gas Atom Pairs *

E. Czuchaj

Institute of Physics, University of Gdańsk

Baylis' semiempirical method has been applied for calculating interatomic potentials and oscillator strengths as a function of internuclear separation of the thallium-noble gas systems. The new potentials for the four lowest molecular states of each diatomic have been compared with the corresponding ones deduced 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 calculated potentials differ considerably from the latter ones. The molecular oscillator strengths have been calculated for both the allowed and the forbidden Tl transitions. The asymptotic values of the first ones are compared with the corresponding atomic oscillator strengths of other calculations and measurements. The agreement is generally quite good.

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. Such atomic processes have been most widely investigated on the alkali-rare gas atom pairs. Recently, several papers have appeared in which some of the above cited processes had been investigated on thallium-noble gas systems [1—4]. Particularly, Cheron et al. have reported on an analysis of the far wing intensities [1] and the shift and broadening of the Lorentzian-shaped line cores of the Tl-rare gas molecules [2]. These authors have also deduced the four lowest potentials of the Tl-rare gas atom pairs from continuum emission intensities. As far as the author knows these thallium-rare gas atom potentials are the most often cited in the literature. So far there were neither scattering data nor theoretical potentials to which the potentials of Cheron et al. could be compared. Therefore, it is still unknown in what relation their potentials remain to other data. This is especially of some importance since the R-positions of Cheron's potentials have been estimated only approximately. Recently, Schlie et al. [3] have reported on the very

strong emission they had observed from the TlXe system at approximately 6000, 4300 and 3650 Å. The electronic transition responsible for the continuum band centered at 3650 Å is assumed to originate in the TlXe molecular states associated with the $6^2D_{3/2,\,5/2}$ states. Up to now no potentials of the Tl-rare gas atom pairs referring to the higher than $7^2S_{1/2}$ atomic states of thallium have been published. Therefore, one may presume that the new results concerning both the potentials and the oscillator strengths of the thallium-rare gas systems enlarge appreciably the information on these systems.

The aim of the present calculations is not to interpret the "measured" potentials of Cheron et al., but rather to provide new results which might be treated as possibly "independent" of the latter ones. This goal could be attained to a certain degree by calculating the adiabatic potentials of the Tl-rare gas atom pairs with the pseudopotential method of Baylis [5]. So far this method has been applied with success to the alkali-rare gas atom pairs [5—7] and to the alkali-Hg molecules [8]. The molecular wave-functions obtained as a result of the calculations have been exploited for computing the oscillator strengths of the Tl-rare gas atom pairs as a function of internuclear separation. These have been calculated for the electronic transitions from the molecular ground-state and from the one associated with $7^2S_{1/2}$ atomic state of Tl to all the other molecular states involved. The Baylis' method along with the modifications made in the present calculations is sketched in the following Section.

The numerical calculations of the adiabatic potentials are described in Sect. 3. The calculation of the oscillator strengths is the subject of the next Section. A general discussion of the results obtained is given in Section 5.

2. Method of Calculation

The method of calculations used here has been described in detail by Baylis [5] and Pascale et al. [6] in application to the alkali-rare gas atom pairs. The calculations will not change much, if an alkali atom be replaced by a thallium atom. Separating the center of mass motion from the relative nuclear motion and then making the Born-Oppenheimer separation, the effective Hamiltonian H_{eff} of the system consisting of a thallium atom and a rare gas atom is put in the form

$$H_{eff} = H_T + H_B + V_{TB}, \qquad (1)$$

where H_T and H_B are the Hamiltonians of the free thallium atom and the rare gas atom, respectively, and V_{TB} stands for the interaction between the atoms. In the case of thermal collisions the perturbation of the thallium core and of the rare gas atom is assumed to be quite small in comparison to the perturbation of the valence electron of the thallium atom. Thereby both the states of the thallium core and of the rare gas atom can be described by unperturbed atomic wavefunctions. In turn, the states of the Tl-valence electron become the molecular states of the diatomic and can be expressed in terms of the unperturbed wavefunctions of thallium as their linear combination. Defining the zero energy of the system when the two atoms are in the ground states and isolated, the problem of calculations reduces to finding the eigenvalues and eigenvectors of the Hamiltonian

$$H_e(\boldsymbol{r}, \boldsymbol{R}) = H_T^e(\boldsymbol{r}) + V(\boldsymbol{r}, \boldsymbol{R}), \qquad (2)$$

where $H_T^e(\boldsymbol{r})$ is the valence electron Hamiltonian of the free thallium atom, $V(\boldsymbol{r}, \boldsymbol{R})$ is the interaction between the atoms and $\boldsymbol{r}$ 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. The interaction term $V(\boldsymbol{r}, \boldsymbol{R})$ consists of two parts: (I) an electrostatic interaction which is taken to be simply that of a polarizable dipole (the rare gas atom) in the field of the thallium valence electron plus thallium core; (II) a repulsive part

which has been introduced to replace the procedure of antisymmetrizing the molecular wavefunctions and dominates at small internuclear distances. This part of the Hamiltonian is expressed in terms of the so-called pseudopotentials $G(\boldsymbol{r}, \boldsymbol{R})$ and $W(R)$ derived on the basis of the Thomas-Fermi statistical model of the atom. Thus we can write

$$V(\boldsymbol{r}, \boldsymbol{R}) = F(\boldsymbol{r}, \boldsymbol{R}) + G(\boldsymbol{r}, \boldsymbol{R}) + W(R), \qquad (3)$$

where $F(\boldsymbol{r}, \boldsymbol{R})$ is the electrostatic interaction between the atoms, which takes the form

$$F(\boldsymbol{r}, \boldsymbol{R}) = -\tfrac{1}{2}\alpha_B e^2 [(\boldsymbol{R}/R^3) - (\boldsymbol{r}'/r'^3)]^2$$

for $r' = |\boldsymbol{R} - \boldsymbol{r}| \geqq r_0$ and

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

for $r' < r_0$. The adjustable parameter r_0 being the radius of a sphere surrounding the noble gas atom is to be determined for each atomic pair separately. For the alkali-rare gas systems this was done by fitting the well depth of the calculated ground state potential to that obtained from atomic beam scattering experiments [5]. However, for the Tl-rare gas systems this procedure could not be used for lack of the corresponding scattering data. Therefore, the radius r_0 had to be determined here in another way (comp. the following Section). The pseudopotential $G(\boldsymbol{r}, \boldsymbol{R})$ which represents the effect of the Pauli exclusion principle and concerns the "Pauli interaction" of the thallium valence electron with the rare gas atom can be expressed in terms of the radial electronic charge density of the noble gas atom $\varrho_B(r')$ as

$$G(\boldsymbol{r}, \boldsymbol{R}) = \frac{\hbar^2}{2\, m_e} [3\,\pi^2 \varrho_B(r')]^{2/3}. \qquad (5)$$

The other pseudopotential $W(R)$ which simulates the Pauli exclusion principle for the repulsion between the thallium core and a rare gas atom can be expressed as

$$W(R) = \frac{3\,\hbar^2}{10\, m_e} (3\,\pi^2)^{2/3} \int d\boldsymbol{r} \qquad (6)$$
$$\cdot \{ [\varrho_T(r) + \varrho_B(r')]^{5/3} - \varrho_T^{5/3}(r) - \varrho_B^{5/3}(r') \},$$

where $\varrho_T(r)$ is the radial electronic charge density of the thallium core and m_e is the electronic mass. The radial electronic densities are expressed in the form

$$\varrho(\varkappa) = \frac{1}{4\,\pi} \sum_s \zeta(s)\, \varkappa^{\alpha(s)} \exp\{-2\,\beta(s)\varkappa\} \qquad (7)$$

and have been calculated by means of the simplified self-consistent field method by Gombas [9, 10]. The sum is taken over all occupied shells of the atom. The parameters $\alpha(s)$ and $\beta(s)$ are determined by a variational calculation and $\zeta(s)$ are normalization coefficients. The Hamiltonian (2) is subsequently diagonalized in the Tl-valence electron wavefunctions *.

These 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 eigenvalues of the Hamiltonian obtained in this manner for various values of the internuclear separation R determine the potential energies of the diatomic. The corresponding eigenvectors are the molecular electronic wavefunctions of the system which depend parametrically on R. Thus the molecular states, which are pure atomic states in the separated atom limit, become a mixture of various atomic states at finite internuclear distances due to the coupling among states. Contrary to the calculations of Baylis [5] and Pascale and Vandeplanque [6] the present calculation differs from the previous ones on two aspects: (I) the atomic radial orbitals used here are the functions suggested by Simons [11] in contrast to the Bates-Damgaard functions applied previously by Baylis and Pascale et al. The Simons' functions differ mainly from the Bates-Damgaard ones as they are finite at the origin and can easily be normalized; (II) the pseudopotential $W(R)$ has been calculated here exactly according to (6) without additional approximations introduced originally by Baylis [5].

---

* In principle, the electronic Hamiltonian (2) should be diagonalized in a complete orthonormal set of eigenfunctions. In practice, one takes a finite basis of atomic states. If the basis states are orthonormal, the problem reduces to diagonalizing the matrix

$$H_{ik} = E_i\,\delta_{ik} + V_{ik} \equiv \delta_{nn'}\,\delta_{ll'}\,\delta_{jj'}\,E_{nlj}$$
$$+ \langle(nls)jm_j|\,V(\mathbf{r},\mathbf{R})\,|(n'l's)j'm_j\rangle$$

for each value of m_j, where E_{nlj} is the energy of the atomic state $|(nls)jm_j\rangle$. As the Simons' functions used here are not orthogonal, there is the small overlap matrix

$$S_{ik} \equiv \langle(nls)jm_j|\,(n'l's)j'm_j'\rangle$$
$$= S_{nl\,n'\,l}\,\delta_{ll'}\,\delta_{jj'}\,\delta_{m_jm_j'}$$

which has to be taken into account in diagonalizing the Hamiltonian (2). Therefore, in the present calculation the matrix H_{ik} has been replaced by $E_iS_{ik} + V_{ik}$. The matrix S_{ik} is regular, thus the problem reduces to diagonalizing

$$E_i\,\delta_{ik} + (S^{-1}V)_{ik}\,.$$

The previous calculations performed by the author for the alkali-rare gas atom systems [7, 17] have indicated that both these refinements of the original Baylis' calculation were made in the right direction. Namely, many of the calculated potentials proved to be in better agreement with the potentials determined experimentally [12] than the potentials of Pascale and Vandeplanque.

3. Calculation of the Adiabatic Potentials

The adiabatic potentials of a thallium-rare gas diatomic are obtained as result of the diagonalization of the effective Hamiltonian (2) in a basis of the eigenfunctions of the free thallium Hamiltonian. The atomic basis used in the present calculation is finite and includes all the Tl-states from $6^2P_{1/2}$ up to $7^2D_{5/2}$. As has been mentioned in the former Section the atomic radial orbitals employed here are the functions suggested by Simons [11] which are normalized but not orthogonal. The other parameters required in the calculation are the thallium energy levels, which are taken from the tables of Moore [13]; the polarizabilities of the rare gas atoms, semiempirically calculated by Dalgarno and Kingston [14] and the coefficients α and β defining the radial electronic charge densities of the rare gas atoms were taken from the work of Gombas [9], but these referring to the thallium core arise from Gombas and Szondy [10]. Next, the pseudopotential $W(R)$ has been calculated by taking into account the two outer core shells of each atom in contrast to the previous calculations [5, 6], where only one shell was taken in the sum (7). The adjustable parameter r_0 defining the "radius" of a noble gas atom (as required by the Baylis' method) could not be determined in the manner as it was done previously for the alkali-rare gas systems (comp. [5, 6]).

For each alkali-rare gas atom pair r_0 has been determined by fitting the well-depth of the calculated ground-state potential to that known from the scattering data. Unfortunately, for the Tl-rare gas atom pairs there are no scattering data and this procedure could not be applied here. What is known for the Tl-rare gas systems are the well-depth of the $(1/2)7S_{1/2}$ potentials of the TlXe, TlKr and TlAr pairs. These quantities have been determined by Cheron et al. from the measured temperature de-

pendence of the fluorescence intensity and they are not affected by the further assumptions (as R_1 assignments, dipole moment $D(R)/D(\infty)$ ratio) which enabled these authors to estimate $V(R)$ (comp. [1]). Therefore, the radius r_0 for the TlXe, TlKr and TlAr systems has been determined here by fitting the well-depth of the calculated $(1/2)7^2S_{1/2}$ potential * to the corresponding one deduced by Cheron et al. The $(1/2)7^2S_{1/2}$ potential depths estimated from [1] for TlXe, TlKr and TlAr are respectively 1320, 850 and 540 cm^{-1}. This procedure, however, could not be applied to the TlNe and TlHe systems, because the corresponding experimental potentials are repulsive. Thus the values of r_0 for these diatomics had to be estimated in another way, and so for TlNe r_0 has been determined by fitting the maximum of the calculated $(1/2)7^2S_{1/2}$ $-(1/2)6^2P_{1/2}$ difference potential to the 3753 Å satellite observed for this system [1]. In turn, the $(1/2)7^2S_{1/2}-(1/2)6^2P_{1/2}$ difference potential calculated for TlHe cannot in any case account for the band centered at 3726 Å as observed experimentally [1]. Therefore, the value of r_0 for TlHe could be estimated only approximately. This has been done by the greatest approach of the calculated $(1/2)7^2S_{1/2}-(1/2)6^2P_{1/2}$ difference potential maximum to the measured 3726 Å satellite. The calculations have also indicated that the maximum of this difference potential changes with r_0 very slowly. The potentials calculated for TlNe and TlHe seem to be of less accuracy than those for the other pairs. They have mainly been reported for completeness of the results. The values of r_0 and the polarizabilities of the rare gas atoms used in the present calculation are given in Table 1.

Table 1. Polarizability α and „radius" r_0 of the rare gas atom.

Rare gas atom	He	Ne	Ar	Kr	Xe
α (cubic bohr)	1.384	2.663	11.080	16.734	27.292
r_0 (bohr)	0.520	0.410	0.720	0.779	0.935

* The adiabatic potentials are usually denoted by the absolute value of the projection of the total angular momentum of the system onto the internuclear axis (quantization axis) taken in parenthesis followed by the corresponding thallium term.

4. Calculation of the Oscillator Strengths

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

$$f_{\Gamma\Omega,\Gamma'\Omega'}(R) = \frac{2\,m_e}{3\,\hbar^2 e^2 g_1} \qquad (8)$$
$$\cdot \Delta V(R) \sum_{MM'\mu} |\langle \Gamma M | D_\mu | \Gamma' M'\rangle|^2,$$

where

$$\langle \Gamma M | D_\mu | \Gamma' M'\rangle$$
$$= -e \int \Psi_{\Gamma M}^*(r, R) r_\mu \Psi_{\Gamma'M'}(r, R)\,dr \qquad (9)$$

is the μ-spherical component of the transition dipole moment of the system. Here $\Delta V(R) = V_{\Gamma'\Omega'}(R)$ $- V_{\Gamma\Omega}(R)$ is the difference potential of the two states between which the transition occurs, r_μ is a spherical component of the position vector of the thallium valence electron with respect to the thallium core, 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 the thallium quantum numbers which along with M specify the molecular state of the diatomic in the separated atom limit, m_e and e stand for electron mass and electron charge, respectively, g_1 is the statistical weight factor for the lower molecular state ($g_1 = 2$) and $\Omega = |M|$. The molecular wavefunctions obtained as a result of diagonalizing the Hamiltonian of the system in the basis of the Tl-wavefunctions $\varphi_{\gamma M}(r)$ are orthonormalized and can be expressed as a linear combination of the latter ones

$$\Psi_{\Gamma M}(r, R) = \sum_\gamma C_{\gamma M}^{\Gamma M}(R)\,\varphi_{\gamma M}(r) \qquad (10)$$

with $C_{\gamma M}^{\Gamma M}(R \to \infty) = \delta(\Gamma, \gamma)$, where δ denotes the Kronecker delta and the summation is over the basis states γ ($\gamma = \{nlsj\}$). From (9) and (10) it follows that the electric dipole moment of a diatomic can be expressed in terms of the atomic dipole moments for transitions between states of the thallium atom

$$d_{\gamma M,\gamma' M'}^\mu = -e \int \varphi_{\gamma M}^*(r) r_\mu \varphi_{\gamma' M'}(r)\,dr.$$

For the atomic dipole moments the well-known selection rules hold. The integrals can easily be calculated from the Simons' radial wavefunctions used

in the present calculation. Thus the calculation of the molecular dipole moments $\langle \Gamma M | D_\mu | \Gamma' M' \rangle$ becomes quite straightforward. For transitions between molecular states the following selection rule holds

$$\Delta M = 0, \pm 1 .$$

The molecular oscillator strengths, as expressed by (8), have been calculated for the transitions from the ground molecular state and from that associated with the $7^2 S_{1/2}$ thallium state (for both $M = \pm 1/2$) to all the other excited molecular states involved in the calculation. Then, the molecular oscillator strengths have been obtained for both the allowed and the forbidden transitions of the thallium atom.

5. Results and Discussion

The present calculations were carried out on the ICL S4-70 computer at ZIPO in Gdansk. For obvious reasons it is impossible to report in this article all the potential energy curves and the oscillator strengths which have been obtained for various thallium-rare gas atom pairs. A full report of the results has been published elsewhere [15] and will be available upon request. Here only their main features will be described and commented. The present calculations have been performed for the internuclear distances varying from 4 a.u. up to 25 a.u. with different step sizes. The four lowest lying potentials for each Tl-rare gas system are demonstrated in Figs. 1—5, where they are also compared with the corresponding ones determined experimentally 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. It is obvious that the stability of the higher potentials is not fully ensured, if a finite atomic basis is used in diagonalizing the diatomic Hamiltonian. This refers particularly to the molecular states correlated asymptotically with the highest states of the basis. However, based on the convergence of the potential energy curves with increasing basis it has been found that the potentials reported here from the ground state up to the ones correlated with the $8^2 S_{1/2}$ level of the thallium atom are stable.

The potentials calculated possess minima at a certain internuclear separation. Particularly, the molecular term $(1/2)7^2 P_{1/2}$ has an extremely deep
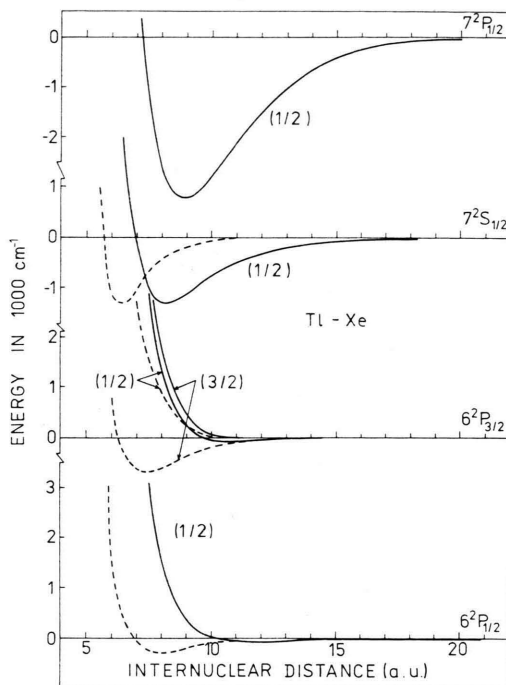

Fig. 1. Potential energy curves for the Tl-Xe pair: —— present results; ----- determined by Cheron et al. [1].
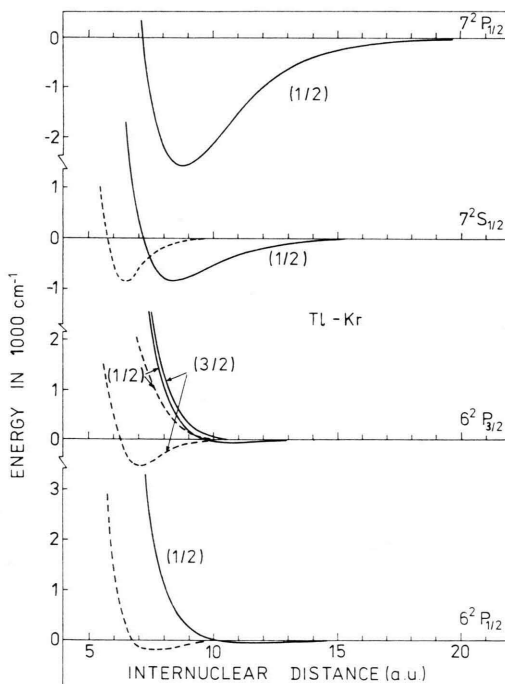

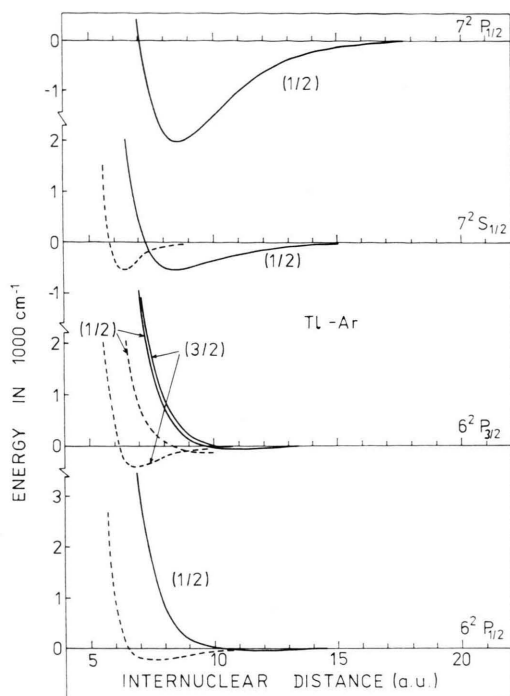Fig. 2. Same as in Fig. 1 for Tl-Kr.
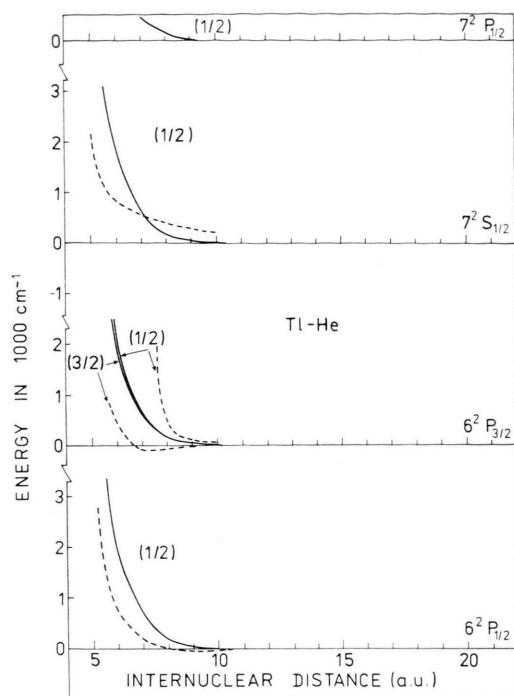
Fig. 3. Same as in Fig. 1 for Tl-Ar.

Fig. 5. Same as in Fig. 1 for Tl-He.

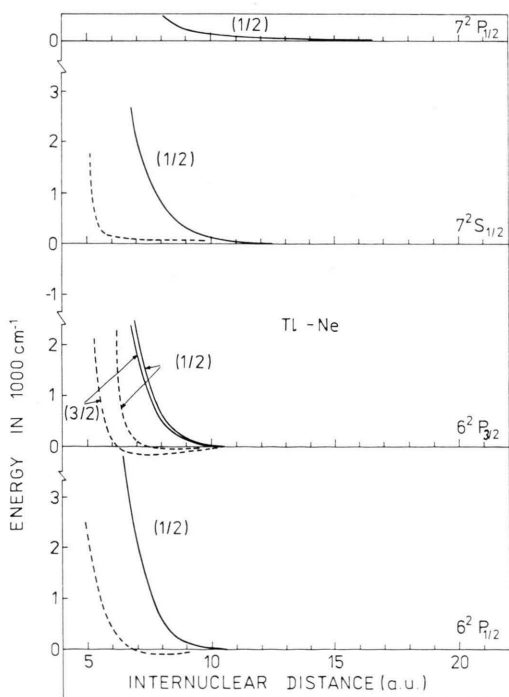Fig. 4. Same as in Fig. 1 for Tl-Ne.

minimum, which respectively for Xe, Kr and Ar amounts to 3214 cm^{-1} at $R = 9 a_0$, 3156 cm^{-1} at $R = 8.75 a_0$ and 2000 cm^{-1} at $R = 8.50 a_0$. Other molecular terms have minima appreciably shallower. Especially, the ones associated with the $6^2 P_{1/2}$ and $6^2 P_{3/2}$ thallium terms are much shallower than the corresponding potentials deduced by Cheron et al. For example, the calculated ground-state potential of the TlXe system has a minimum of only 42 cm^{-1}, whereas the minimum of the corresponding measured potential amounts to 300 cm^{-1}. In the light of the present calculation such shallow potentials associated with the $6^2 P_{1/2, \, 3/2}$ thallium terms can be understood as a result of the existence of the $6 s^2$ electrons, the influence of which on the calculated $W(R)$ pseudopotential is appreciable. For example, $W(R)$ calculated for CsXe [7] tended to zero at about 7 a.u., whereas for TlXe it tends to zero only at 13 a.u. In general, the minima of the potential curves increase as one goes from lighter to heavier rare gas atoms. This can be explained by the increase of polarizabilities with heavier rare gas atoms. It is worth noticing that the calculated potentials have minima considerably shifted towards larger R in comparison to that estimated by

Cheron et al. However, it is necessary to remember that these authors were not able to give the right R-position of their potentials because the method used by them did not allow this. They could only deduce the depth of the $(1/2)7^2S_{1/2}$ potential and the relationships between this potential and the lower ones. The R-positions of their potentials have been estimated less accurately. From Figs. 1—5 we also see that the attractive portions of the calculated $(1/2)7^2S_{1/2}$ potentials possess considerably smaller slopes than those of the measured potentials.

One also cannot understand why the calculated $(3/2)6^2P_{3/2}$ potential lies somewhat higher than the $(1/2)6^2P_{3/2}$ term, although Cheron et al. suggest that it should be the opposite. If they are right this would mean that the inversion of the calculated terms is rather the result of an inaccuracy of the pseudopotential method. Particularly, the Gombas parameters defining the radial electronic densities of the atoms seem to be of little accuracy. The little accurate Gombas parameters could also explain the fact that the calculated potentials associated with the $6^2P_{1/2, 3/2}$ atomic terms of thallium are so shallow.

Regarding the oscillator strengths calculated here, they prove to behave similarly to the ones calculated by Pascale [16] and by this author [17] for the alkali-rare gas atom systems. It is impossible to compare them with any others because, as far as the author knows, the oscillator strengths reported here are the first ones ever published. However, we can compare the asymptotic values of the molecular oscillator strengths calculated for the transitions which correspond to the allowed thallium transitions with the proper atomic oscillator strengths. This is demonstrated in Table 2, where some of the thallium oscillator strengths calculated

here are compared with others, both those calculated fairly accurately [18] and those measured experimentally [19]. We see that the agreement between our oscillator strengths and the others is quite good. This confirms also the validity of the use of the Simons' functions in the present calculation instead of the Bates-Damgaard ones. The Simons' functions enable one to take into account the contribution from small radial distances of the thallium valence electron, which in the Coulomb approximation is neglected. Some insufficiency of the Bates-Damgaard functions in calculations of transition moments, particularly for the lowest transitions in the thallium atom, is also discussed by Bardsley and Norcross [18]. The oscillator strengths calculated for the resonance lines of thallium perturbed by rare gas atoms are demonstrated diagrammatically on a semilogarithmic scale in Figures 6—10. Those associated with allowed atomic transitions depend strongly on R in the range of small internuclear distances (up to about $6a_0$) and tend with increase of R gradually to the corresponding atomic values. In turn, the oscillator strengths corresponding to the forbidden atomic transitions reach quite large values at a certain internuclear distance (in the range of $5-6a_0$) and then with increasing R decrease rapidly to zero in the separated atom limit. It is worthwhile to notice that the calculated molecular oscillator strengths for the forbidden thallium transitions (P-P, S-S

Table 2. Absorption oscillator strengths for some transitions of thallium.

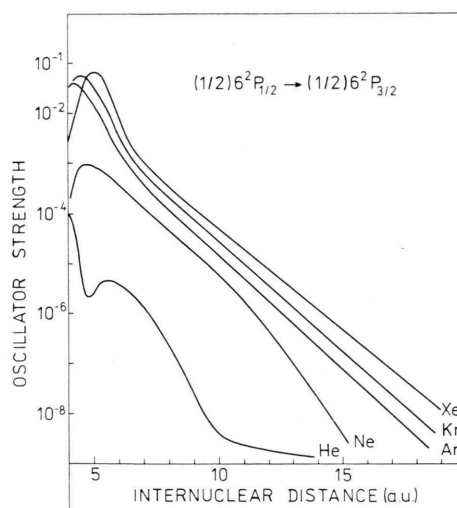| Transition	Present calcula-tion	Relativ-istic cal-culation [18]	Coulomb approxi-mation [19]	Experi-mental values [19]
$6^2P_{1/2} - 7^2S_{1/2}$	0.185	0.135	0.070	0.133
$6^2P_{1/2} - 8^2S_{1/2}$	0.0184	0.0188	0.017	0.0176
$6^2P_{3/2} - 7^2S_{1/2}$	0.130	0.163	0.100	0.151
$6^2P_{1/2} - 6^2D_{3/2}$	0.220	0.278	0.220	0.290
$6^2P_{1/2} - 7^2D_{3/2}$	0.0632	0.0742	0.064	0.074
$7^2S_{1/2} - 7^2P_{1/2}$	0.332	0.416 (0.315 [20]) —	—	—

Fig. 6. Oscillator strengths for the $(1/2)6^2P_{1/2} - (1/2)6^2P_{3/2}$ transition of the Tl-rare gas atom pairs as a function of internuclear separation.
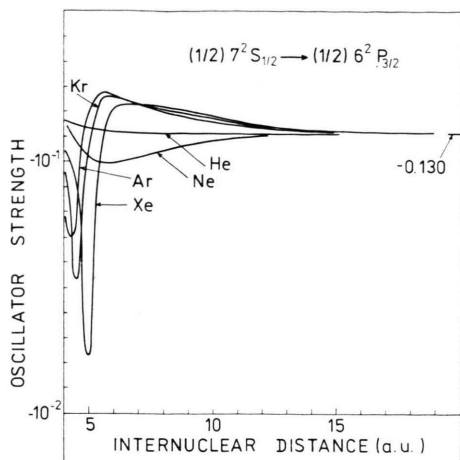
Fig. 7. Same as in Fig. 6 for the $(1/2)\,7^2S_{1/2} - (1/2)\,6^2P_{3/2}$ transition.

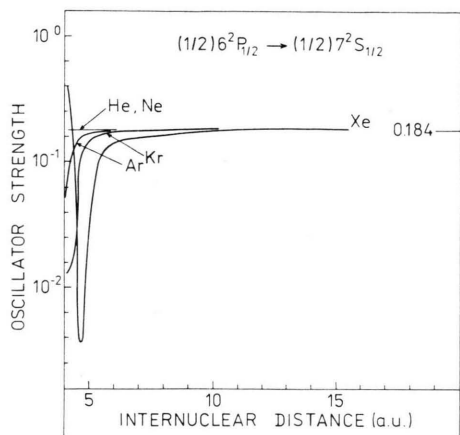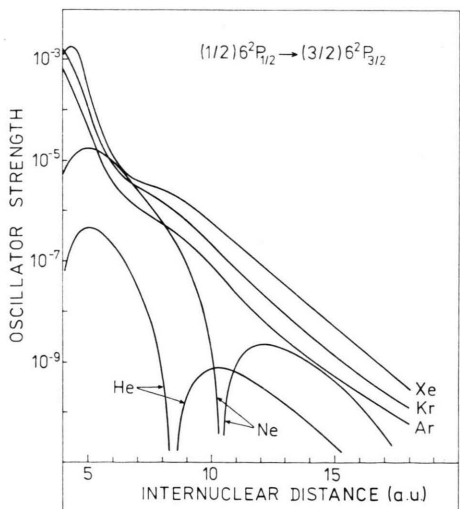Fig. 8. Same as in Fig. 6 for the $(1/2)\,6^2P_{1/2} - (1/2)\,7^2S_{1/2}$ transition.

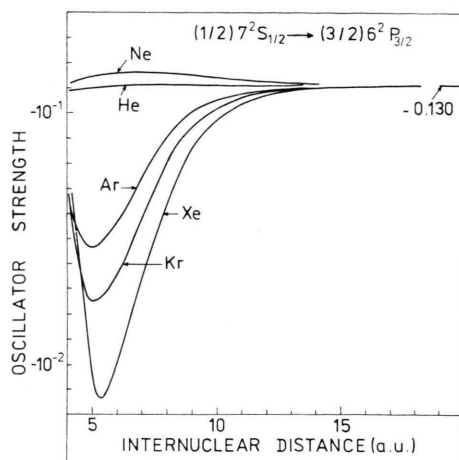Fig. 9. Same as in Fig. 6 for the $(1/2)\,6^2P_{1/2} - (3/2)\,6^2P_{3/2}$ transition.

Fig. 10. Same as in Fig. 6 for the $(1/2)\,7^2S_{1/2} - (3/2)\,6^2P_{3/2}$ transition.

and S-D) are of the same order as those calculated by Pascale [16] for the alkali-rare gas atom pairs. This allows to expect that as in the case of the alkali-rare gas systems also in the thallium-rare gas mixtures the collisionally induced molecular bands and satellite lines should be observed.

6. Conclusion

Baylis' semiempirical method has been applied to calculate both the adiabatic potentials and the oscillator strengths as a function of internuclear separation of the thallium-rare gas systems. The potential energy curves obtained differ considerably from those deduced by Cheron et al. from the measurements of continuum emission intensities. There are many possible reasons for this disagreement on both the computational and the experimental side. It is quite impossible at present to establish which of them are essential. It is noticeable to compare the C_6-coefficients for the $Tl(7^2S_{1/2})$-noble gas atom pairs determined by Cheron et al. [2] from the measured broadening rates of the Tl $7^2S_{1/2} - 6^2P_{1/2}$ (3776 Å) line with the ones estimated from both their $(1/2)7^2S_{1/2}$ potentials and the potentials calculated here. The "measured" C_6-coefficients in atomic units for Xe, Kr and Ar are, respectively, 2800, 1900 and $1500\,e^2a_0^5$. On the other hand, having the well-depth ε_m and the equilibrium internuclear separation R_m of a potential one can put the C_6 coefficient simply as $C_6 = 2\,\varepsilon_m R_m^6$ (Lennard-Jones 12,6 potential). In this way the present calculations give the C_6 coefficients, re-

spectively, 3.150, 2.200 and $1.600 e^2 a_0^5$, whereas those estimated from the Cheron's potentials [1] are only 900, 550 and $300 e^2 a_0^5$. Clearly, further investigations are desirable in order to reach more definite conclusions. It seems, however, that the results reported in this paper can serve as a guide in future use of the thallium-rare gas atom excimers as potential laser systems. Particularly, this con-

cerns the possibility of obtaining a lasing action on the Tl forbidden transition from the metastable $6P_{3/2}$ level to the ground state at 1.28 microns. The population of the Tl metastable state is expected to be sufficiently large to obtain the required population inversion [3]. Lasing actions on Tl transitions originating in some upper levels ($6^2D_{3/2, 5/2}$) are also to be expected.

[1] B. Cheron, R. Scheps, and A. Gallagher, J. Chem. Phys. **65**, 326 (1976).
[2] B. Cheron, R. Scheps, and A. Gallagher, Phys. Rev. A **15**, 651 (1977).
[3] L. A. Schlie, L. E. Jusinski, R. D. Rathge, R. A. Hamil, and D. L. Drummond, J. Chem. Phys. **72**, 4529 (1980).
[4] B. Gelbhaar, Z. Physik A **272**, 53 (1975).
[5] W. E. Baylis, J. Chem. Phys. **51**, 2665 (1969).
[6] J. Pascale and J. Vandeplanque, J. Chem. Phys. **60**, 2278 (1974).
[7] E. Czuchaj and J. Sienkiewicz, Z. Naturforsch. **34a**, 694 (1979).
[8] R. Düren, Chem. Phys. Lett. **39**, 481 (1976).
[9] P. Gombas, Pseudopotentiale, Springer, New York 1967.
[10] P. Gombas and T. Szondy, Solution of the simplified SCF for all atoms of the periodic system of elements from Z = 2 to Z = 92, Hilger, London, 1970.
[11] G. Simons, J. Chem. Phys. **60**, 645 (1974).
[12] B. Sayer, M. Ferray, J. P. Visticot, and J. Lozingot, J. Phys. B **13**, 177 (1980).
[13] C. E. Moore, Atomic Energy Levels, Nat. Bur. Stand. U.S. Cir. 467, U.S. Government Printing Office, Washington D.C. 1958, Vol. 3.
[14] A. Dalgarno and A. E. Kingston, Proc. Roy. Soc. London A **259**, 424 (1961).
[15] E. Czuchaj, Adiabatic Potentials and Oscillator Strengths of Thallium-Noble Gas Atom Pairs (Numerical Results), Preprint of the Institute of Physics of the Gdansk University, No. 14 (1981).
[16] J. Pascale, J. Chem. Phys. **67**, 204 (1977).
[17] E. Czuchaj, Z. Physik A **292**, 109 (1979).
[18] J. N. Bardsley and D. W. Norcross, J. Quant. Spectrsc. Radiat. Transfer **23**, 575 (1980).
[19] A. Gallagher and A. Lurio, Phys. Rev. **136**, A 87 (1964).
[20] D. V. Neuffer and E. D. Commins, Phys. Rev. A **16**, 844 (1977).