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DIPOLE MOMENTS OF S–P TRANSITIONS IN ALKALI ATOMS PERTURBED BY RARE GASES*

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Dipole moments of S–P transitions in alkali atoms perturbed by rare gases were calculated as a function of the internuclear distance, R, based on the pseudopotential model calculation of Baylis. Several of the results obtained are demonstrated graphically. The calculated transition dipole moments depend strongly on R at small and intermediate internuclear distances ($R \sim 4$–$20a_0$). However, the line strengths of the corresponding transitions turn out to be approximately constant.

1. *Introduction*

The broadening of the resonance lines of alkali atoms perturbed by rare gases have been studied extensively for many years. An interest in the spectroscopy of these lines has been increased since Hedges et al. [1] demonstrated that the light radiated in the far spectral wings of these lines, as much as 1000 Å from the line centre, can be used to determine the molecular potential energies for alkali-noble gas systems. Recent studies both theoretical [2, 3] and experimental [4–7] indicate that although an alkali atom and a noble gas atom repel each other (except for a weak Van der Waals attraction) when the alkali atom is in its ground ${}^2S_{1/2}$ state, the two atoms may bind together to form a molecule when the alkali atom is in an excited P, D or S state. Such bound diatomic systems possess a short lifetime and are usually called quasimolecules. Since population inversion of the ground state and an excited bound state is in a natural way assured, the radiative transitions from the upper state to the repulsive ground state of these systems are of interest for excimer laser purposes [8, 9]. Moreover, some experimental results [10, 11] indicate that for resonance doublets of the alkali atoms one observes changes in the intensity of each component under the influence of foreign gas perturbation. This fact cannot be explained in terms of phase-shift theories of spectral line broadening. When considering the integrated intensity

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of a line, contributions from the satellite structures must be taken into account [12]. Both the occurrence of the satellites and their intensities depend on transition probabilities, which, as was shown by Granier et al. [13], vary with the internuclear distance, R, of the interacting atoms. To calculate the probability of dipole transition in a diatomic system it is necessary to know the corresponding transition moment. So far one has assumed that the transition moments of the alkali-noble gas atom systems associated in the separated atom limit with allowed alkali atom transitions are independent of the internuclear distance R. In calculations these were usually replaced by the corresponding atomic transition moments. In this work we have calculated the dipole moments as a function of R for various alkali-noble gas atom pairs for molecular transition associated in the separated atom limit with $S-nP$ electric dipole transitions in the alkali atom. The molecular electronic wavefunctions required for this purpose were obtained using the pseudopotential model calculation of Baylis [2]. The Baylis method together with the modifications made during the present calculations are described briefly in Section 2. Sections 3 and 4 are devoted to the calculation of the transition dipole moments. The results and discussion are found in Section 5.

2. *Pseudopotential model calculation*

The pseudopotential method used to calculate the electronic wavefunctions of alkali-rare gas atom systems consists in finding the eigenvalues and eigenvectors of an effective Hamiltonian of the system, which depends on the internuclear distance of interacting atoms. It is assumed that for thermal collisions the perturbations of the alkali core and of the rare gas atom are quite small. Thus, both the state of the alkali core and of the rare gas atom may be described by unperturbed atomic wavefunctions. Only the valence electron of the alkali atom suffers the perturbation. Therefore, defining the zero energy of the system when both the atoms are in the ground states and isolated, the Hamiltonian of the system consists of the alkali valence electron Hamiltonian and the interaction between the atoms. The interaction term consists, in turn, of two parts: (*i*) an electrostatic interaction which is taken to be that of a polarizable dipole (the rare gas atom) in the field of the alkali valence electron and alkali core; (*ii*) a repulsive part which simulates the effect of the Pauli exclusion principle and dominates at small internuclear distances. The latter part of the interaction term is expressed in terms of two so-called "pseudopotentials" derived based on the Thomas–Fermi statistical model of the atom. One of these provides for the alkali core-rare gas atom repulsion and the second one tends to exclude the valence electron from the neighbourhood of the noble gas atom. Subsequently, one obtains the matrix representation of the Hamiltonian in the basis of the alkali valence electron wavefunctions and diagonalizes the matrix. The diagonal elements of the diagonalized matrix are the eigenvalues of the Hamiltonian, whereas the columns of the transformation matrix which diagonalizes the Hamiltonian are the corresponding molecular eigenvectors. The present calculation differs from the calcuations of Baylis [2] and of Pascale et al. [3] in two respects: (*i*) Firstly, the Pauli exclusion pseudopotential for the repulsion between the alkali core and rare gas atom was now evaluated exactly instead of using the approximation proposed by Baylis, (*ii*) Secondly, the atomic radial orbitals needed to form an atomic basis were taken to be the functions suggested by Simons [14] instead of the Bates–Damgaard type [15]. The functions proposed by Simons behave asymptotically like the latter ones but, in contrast to these, they are finite at the origin and can be normalized easily.

3. Transition dipole moment

An orthonormalized molecular electronic wavefunction of an alkali-rare gas atom system obtained based on the pseudopotential calculation is expanded in terms of the alkali valence electron bound states as:

$$\Psi_{\Gamma M}(\boldsymbol{r}, \boldsymbol{R}) = \sum_{\gamma} C_{\gamma M}^{\Gamma M}(R)\psi_{\gamma M}(\boldsymbol{r}), \tag{1}$$

where Γ stands for the set of the quantum numbers $(NLSJ)$ which refer to the atomic state correlated, in the separated atom limit, with the given molecular state, γ denotes the set of quantum numbers $(nlsj)$ which specify a definite atomic state in the expansion, $\boldsymbol{r}$ is the position vector of the alkali valence electron with respect to the alkali nucleus and $\boldsymbol{R}$ is the position vector of the rare gas atom relative to the alkali nucleus. M is the projection of the total angular momentum of the system along the internuclear axis.[1] In the asymptotic limit $R \to \infty$, all the expansion coefficients reduce to the Kronecker delta, i.e., $C_{\gamma M}^{\Gamma M}(R \to \infty) = \delta(\Gamma, \gamma)$. The summation is over all the states included in the basis. The electric dipole moment of an alkali-rare gas atom system is given, generally, by the expression:

$$\boldsymbol{\mu} = -e\boldsymbol{r} + \alpha\boldsymbol{E}, \tag{2}$$

where $\boldsymbol{E}$ is the electric field at the noble gas centre due to the alkali electron and the core (assumed to have a charge $+e$) and α stands for the polarizability of the noble gas atom. During the calculation it was found that the contribution to the moleclar transition moments arising from the dipole moment of the rare gas atom is negligible compared to that of the alkali electron. Thus the corresponding term in (2) has been dropped in the present considerations. Denote the components of $\boldsymbol{r}$ by x, y, z (z along the internuclear axis), then the spherical components of the dipole moment are expressed as follows:

$$\begin{aligned} \mu_1 &= e\frac{1}{\sqrt{2}}(x+iy) = -er\sqrt{\frac{4\pi}{3}}\,Y_1^1(\vartheta, \varphi), \\ \mu_0 &= -ez = -erP_1(\cos\vartheta), \\ \mu_{-1} &= -e\frac{1}{\sqrt{2}}(x-iy) = -er\sqrt{\frac{4\pi}{3}}\,Y_1^{-1}(\vartheta, \varphi), \end{aligned} \tag{3}$$

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[1] The molecular state $|\Gamma M\rangle$ is also denoted by the quantum number M (in parenthesis) followed by the alkali state to which it separates for large R's.

where ϑ is the angle between the vectors $\boldsymbol{r}$ and $\boldsymbol{R}$. The matrix element of a spherical component of the dipole moment operator taken between two molecular states $|\Gamma M\rangle$ and $|\Gamma' M'\rangle$ is:

$$\langle \Gamma M|\mu_m|\Gamma' M'\rangle = \int \Psi^*_{\Gamma M}(\boldsymbol{r}, \boldsymbol{R})\mu_m \Psi_{\Gamma' M'}(\boldsymbol{r}, \boldsymbol{R})d\boldsymbol{r}, \tag{4}$$

where the following selection rule $\Delta M = 0, \pm 1$ still holds. In this calculation we considered the transitions from the ground molecular state for which $M = \pm 1/2$ to the excited states with $M' = \pm 1/2$ and $M' = \pm 3/2$. As is known, the molecular adiabatic potentials for opposite values of M and with the same set of other quantum numbers Γ are identical. However, the two states $|\Gamma M\rangle$ and $|\Gamma - M\rangle$ differ from each other. Since the state $|\Gamma - M\rangle$ is obtained from $|\Gamma M\rangle$ by a reflection of the system at a plane passing through the internuclear axis which can be regarded as a combined effect of parity followed by rotation through π about an axis perpendicular to the plane it can be shown that the following relation holds

$$C^{\Gamma, -M}_{\gamma, -M}(R) = (-1)^{J-j+L-l} C^{\Gamma M}_{\gamma M}(R).$$

General considerations show also that:

$$\langle \Gamma + 1/2|\mu_0|\Gamma' + 1/2\rangle = \langle \Gamma - 1/2|\mu_0|\Gamma' - 1/2\rangle,$$

$$\langle \Gamma + 1/2|\mu_{+1}|\Gamma' - 1/2\rangle = -\langle \Gamma - 1/2|\mu_{-1}|\Gamma' + 1/2\rangle,$$

and

$$\langle \Gamma + 1/2|\mu_{-1}|\Gamma' + 3/2\rangle = -\langle \Gamma - 1/2|\mu_{+1}|\Gamma' - 3/2\rangle.$$

Finally, inserting (1) into (4) we find that the molecular transition moment can be expressed in terms of the alkali transition dipole moments

$$d^{\mathrm{m}}_{\gamma M, \gamma' M'} = \int \psi^*_{\gamma M}(\boldsymbol{r}) d_{\mathrm{m}} \psi_{\gamma' M'}(\boldsymbol{r}) d\boldsymbol{r}$$

where $\boldsymbol{d} = -e\boldsymbol{r}$. For the atomic dipole moments the usual selection rules hold, and their values can be easily calculated from both the Bates–Damgaard radial wavefunctions [15] and the functions sugested by Simons [14] which have been involved in the calculation.

4. *Calculation*

In order to obtain the molecular electronic wavefunctions needed for the present calculation, the Hamiltonian of the system was diagonalized in the basis of the alkali valence electron wavefunctions. The atomic basis used for each of the alkali atoms was large enough to ensure the stability of several of the lowest excited molecular terms for each pair of the atoms considered. For example, for sodium the following atomic states were taken: $3S_{1/2}$, $3P_{1/2}$, $3P_{3/2}$, $4S_{1/2}$, $3D_{5/2}$, $3D_{3/2}$, $4P_{1/2}$ and $4P_{3/2}$. Based on the convergence of the molecular terms with an increasing basis, which was checked by Pascale et al. [3] and Granier et al. [13], we believe that the calculated adiabatic potentials for sodium are stable from the ground state up to those associated, in the separated atom limit, with the $3D_{3/2}$ level. The atomic bases for the other alkali atoms were formed analogically. The parameters required in the calculation of molecular terms are the alkali energy levels, which were taken from the tables of Moore [16], the polarizabilities of the rare gas atoms, semiempirically calculated by Dalgarno and Kingston [17] and the adjustable parameter, r_0, involed in the calculation of the electrostatic interaction between the alkali and the rare gas atom treated as a characteristic radius of the rare gas atom. The value of r_0 was determined by fitting the depth of the calculated ground state potential of the diatomic system to that calculated by Pascale et al. [3]. The adiabatic potentials calculated for various alkali-noble gas atom pairs will be published elsewhere [18]. The present work concerns only the calculation of the dipole moments for the molecular transitions between the ground state and the nearest excited states correlated, in the separated atom limit, with n^2P alkali atom states. The atomic functions $\psi_{\gamma M}(r)$ involved in the calculation are taken in the $|(nls)jm_j\rangle$ — representation, where an alkali wavefunction is the product of a radial part multiplied by a spin-orbit coupling function, i.e.,

$$|(nls)jm_j\rangle = \sum_{m_s} (l1/2m_lm_s|jm_j)R_{nl}(r)Y_l^{m_l}(\vartheta,\varphi)\chi_{1/2,m_s}.$$

The atomic orbitals, $R_{nl}(r)$, are the functions suggested by Simons [14] which can be expressed in terms of the generalized Laguerre polynomials:

$$R_{nl}(r) = \mathcal{N}(-1)^{n-l-1-\mathrm{Int}(\delta)}\left(\frac{2Z_{\mathrm{net}}}{n-\delta}\right)^{l+3/2-\delta+\mathrm{Int}(\delta)} e^{-\frac{Z_{\mathrm{net}}r}{n-\delta}} r^{l+1-\delta+\mathrm{Int}(\delta)}$$

$$\times L_{n-l-1-\mathrm{Int}(\delta)}^{2l+1-2\delta+2\,\mathrm{Int}(\delta)}\left(\frac{2Z_{\mathrm{net}}r}{n-\delta}\right),$$

with

$$\mathcal{N} = \sqrt{\frac{(n-l-1-\mathrm{Int}(\delta))!}{2(n-\delta)\Gamma(n+l+1-2\delta+\mathrm{Int}(\delta))}},$$

where Int (δ) is the rounded nearest integer of the quantum defect δ. It is worthwhile to note that these functions are normalized but not orthogonal. For the diagonalization of the Hamiltonian one can use the well-known Jacobi's procedure.

5. *Results and discussion*

The dipole moments were calculated for all the alkali-rare gas atom systems for transitions from the ground molecular state, correlated, in the separated atom limit, with the $n^2S_{1/2}$ alkali atom ground state to the excited states which dissociate to the $n^2P_{1/2,3/2}$ states of the alkali atom. All the calculations were carried out for the values of R from $R = 4a_0$ up to $R = 22a_0$. It is impossible to report here all the results obtained. They will be available upon request. However, in order to illustrate the present calculations some of the results are presented graphically. The molecular electronic wavefunctions obtained in the pseudopotential calculation are pure atomic states in the separated atom limit, but they are a mixture of various atomic states at finite internuclear distances because of the coupling amoung states. In this way the transition dipole moments of a diatomic system depend on the internuclear distance, R, of the atoms as well. Figures 1–2 show the coefficients $C_{\gamma M}^{\Gamma M}(R)$ of expansion (1) as a function of R for the ground $X^2\Sigma_{1/2}$ state and

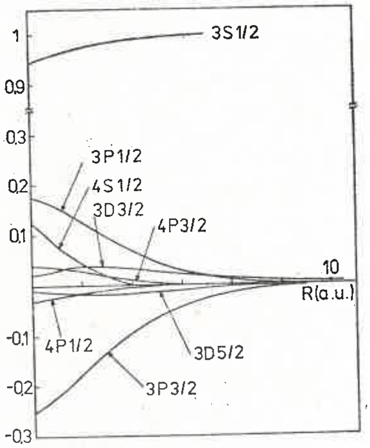

Fig. 1. Coefficients $C(R)$ of the atomic state expansion of the molecular ground state $X^2\Sigma_{1/2}$ versus the internuclear distance R, for the NaAr system

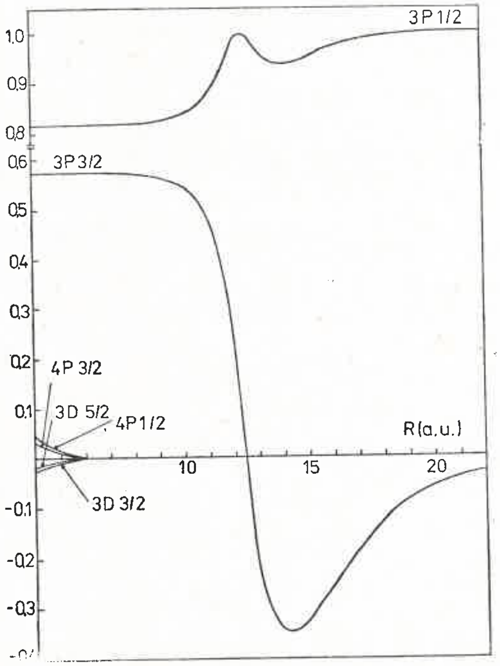

Fig. 2. Same as in Fig. 1 for the $A^2\Pi_{1/2}$ state

the first excited $A^2\Pi_{1/2}$ state of the NaAr system. These molecular states are correlated respectively with the $3^2S_{1/2}$ and $3^2P_{1/2}$ atomic states of Na. The mixing of various atomic states in the case of the ground molecular state is seen to be important at small R. On the other hand, for the $A^2\Pi_{1/2}$ state only the coefficients correlated with the $3^2P_{1/2}$ and $3^2P_{3/2}$ atomic states are significant in the expansion. All the remaining coefficients are small and tend to be zero at R as small as $5a_0$. Therefore, they have a negligible contribution to the molecular transition moment. In Fig. 3 the dipole moments versus R are shown for the NaAr system. In order to relate the present results to other

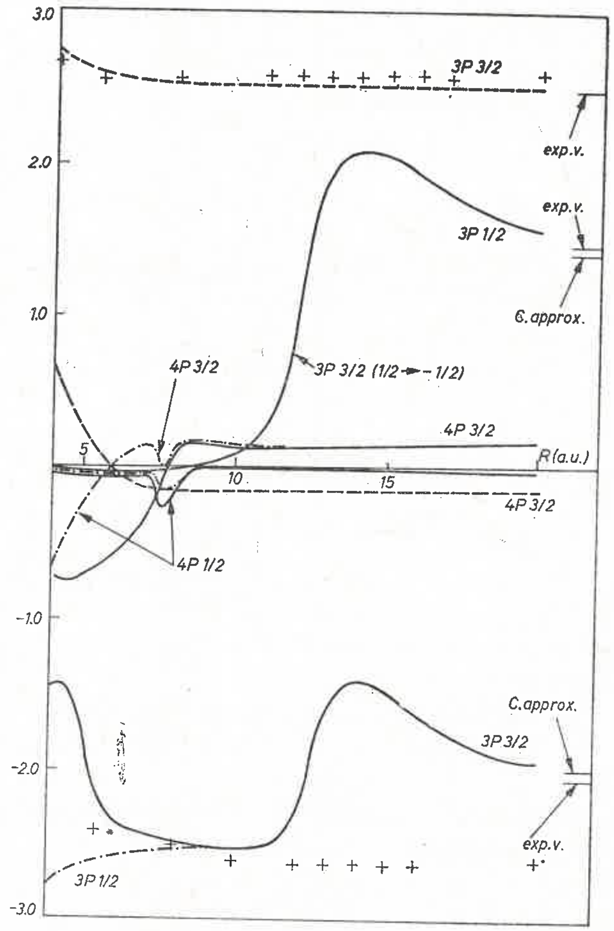

Fig. 3. Dipole moments versus the internuclear distance, R, in atomic units (ea_0) for transitions in the NaAr system from the ground state $(1/2)3^2S_{1/2}$ to excited states associated, in the separated atom limit, with the $3P_{1/2,\,3/2}$ and $4P_{1/2,\,3/2}$ atomic levels of Na. ——— $|\Gamma+1/2\rangle \to |\Gamma'+1/2\rangle$-transition, - - - - - $|\Gamma+1/2\rangle \to |\Gamma'+3/2\rangle$-transition and – · – · – $|\Gamma+1/2\rangle \to |\Gamma'-1/2\rangle$ -transition. The pluses (+) are the values calculated by Saxon et al. [20]. The values of the atomic transition moments calculated in the Coulomb approximation (C. approx.) [15] and experimentally determined by Minkowski (exp. v.) [19] are marked on the left-hand side of the figure

available data we marked also their asymptotic values obtained both theoretically (with the Bates–Damgaard functions) and experimentally (determined by Minkowski [19]). A comparison is also made with the recent results of Saxon et al. [20] obtained using the configuration interaction CI calculation. It can be seen that the present calculated dipole moments depend strongly on R. In the limit $R \to \infty$ they converge asymptotically to the corresponding atomic transition moments. It is also noteworthy that the so-called line strengths of the transitions defined as:

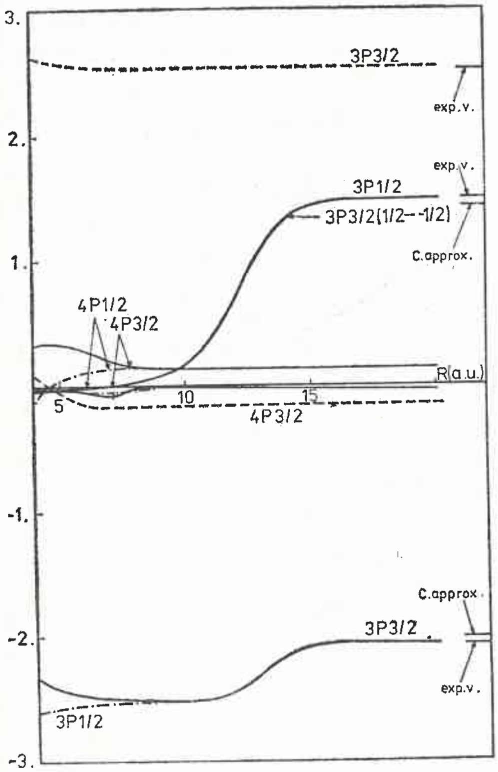

Fig. 4

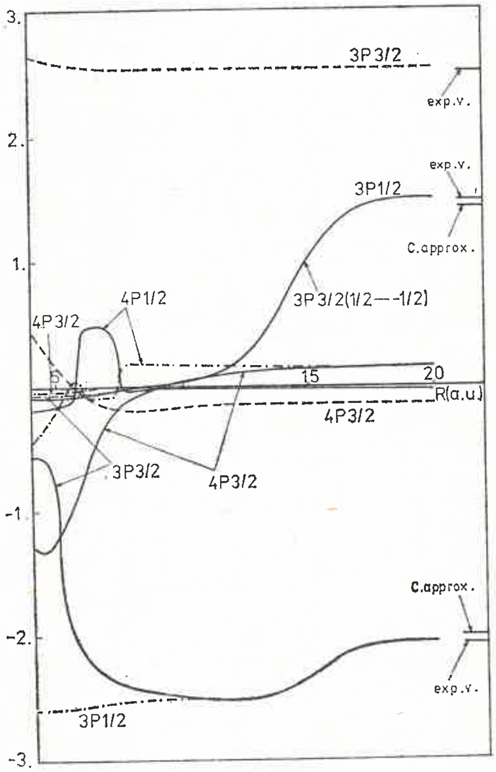

Fig. 5

Fig. 4. Same as in Fig. 3 for the NaHe system
Fig. 5. Same as in Fig. 3 for the NaNe system

$$S_{\Gamma\Omega,\Gamma'\Omega'} = \sum_{MM'm} |\langle \Gamma M|\mu_m|\Gamma' M'\rangle|^2$$

seem to be rather constant from large R's up to about $5a_0$. On the other hand the dipole moments calculated by Saxon et al. display only a slight variation with R. However, the transition dipole moment $X^2\Sigma \to B^2\Sigma$, in the present notation $(1/2)3^2S_{1/2} \to (1/2)3^2P_{3/2}$, calculated by them does not tend to its asymptotic value at large R's($R \sim 20a_0$). Therefore, quite reasonable results obtained for the NaAr system permit us to believe that the present calculations also provide acceptable transition dipole moments for other alkali-noble gas atom pairs for which one cannot make any comparison because of a lack of corresponding data. Figures 4–7 present the dipole moments of Na perturbed, in turn, by He, Ne, Kr and Xe. The behaviour of the transition dipole moments with R in all these systems is analogical to that of NaAr. The dipole moments exhibit a structure at small values of R, where the adiabatic potential curves of the excited states have a well because of coupling with neighbouring states. Some oscillations in dipole moments observed, for example, for NaAr and NaNe are probably associated with the oscillations in the coefficients $C(R)$, which largely contribute to the calculated transition moments. Figures 8–11 present the transition moments for various alkali atoms perturbed by Ar. A discontinuity observed in the LiAr system for $R \sim$ 11-12 a_0 is probably due to the fact that the potential curves of the $(1/2)2P_{1/2}$ and $(1/2)2P_{3/2}$ molecular states have a pronounced avoided crossing in the region of R considered. In this case the two molecular states exchange their wavefunctions. The calculated transition dipole moments provide interesting information about

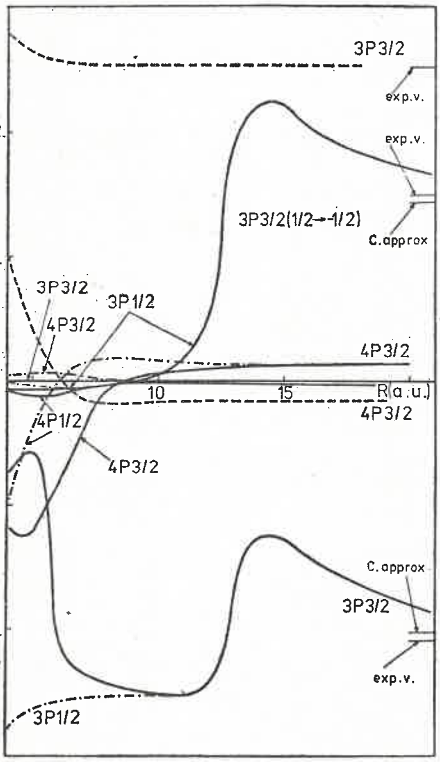

Fig. 6

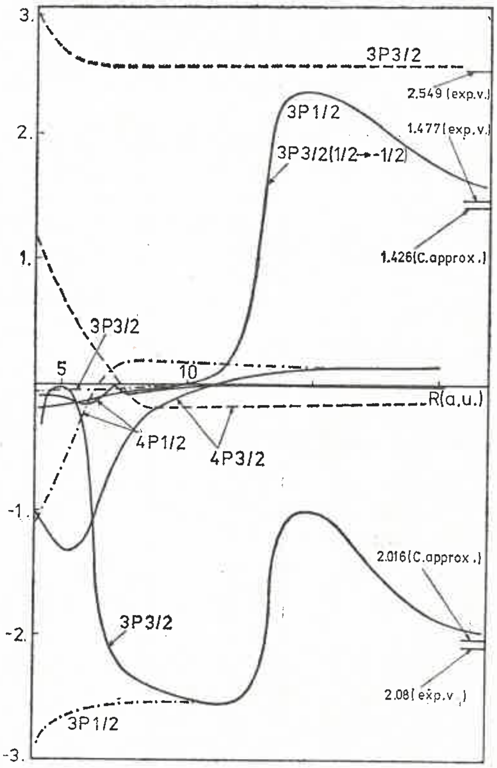

Fig. 7

Fig. 6. Same as in Fig. 3 for the NaKr system
Fig. 7. Same as in Fig. 3 for the NaXe system

these systems. Knowing the transition moments one can calculate the corresponding line strengths, S, as a function of R. Subsequently, multiplying the line strength by the Boltzmann factor (also as a function of R) one obtains a quantity which is proportional to the transition probability of absorption measured by a decrease in the photon flux. Using the Einstein A/B relation one can get the probability of the spontaneous emission of the system considered. Having the calculated line strengths one can also evaluate the corresponding electronic absorption oscillator strengths as a function of R and the lifetimes of the excited states of the alkali-noble gas systems.

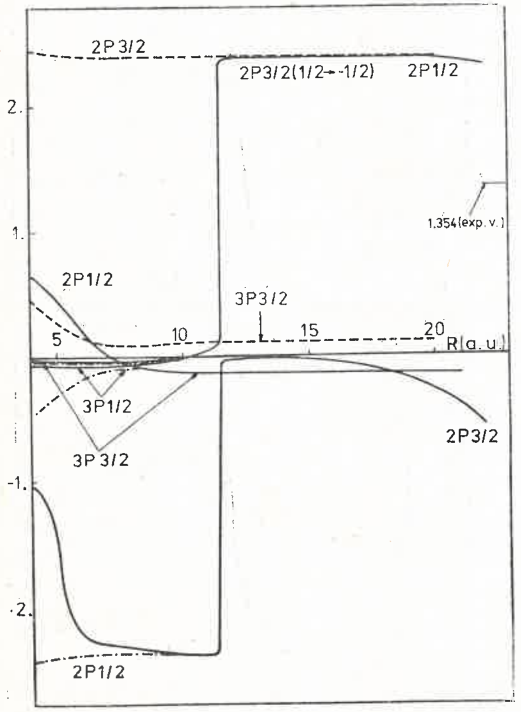

Fig. 8

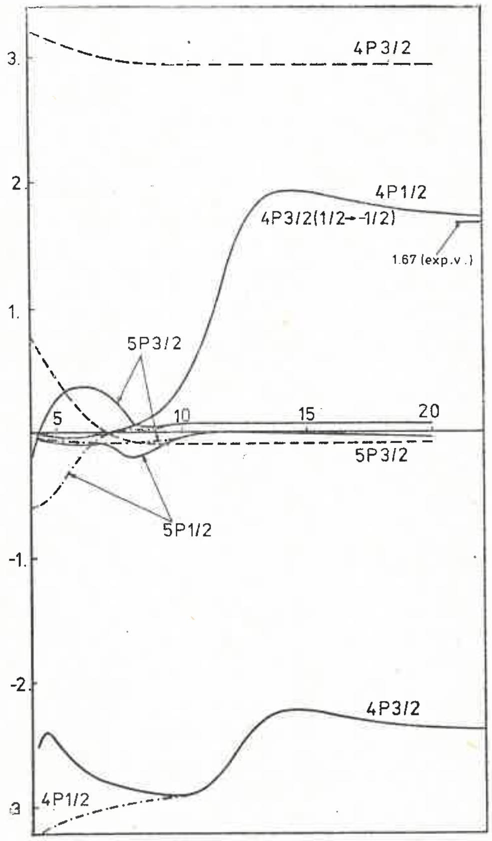

Fig. 9

Fig. 8. Same as in Fig. 3 for transitions in LiAr from the ground state (1/2)$2^2S_{1/2}$ to excited states associated in the separated atom limit with $2^2P_{1/2,\,3/2}$ and $3^2P_{1/2,\,3/2}$ states of Li

Fig. 9. Same as in Fig. 3 for transitions in KAr from the ground state (1/2)$4^2S_{1/2}$ to excited states associated in the separated atom limit with $4^2P_{1/2,\,3/2}$ and $5^2P_{1/2,\,3/2}$ states of K

The calculation of the lifetimes seems to be of particular interest. So far they were assumed to be equal to the lifetimes of the corresponding excited states of alkali atoms. Now there is a possibility to verify that assumption.

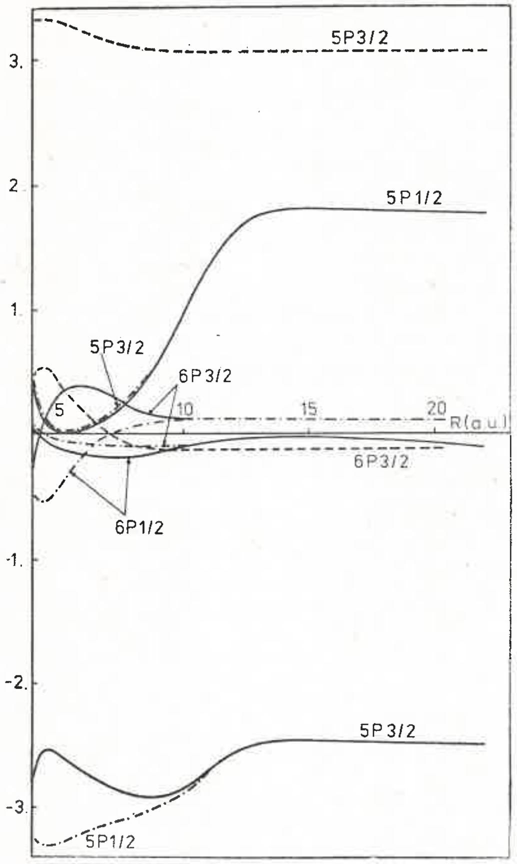

Fig. 10

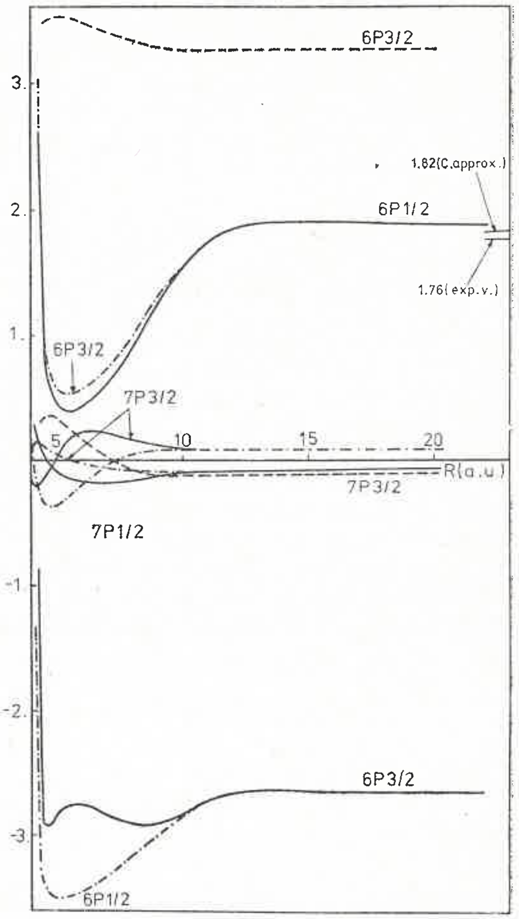

Fig. 11

Fig. 10. Same as in Fig. 3 for transitions in RbAr from the ground state $(1/2)5^2S_{1/2}$ to excited states associated in the separated atom limit with $5^2P_{1/2,\,3/2}$ and $6^2P_{1/2,\,3/2}$ states of Rb

Fig. 11. Same as in Fig. 3 for transitions in CsAr from the ground state $(1/2)6^2S_{1/2}$ to excited states associated in the separated atom limit with $6^2P_{1/2,\,3/2}$ and $7^2P_{1/2,\,3/2}$ states of Cs

6. Conclusion

The dipole moments versus R in alkali-rare gas systems for transitions from the ground state to the first excited states associated in the separated atom limit with n^2P states of alkali atoms have been calculated based on the Baylis pseudopotential method. Some of the results have been presented graphically. The transition moments obtained should be useful in the interpretation of molecular bands and satellite lines which have been observed recently both in emission and absorption of alkali-rare gas mixtures. A comparison between the calculated and observed line profiles would lead to more complete information concerning the adiabatic potential energies of the excited states.

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