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Analysis of rotational coupling in collisions of Li^+ with Ne leading to double excitation of Ne

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Abstract. Electron angular distributions due to autoionization of Ne, doubly excited to the $(2p^43s^2)^1D$ state in collisions with Li^+ in the energy range 1.2–2.2 keV, are measured in coincidence with Li^+ scattered into a well defined direction ($\Phi = 0°$, $\Theta_{cm} = 10.8°$). The experimental findings are analysed with the help of a collision model proposed earlier. In this model the initial excitation occurs by radial diabatic coupling to a molecular Σ-state at small distances, followed by rotational coupling to Π- and Δ-states at intermediate distances in the second half of the collision. The energy splitting between the Σ-, Π- and Δ-states is described by a model function. By adapting two parameters of this model function, the experimental findings can be reproduced within the experimental error in numerical calculations involving the relevant set of coupled differential equations.

1. Introduction

In a recent publication (Oud *et al* 1993) we have published angular distributions of electrons emitted by autoionization of Ne atoms that were doubly excited into the $(2p^43s^2)^1D$-state in collisions with Li^+ ions. By measuring the electrons in coincidence with Li^+ ions scattered into a well defined solid angular range, the angular distributions were specified for collision events with defined scattering plane and impact parameter. Since the autoionization occurs long after the collision, excitation and decay by electron emission are well separated steps, and the electron angular distribution reflects directly the 'orientation and shape' of the collisionally excited atom. Orientation and shape of the atom, on the other hand, are a direct consequence of the dynamics of the excitation during the collision, which can thus be studied by measuring the angular distributions for well selected collision events. Results were presented for four collision energies, 1.2, 1.5, 2.0 and 2.5 keV. The distributions were found to have a near rotational symmetry with respect to an axis lying in the collision plane and forming an angle (γ) with the direction of the primary beam dierction. The anisotropic shape of the distributions was evaluated in terms of the complex sublevel population amplitudes of the decaying atom. It was found that, in a coordinate system with z-axis in direction (γ) of the symmetry axis, only the $M = 0$ sublevel is populated appreciably at all four collision energies, while the angle (γ) showed some variation with collision energy.

These results were qualitatively interpreted on the basis of a molecular state correlation diagram we proposed for the collision system. For convenience it is reproduced in

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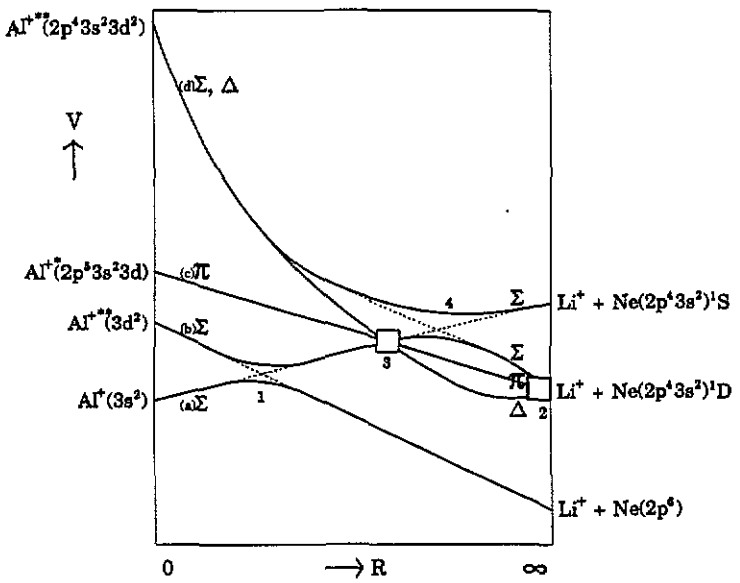

Figure 1. Schematic molecular-state correlation diagram for the system (Li–Ne)$^+$. Adiabatic potential curves are given by full curves. Broken lines labelled (*a*) to (*c*) indicate diabatic curves constructed from the one-electron correlation diagram. The configurations of these diabatic curves are: (*a*) $(1s\sigma^2)(2s\sigma^2)(2p\sigma^2)(2p\pi^4)(3s\sigma^2)\,^1\Sigma$, (*b*) $(1s\sigma^2)(2s\sigma^2)(2p\sigma^2)(2p\pi^4)(3d\sigma^2)\,^1\Sigma$, (*c*) $(1s\sigma^2)(2s\sigma^2)(2p\sigma^2)(2p\pi^3)(3s\sigma^2)(3d\sigma)\,^1\Pi$, (*d*) $(1s\sigma^2)(2s\sigma^2)(2p\sigma^2)(2p\pi^2)(3s\sigma^2)(3d\sigma^2)\,^1\Sigma, {}^1\Delta$.

figure 1. As suggested by the 'topology' of this diagram, it was proposed that the excitation to the doubly excited ^{1}D-state of Ne proceeds as follows. The double excitation occurs at small distances (label 1 in the diagram) by radial coupling between the initial state $^1\Sigma$-curve and the $^1\Sigma$-curve that correlates diabatically to the doubly excited $Ne(2p^43s^2)\,^1S$ state. The system then follows the adiabatic path at the indicated avoided crossing with the next higher $^1\Sigma$-state (label 4 in the diagram), which would result in the population of a 'pure' $M=0$ sublevel of the ^{1}D-state in a coordinate system with the z-axis oriented along the asymptotic direction ($\Theta_{cm}=10.8°$) of the collision system. To explain the significant deviation of the observed direction ($\gamma=35°$–$45°$) of the $M=0$ sublevel from Θ_{cm}, rotational coupling with the Π- and Δ-molecular states converging asymptotically to the Li^+–$Ne(2p^43s^2)\,^1D$ state of the system was invoked. It was argued that especially at the crossing of these states (label 3), and at large distance where these states become degenerate (label 2), rotational coupling might lead to a 'slipping' of the $M=0$ state with respect to the rotating molecular axis, thus leading to a final direction angle (γ) which is larger than the asymptotic angle of the internuclear axis ($\Theta_{cm}=10.8°$).

The goal of the present work has been to test the collisional excitation model sketched above in a more quantitative way. For this purpose, new measurements of the direction angle $\gamma(E_{coll})$ have been carried out in the energy range extending from $E_{coll}=1.2$ keV to $E_{coll}=2.2$ keV. In addition, theoretical calculations of the rotational coupling occurring for a collision system described by the proposed molecular correlation diagram (see figure 1) have been performed. The result of these calculations is compared with the new experimental data.

2. Experimental procedure and results

The experimental set-up used has been described in detail in our earlier publication (Oud *et al* 1993). Here we therefore only give an outline of the experimental procedure. The ion–electron coincidence technique allows us to detect electrons at well defined angles (ϑ, ϕ) with respect to the collision plane determined by the primary ion beam and the position of the ion detector. At a given polar angle (ϑ) with respect to the primary-beam direction, electrons are detected with respect to four azimuthal angles, $\phi = 0°$, 180° (detection in the collision plane) and $\phi = 90°$, 270° (detection perpendicular to the collision plane). For each collision energy, measurements are carried out at polar angles $\vartheta = 45°$, 75°, 105° and 135°. So at each energy 16 points of the angular distribution are measured. To these 16 experimental points the theoretical expression of the angular distribution is fitted, yielding the values of the free parameters in this expression. The theoretical expression and details on the fitting procedure are given in the earlier publication (Oud *et al* 1993). The free parameters in this expression are the asymptotic population amplitudes for the Σ-, Π- and Δ-states that correlate to the atomic ^{1}D-state. In all cases the fit was possible with no statistically significant discrepancies. With the adapted parameters the orientation angle $\gamma(E_{coll})$ of the distribution is calculated. The resulting 'experimental' orientation angles for 17 values of the collision energy E_{coll} are shown

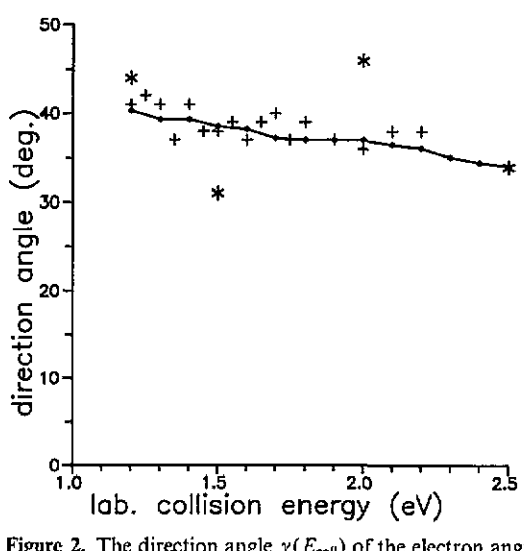

Figure 2. The direction angle $\gamma(E_{coll})$ of the electron angular distribution of autoionization electrons emitted by $Ne(2p^43s^2)\,^1D$ atoms excited in collisions with Li^+ ions at various collision energies E_{coll}. The angular distributions are measured in coincidence with Li^+ ions scattered into a well defined direction ($\Theta_{cm} = 10.8°$, $\Phi = 0°$). The angle $\gamma(E_{coll})$ is given relative to the primary Li^+ beam direction. (+) present experimental results; (*) experimental results from Oud *et al* (1993); (——) results from present model calculations.

in figure 2. Also shown in figure 2 are the four values of our earlier measurements. One can see that the points at 1.5 keV and 2 keV deviate somewhat from our present results. We believe that these deviations are a result of small systematic errors in the earlier measurements. It is very difficult to avoid such systematic errors completely, especially if the apparatus has to be readjusted between measurements. Such readjustments, on the other hand, had been necessary partly because of the long duration of a complete coincident angular distribution containing 48 data points. By reducing the number of

data points per collision energy to 16, it was possible to obtain the present data set without such a readjustment. We therefore believe that the present data are mutually consistent in giving the energy dependence $\gamma(E_{coll})$.

The present data clearly show that the orientation angle (γ) does not oscillate with any appreciable amplitude. Such an oscillation could not be excluded on the basis of the earlier measurements. On the other hand, a significant decrease of the orientation angle with increasing collision energy can be observed. Regarding the shape of the distributions it is found that at all energies it is consistent with an autoionizing transition of the type $^1D \rightarrow {}^2P_{1/2,3/2}$, where the ^1D-atom is populated strongly in the $M=0$ sublevel in a quantization system with z-axis parallel to the orientation of the distribution. The $M=0$ population probabilities lie between 80% and 100% for all 17 collision energies. This is in agreement with the earlier measurements.

In the next section we will confront these experimental findings with theoretical calculations carried out on the basis of the proposed molecular correlation diagram.

3. Rotational coupling analysis

According to the correlation diagram proposed to explain double excitation into the $Ne(2p^43s^2)^1D$ state in collisions with Li^+ (see figure 1), the population of the $^1\Sigma$-molecular state correlating asymptotically to doubly excited $Ne(2p^43s^2)^1D$, occurs at small distances of the collision partners. The smallest distance for the scattering events studied in the present experiments arises for collisions at 2.2 keV and amounts to 0.73 au, as calculated from the scattering potential we will use. For all lower collision energies the distance of closest approach for scattering by a centre of mass scattering angle of 10.8° is larger. The rotational coupling between the initially populated $^1\Sigma$-state to the Π- and Δ-states thus occurs in the second half of the collision at distances that are rather large compared to the size of the anisotropic $2p^4$-core of the Ne atom which causes this coupling. Using 'Slater's rules' (Slater 1930) one estimates a radius of 0.61 au. We therefore use an atomic basis to describe the time evolution of the excited-state wavefunction after the initial excitation by radial coupling. Restricting the description to rotational coupling between atomic states $|LM\rangle$ belonging to just one value of the orbital angular momentum—$L=2$ in the present case—the coupled differential equations describing the time evolution may then be written as (Nikitin and Umanski 1984):

$$i\hbar\dot{a}_M(t) = \sum_{M'=M\pm1} \tfrac{1}{2} c_{\pm}^{L} \dot{\vartheta}(R(t)) \exp\left\{-\frac{i}{\hbar}\int_{-\infty}^{t} (E_M(R(t')) - E_{M'}(R(t')))\,dt'\right\} a_M(t) \qquad (1)$$

$$c_{\pm}^{L} = [L(L+1) - M(M\pm1)]^{1/2}\hbar. \qquad (2)$$

Here $a_M(t)$ are the population amplitudes, $E_M(R(t))$ the distance dependent energies of the states, with M running from -2 to 2, and $\dot{\vartheta}(R(t))$ is the angular velocity of the internuclear axis which coincides with the quantization axis. Due to the cylindrical symmetry of the collision system with respect to this axis, the energies E_M do not depend on the sign of M. With this condition the system of five coupled differential equations reduces to a system of three coupled equations corresponding to $|M| = 0, 1, 2$, i.e. the coupled equations for the Σ-, Π- and Δ-states. If the trajectory $R(t)$ is known, these coupled equations can be solved numerically for model functions describing the energy splitting between these states. In our case we need trajectories leading to a centre of mass scattering angle of 10.8°, as fixed by the ion detector. These trajectories are selected

by choosing the corresponding impact parameter at the various collision energies from the classical deflection function calculated with an estimated scattering potential. As scattering potential we use a screened Coulomb potential of the general form proposed by Ziegler, Biersack and Littmark (Overbury and Huntley 1985) (in au):

$$V(r)=\frac{Z_1Z_2}{R}\{0.1818\exp(-3.200\,R/a)+0.5099\exp(-0.9423\,R/a)$$
$$+0.2802\exp(-0.4029\,R/a)+0.02817\exp(-0.2016\,R/a)\}$$
$$a=0.8853\,(Z_1^{0.23}+Z_2^{0.23})^{-1}. \tag{3}$$

For our Li^+–Ne system, the nuclear charges are $Z_1=3$ and $Z_2=10$. The resulting impact parameters in atomic units are listed in the table below for some collision energies.

Energy (keV)	1.20	1.30	1.40	1.50	1.60	1.70	1.80	1.90	2.00	2.10	2.20	2.30	2.40	2.50
Impact parameters (au)	0.950	0.920	0 892	0.865	0.843	0.821	0.801	0.783	0.765	0.749	0.733	0.718	0.704	0.690

The accuracy of the impact parameter values given in the table is difficult to estimate. Overbury and Huntly (1985) found that, for collisions at 2.5 keV of Li^+ with a variety of target atoms, a scattering angle of a value around 10 to 20 degrees is predicted with an accuracy of at least 1 degree by the universal potential given in relation (3). From this we derive on the basis of the deflection function an estimated possible error of the impact parameter values given in the table of less than 5%. This possible error is small enough to be irrelevant for our analysis, whose main purpose is to investigate whether the proposed model is consistent with the experimental data.

To obtain the theoretical asymptotic population amplitudes predicted for collisions selected in the experiment, the coupled differential equations are solved along the trajectory belonging to the appropriate impact parameter. The initial conditions according to the proposed correlation diagram are: population amplitude $a(\Sigma)=1$, $a(\Pi)=0$, $a(\Delta)=0$, at the distance of closest approach.

The main difficulty is, of course, to devise physically reasonable model functions for the energy splitting between the three molecular states. At large distances this splitting is given by the interaction of the charge of the Li^+ ion with the quadrupole moment of the $(2p^4)^1D$-core of the Ne atom. Assuming the quadrupole moment to be due to the hole corresponding to two missing independent 2p-electrons coupled to a $L=2$ angular momentum state, one readily derives from the expression for one 2p-electron (Flügge 1971) the following expression for the charge-quadrupole interaction potentials in the present case (au):

$$U_M=\langle r^2\rangle(2-M^2)/(5R^3). \tag{4}$$

The expectation value $\langle r^2\rangle$ of the square or the distance of the 2p-electron we estimate using a hydrogenic wavefunction for an effective charge 'seen' by the 2p electron in $Ne^{2+}(..2p^4)$. In this way we obtain $\langle r^2\rangle=0.70$ au. The splittings resulting with this value from relation (4) are used at large distances in the calculations. The order on the energy scale at these distances is Σ, Π, Δ with Σ having the highest energy.

At small distances the order of the molecular states is reversed, with Σ having the lowest energy. As outlined in our earlier paper, this is a consequence of the one electron

correlation diagram. To model this situation we use the following functions:

$$V(\Sigma)=2F(R) \qquad V(\Pi)=F(R) \qquad V(\Delta)=-2F(R)$$
$$F(R)=S_1(R, d_1)0.14/(R+d_1)^3-S_2(R, d_2)C \tag{5}$$

and $S_1(R)$ and $S_2(R)$ appropriate functions that switch off the quadrupole (Q), and switch on the Pauly-type and chemical interactions, respectively, when the distance decreases below the corresponding characteristic values d_1 and d_2, respectively. The $1/R^3$ dependence of relation (4) is replaced by the $1/(R+d_1)^3$ dependence in relation (6) to achieve vanishing of the charge-quadrupole interaction term in relation (5) for $R\to 0$. We have chosen the following form for these switching functions:

$$S_1(R, d_1)=1-\frac{(1+\exp(-\alpha d_1))}{(1+\exp(\alpha(r-d_1)))}$$
$$S_2(R, d_2)=\frac{(1+\exp(-\alpha d_2))}{(1+\exp(\alpha(r-d_2)))}. \tag{6}$$

For d_1 we use the estimated radius of the 2p-orbital in $Ne^{2+}(2p^4)$, $d_1=0.61$ au and for d_2 we use the sum of d_1 and the estimated radius of the 1s-orbital in $Li^+(1s^2)$, $d_2=1.01$ au. The constants (C, α) are treated as free parameters. By choosing their values, the cross-over of the states—the point labelled '3' in the correlation diagram—is determined.

We are of course aware of the fact that our model functions are somewhat arbitrary. But, on the other hand, we only want to find out whether the proposed model is consistent with the experimental data. Since the experimental data we want to reproduce are very detailed—for every collision energy the measured shape and orientation of the angular distribution contains the values of four independent parameters, namely the relative values and phases of the complex population amplitudes of the three states—a possible reproduction appears certainly significant.

With the functions defined in this way calculations are carried out in the described way with varied parameters (C, α). By trial and error it is attempted to reproduce the experimental findings with one set of values of these parameters. The experimental findings are: (i) the observed values of the orientation angles $\gamma(E_{coll})$ for all collision energies and (ii) the fact that, at all collision energies, the final population of the Σ-, Π- and Δ-state corresponds to a nearly pure Σ-population in a quantization system with the z-axis pointing in the direction given by $\gamma(E_{coll})$. It is found that parameter sets in a rather narrow region around the values $C=2.0$ au, and $\alpha=2.85$, yield an excellent reproduction of the experiment. The orientation angles $\gamma(E_{coll})$ calculated with these parameter values for collisions selected in the experiment are compared in figure 2 to the experimental data. The calculated population probabilities of the Σ-, Π- and Δ-states are shown in figures 3(a) and (b), for the two extreme collision energies 1.2 keV and 2.5 keV, respectively. In figure 4(a), the shapes and orientations of the d-wavefunction reconstructed from the complex population amplitudes for these collision energies are shown. The squared electron density as a function of the polar angle in the collision plane is plotted. For comparison, the shape and orientation corresponding to a pure Σ-population, as it arises in the case of degenerate Σ-, Π- and Δ-states for collision with centre of mass scattering angle of 10.8°, is shown in figure 4(b). Finally, the energy splitting between the Σ-, Π- and Δ-states as calculated with the adapted parameters is

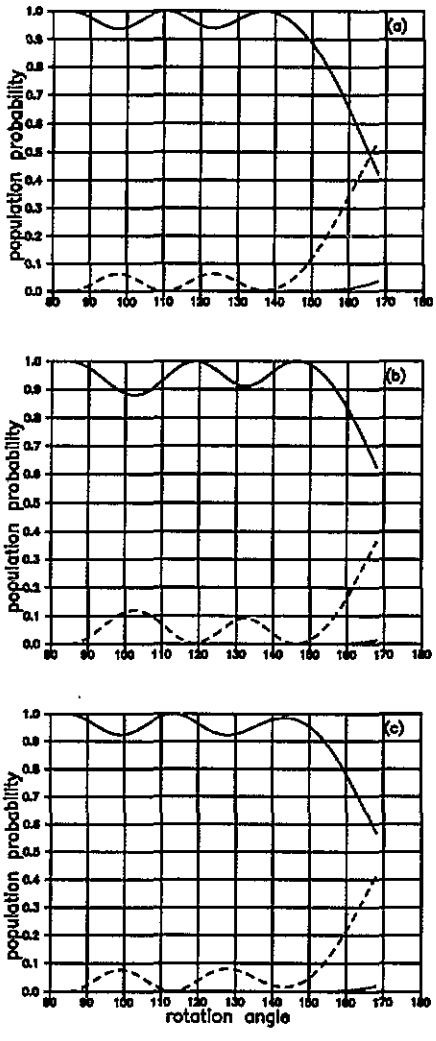

Figure 3. The population probabilities of the Σ-, Π- and Δ-state converging to Li^+-$Ne(2p^4 3s^2)^1D$ as a function of the rotation angle of the collision system during the collision. (*a*) Results for the parameter set ($C = 2.0$ au, $\alpha = 2.85$) and for $E_{coll} = 1.2$ keV. Full line: Σ-state; long dashes: Π-state; short dashes: Δ-state. (*b*) Same as (*a*) but for $E_{coll} = 2.5$ keV. (*c*) Results for the parameter set ($C = 1.8$ au, $\alpha = 2.85$) and for 1.2 keV.

shown in figure 5. The distance of the crossing of the three states (labelled '3' in the correlation diagram) lies at $R_c = 3.50$ au.

4. Discussion

In the attempt to find the best set of the two free parameters (C, α), we found that the most crucial condition is the observed nearly constant 'Σ-shape' of the angular distributions for all collision energies. It turns out that this condition can only be realized if the parameters are chosen in such a way that the in anti-phase oscillating population probabilities for the Σ- and Π-state (see figures 3(*a*) and (*b*)) have a 'last maximum'

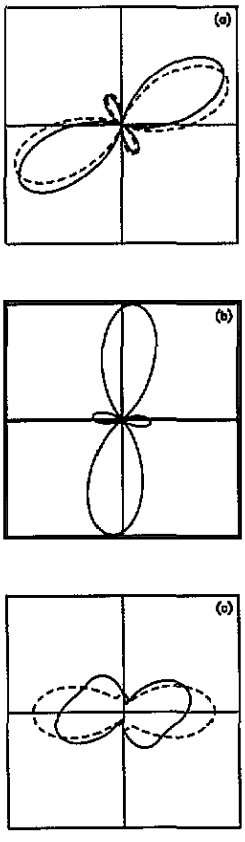

Figure 4. Polar intensity plots showing the shape and the orientation of the d-wavefunction reconstructed from the population amplitudes calculated on the basis of the model. The direction of the horizontal axis coincides with the asymptotic direction of the collision system. Solid line: $E_{coll}=1.2$ keV; dashed line: $E_{coll}=2.5$ keV. (*a*) Calculations for the parameter set ($C=2.0$ au, $\alpha=2.85$). (*b*) Degenerate Σ-, Π- and Δ-curves. In this case a 'pure' $M=0$ distribution oriented along the direction given by half the overall rotation angle $\gamma=(180°-10.8°)/2$ is obtained. (*c*) Parameter set ($C=1.8$ au, $\alpha=2.85$).

and, respectively, a 'last minimum' at a rotation angle which is close to the orientation angle $\gamma\sim40°$. So far, the result of the analysis does not seem to contradict the simple picture of a 'locking radius'. The locking radius would have to have a value of about $R_l=2$ au to explain the observed orientation angles ($\gamma=\Theta_{cm}+\sin^{-1}(b/R_l)$), a value which seems to be reasonable for the energy splittings shown in figure 5. But the possibility to explain the experimental data in this way must be viewed as accidental. To demonstrate this, we show in figure 3(*c*) the population probabilities for the slightly modified set ($C=1.8$, $\alpha=2.85$). The probabilities do not seem to have changed much compared to the ones of figure 3(*a*). The crossing distance is, with $R_c=3.4$ au, also essentially unchanged, so that an effective 'locking radius' would still have to be about 2 au. On the other hand, the angular distribution has changed drastically, as evident from figure 4(*c*). The orientation of the angular distribution is not anymore approximately explained by the simple model of a 'locking radius' which would predict an orientation angle around 38°. Also, the shape of the distribution is now strongly dependent on the collision energy (see figure 4). From this it has to be concluded that the

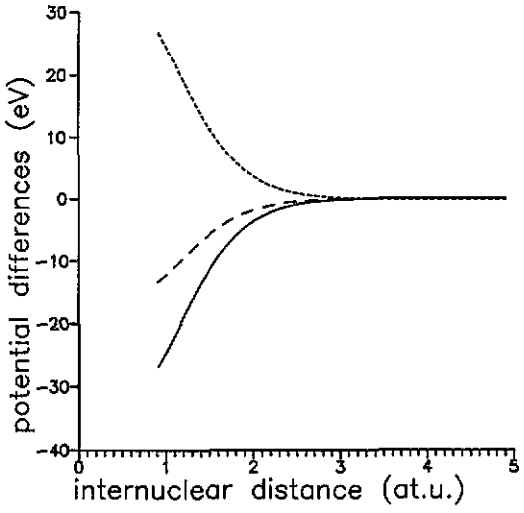

Figure 5. Energy splitting between the Σ-, Π- and Δ-states as calculated with the parameter set ($C=2.0$ au, $\alpha=2.85$). Solid line: Σ-state; long dashes: Π-state; short dashes: Δ-state.

concept of a 'locking radius' is too simple to explain the effects of rotational coupling in real collision systems.

For the parameters ($C=2.0$ au, $\alpha=2.85$) the *second* 'Σ-maximum' (Π-minimum) is located at rotation angles close to (γ). We have also tried parameters for which the *first* 'Σ-maximum' (Π-minimum) is located there. For the corresponding set ($C=0.95$, $\alpha=2.8$), the experimental $\gamma(E_{coll})$ data were reasonably well reproducible, however, the shapes of the angular distributions were more strongly dependent on the collision energy, leading for some energies to significantly less pure 'Σ-shapes' than observed in the experiment.

We have not tried parameter sets for which the *third* 'Σ-maximum' (Π-minimum) is located close to (γ). Such parameters are unrealistic because they lead to energy splittings between the Σ-, Π- and Δ-states which for small distances become larger than the energy difference between the united atom states to which they correlate according to the diagram in figure 1. Using 'Slater's rules' (Slater 1930) we estimate for the united atom limit of the $\Delta-\Sigma$ energy difference a value of 173 eV. From figure 5, we see that the energy splitting obtained from the adapted parameters is consistent with this value.

5. Conclusion

We have shown that our present and earlier experimental data on the coincident angular distribution of electrons emitted by Ne atoms doubly excited into the $(2p^4 3s^2)\,^1D$-state in collisions with Li^+ can be reproduced quantitatively within a collision model based on a proposed molecular orbital correlation diagram. Rotational coupling to Π- and Δ-states after initial population of a Σ-state is found to explain the shape and the orientation of the angular distributions. The evolution of the population amplitudes in the second half of the collision is well described at all collision energies by Σ-, Π- and Δ-energy splittings described by model functions in which two parameters are adapted. The population probabilities for Σ- and Π-states oscillate in antiphase as a function of the rotation angle of the collision system. The experimental data can only be reproduced

within the experimental error if the *second* 'Σ-maximum' (Π-minimum) of these oscillating population probabilities is located close to the observed orientation angle (γ). This condition appears to be rather independent of the model functions. For the chosen form of the model functions, the parameters ($C = 2.0$, $\alpha = 2.85$) are accurately determined, leading to splittings (shown in figure 5) which support the proposed molecular correlation diagram. From the model functions it is concluded that the charge–quadrupole interaction in the second half of the Li^+–Ne collisions leading to excitation of $Ne(2p^43s^2)^1D$ has only negligible influence on the excitation dynamics in the keV collision energy range.

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