

van der Waals and resonance interaction in the quasimolecular system Eu-Sr

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The authors outline an asymptotic calculation of adiabatic potential curves for diatomic quasimolecular systems that happens to be quite accurate in the domain of long-range forces, even for atoms with complex electronic configurations. A formula for the molecular oscillator strength expressed via the oscillator strengths of the constituent atoms and the eigenfunctions of the effective Hamiltonian is presented. Quite general theoretical results on the electrostatic interaction within these quasimolecular systems are then applied to a calculation of the dipole-dipole interaction for the quasimolecule Eu-Sr, leading to the adiabatic potentials in the region of interatomic distances larger than approximately 1.0 nm. These results are checked by comparing the quasistatic absorption coefficient for the blue quasistatic wing of the Eu resonance line broadened by the influence of Sr atoms to the experimentally derived profile [K. Niemax, *Phys. Rev. Lett.* **55**, 56 (1985)]. Excellent agreement is obtained. A great influence of the molecular oscillator strengths on the shape of the quasistatic profile is found, so that, in general, the character of the interaction potential could not be judged from log-log plots of the absorption coefficient alone.

I. INTRODUCTION

Not long ago Niemax¹ reported on the transition from second- to first-order dipole-dipole interaction (van der Waals to resonance) in the excited molecule Eu-Sr. This is quite a rare behavior, but possible for heteronuclear systems.^{2,3} In this theoretical approach we have performed asymptotic calculations of adiabatic potential curves for the quasimolecule Eu-Sr, assuming that exchange effects could be neglected in the region of large interatomic distances. Also, the molecular electronic-transition oscillator strengths were calculated as functions of interatomic distance. With this as a basis, quasistatic absorption coefficients were calculated for the europium resonance triplet ($4f^7 6s^2 {}^8S_{7/2} - 4f^7 6s 6p {}^8P_J$) for which we shall use the notation⁴ ($a {}^8S_{7/2} - y {}^8P_J$), with wavelengths 459.53, 462.85, and 466.32 nm for $J=9/2$, $7/2$, and $5/2$, respectively, broadened by strontium; and for the 460.86-nm strontium resonance line ($5s^2 {}^1S_0 - 5s 5p {}^1P_1$) broadened by europium, both perturbers being in their ground states. Eu and Sr atoms have two valence electrons and, furthermore, europium exhibits complicated electronic structure. For such systems, which include atoms with unfilled inner shells, *ab initio* methods would require a lot of computing time with a risk of numerical failure, while the relatively simple perturbation treatment can provide a good theoretical approach.

For proper calculation of an absorption coefficient of spectral lines for certain atoms A and B , within the general mixture of a two-component gas or vapor A - B , consideration of all three diatomic molecules A - A , A - B , and B - B is needed. Let us denote by $L_A^{(B)}$ the reduced line profile of atom A broadened by the electrostatic influence of atom B in a quasimolecular system A - B , and by N_A (N_B) the concentrations of atoms A (B). Then for the absorption coefficient we write

$$k(\Delta\lambda) = N_A^2 L_A^{(A)} + N_A N_B L_A^{(B)} + N_B N_A L_B^{(A)} + N_B^2 L_B^{(B)}. \quad (1)$$

In the physical conditions where the concentration of perturbing atoms (let us say B) greatly exceeds the concentration of emitting atoms (A), only the second and the last term in (1) will be important. This is exactly the case of an experiment¹ where the vapor pressure of Eu was five to six orders of magnitude smaller than that of Sr. In the quasistatic wings of europium resonance lines, the contribution of the far wings of the strontium resonance line [corresponding to the last term in (1)] is shown to be small.¹ However, this contribution is subtracted in Niemax's work, and thereafter reproduces a spectrum such that it is sufficient to analyze the quasimolecule Eu-Sr. This will also give us information on the Sr resonance line broadened by europium in vapor mixtures with reverse concentrations.

For the system Eu-Sr not only are the atomic resonance energy levels close to each other, but, moreover, the Sr resonance singlet level $5s 5p {}^1P_1$ falls between the $J=\frac{9}{2}$ and $\frac{7}{2}$ components of the Eu resonance triplet $4f^7 6s 6p {}^8P_J$. Corresponding energy differences $E(\text{Eu}^*(J)) - E(\text{Sr}^*)$ are 62.78 and -93.31 cm^{-1} for $J=\frac{9}{2}$ and $\frac{7}{2}$, respectively. This results in a strong coupling between the two resonance states (marked by asterisks), and, consequently, the molecular oscillator strengths will become exceedingly important for the behavior of the quasistatic absorption coefficient.

II. PERTURBATION TREATMENT OF ELECTROSTATIC INTERACTION

The electronic Hamiltonian under consideration will now be written in the form of an effective Hamiltonian, suitable for the perturbation calculation of quasidegenerate levels.^{2,5}

$$H_{\text{eff}}(R) = W_{\text{es}}(R) + V_{\text{dis}}(R) + H_A + H_B, \quad (2)$$

where W_{es} denotes the electrostatic interaction between two multipoles separated by distance R and H_I ($I = A, B$) is the Hamiltonian of the unperturbed atom. V_{dis} is the dispersive contribution of the polarization interaction, and is defined by

$$V_{\text{dis}} = \sum_{\substack{k, k \neq k_0 \\ l, l \neq l_0}} \frac{W_{\text{es}} |\phi'_k\rangle_A |\phi'_l\rangle_B \langle \phi'_l|_A \langle \phi'_k|_B W_{\text{es}}}{E_{k_0}^A + E_{l_0}^B - E_k^A - E_l^B}. \quad (3)$$

In (3), $E_{k(l)}^{A(B)}$ represents the energy of unperturbed atomic levels and the subscript zero refers to initial (not necessarily ground) states of atoms before the electronic transition in a quasimolecule has happened. Also, we have assumed the molecular electronic wave functions to be of the product form $|\Psi\rangle = |\phi_A\rangle |\phi_B\rangle$ which is justified in regions where exchange effects, i.e., the overlapping of the wave functions of the two atoms, are small.⁶ To estimate the limits of the domain where exchange effects do become important, one can calculate the sum of average atomic radii in a molecular state under consideration (one atom in resonance and the other in the ground state). By the use of the tables of atomic radii⁷ we have found that for distances 0.6–0.7 nm the electrons' orbits will come "in touch." To be sure, we shall take the domain of our calculation as the distances $R > 1.0$ nm.

The electronic Hamiltonian in the form (2) is very practical because electronic energies of the quasimolecule are obtainable up to the correction of second order by

simply calculating the matrix elements between desired quantum states:

$$\begin{aligned} \langle \Psi | H_{\text{eff}}(R) | \Psi'' \rangle &= \langle \Psi | W_{\text{es}}(R) | \Psi'' \rangle \\ &\quad + \langle \Psi | V_{\text{dis}}(R) | \Psi'' \rangle + E_I^0 \delta_{\Psi\Psi''}, \\ E_I^0 &= \begin{cases} E_A^0 & \text{for } |\Psi\rangle \text{ of type } |A^*B\rangle \\ E_B^0 & \text{for } |\Psi\rangle \text{ of type } |AB^*\rangle. \end{cases} \end{aligned} \quad (4)$$

The first step of our work is the calculation of angular parts of matrix elements in (4). They can be derived "exactly," keeping in mind the approximation of $|\Psi\rangle$ as a nonantisymmetrized product. To account for the levels that correspond to the components of fine structure of atomic terms, we shall use the so-called coupled representation (Hund's case *c*, i.e., the spin-orbit coupling stronger than the electrostatic interaction). In other words, we can write electronic wave functions of a particular atom I as kets $|n; LSJM\rangle_I$, where J is the total angular momentum formed by addition of orbital (L) and spin (S) atomic angular momenta. M is the projection of J on the axis of a quasimolecule. Therefore, the total asymptotic wave function will be of the form

$$\begin{aligned} |\Psi\rangle &= |n_A; L_A S_A J_A M_A\rangle |n_B; L_B S_B J_B M_B\rangle \\ &= |n; LSJM\rangle_A |n; LSJM\rangle_B. \end{aligned} \quad (5)$$

The symmetry of the molecular state in the coupled approximation is characterized by the quantum number $\Omega = |M_A + M_B|$. For the electrostatic interaction the most appropriate expression is the multipole expansion

$$W_{\text{es}} = \sum_{i,j} \sum_{a,b,\alpha} \frac{4\pi e^2 (-)^b (a+b)! r_i^a r_j^b Y_a^{-\alpha}(\hat{r}_i) Y_b^{\alpha}(\hat{r}_j)}{R^{a+b+1} (2a+1)(2b+1) [(a-\alpha)!(a+\alpha)!(b-\alpha)!(b+\alpha)!]}, \quad (6)$$

where r_i and r_j are distances of electrons from the corresponding atoms A and B , \hat{r}_i and \hat{r}_j are unit vectors pointing from atoms to electrons, a (b) is the order of multipole for atom A (B), and $Y_{a(b)}^{\alpha}$ denotes the spherical harmonic with α as the projection value of the smaller of the two numbers a and b . For neutral species, $a, b \geq 1$, and the lowest possible interaction is of the dipole-dipole type. In practice, the sum $\sum_{i,j}$ reduces to the outer (valence) electrons only. Here we deal with atoms which have two outer electrons. This approximation is a bit less applicable to the electronic configuration of Eu where the $4f$ subshell is half-filled, but, nevertheless, the interaction between the deep-lying $4f$ electrons and the outer electrons can be considered as negligible.^{4,8-10}

The summation of valence electrons can be separated, so that, for a particular atom,

$$\sum_{k=1}^{\mu} e r_k^a Y_a^{\alpha}(\hat{r}_k) \equiv \sum_{k=1}^{\mu} e \mathcal{Y}_a^{\alpha}(\hat{r}_k) \equiv \mathcal{M}_a^{\alpha} \quad (7)$$

represents a multipole moment of order a for the atom with μ valence electrons. For $a = 1$ we shall have the dipole moment operator $\mathcal{M}_1^{\alpha} = \mathcal{D}^{\alpha}$. Here we deal with the states where equivalent electrons exist and (fractional) parentage coefficient schemes⁶ ought to be used for a description of the atomic quantum states. Because the radial integrals will be expressed via oscillator strengths, the angular parts of matrix elements will be calculated down to the reduced matrix elements of a multipole moment for the atom as a whole. In that way we ensure the clear separation between the part of our calculation where the known angular parts of wave functions appear, and the part where experimental values or semiempirical methods (Coulomb approximation, see Appendix) enter for the radial integrals.

By use of the Wigner-Eckart theorem and the concept of the relative line strength,^{5,11} one can derive the following expression for the matrix elements of the first-order electrostatic interaction in the general case:

$$\begin{aligned}
\langle \Psi | W_{\text{es}} | \Psi' \rangle = & (-)^{S_A+S_B-\Omega} \sum_{a,b} \frac{4\pi}{R^{a+b+1}} \frac{(-)^b (a+b)!}{[(2a+1)(2b+1)]^{1/2}} \\
& \times \left[\frac{(2J_A+1)(2J'_A+1)}{(2S_A+1)} \right]^{1/2} \begin{Bmatrix} L_A & J_A & S_A \\ J'_A & L'_A & a \end{Bmatrix} \langle nL(S) || \mathcal{M}_a(\mathbf{r}_A) || n'L'(S') \rangle_A \delta_{S_A S'_A} \\
& \times \left[\frac{(2J_B+1)(2J'_B+1)}{(2S_B+1)} \right]^{1/2} \begin{Bmatrix} L_B & J_B & S_B \\ J'_B & L'_B & b \end{Bmatrix} \langle nL(S) || \mathcal{M}_b(\mathbf{r}_B) || n'L'(S') \rangle_B \delta_{S_B S'_B} \\
& \times \sum_{\alpha} \begin{Bmatrix} J'_A & a & J_A \\ M'_A & -\alpha & -M_A \end{Bmatrix} \begin{Bmatrix} J'_B & b & J_B \\ M'_B & \alpha & -M_B \end{Bmatrix} \frac{1}{[(a-\alpha)!(a+\alpha)!(b-\alpha)!(b+\alpha)!]^{1/2}}, \tag{8}
\end{aligned}$$

with the notation abbreviated as in (5):

$$\langle n_A L_A(S_A) || \mathcal{M}_a(\mathbf{r}_A) || n'_A L'_A(S'_A) \rangle = \langle nL(S) || \mathcal{M}_a(\mathbf{r}_A) || n'L'(S') \rangle_A.$$

Here, $|\Psi\rangle$ and $|\Psi'\rangle$ are of form (5). We have put the spin number (S) in parentheses to remind us that the reduced matrix element (relative multiplet line strength) depends on the way of coupling of the electronic angular momenta in a total orbital (L) and spin (S) angular momentum of the atom. The specialization for the dipole-dipole interaction ($a=b=1$) gives

$$\begin{aligned}
\langle \Psi | W_{\text{es}}(a=b=1) | \Psi' \rangle = & (-)^{S_A+S_B-\Omega+1} \frac{1}{R^3} \\
& \times \left[\frac{(2J_A+1)(2J'_A+1)}{(2S_A+1)} \right]^{1/2} \begin{Bmatrix} L_A & J_A & S_A \\ J'_A & L'_A & 1 \end{Bmatrix} | \langle nL(S) || D_A || n'L'(S') \rangle_A | \delta_{S_A S'_A} \\
& \times \left[\frac{(2J_B+1)(2J'_B+1)}{(2S_B+1)} \right]^{1/2} \begin{Bmatrix} L_B & J_B & S_B \\ J'_B & L'_B & 1 \end{Bmatrix} | \langle nL(S) || D_B || n'L'(S') \rangle_B | \delta_{S_B S'_B} \\
& \times \sum_{\alpha} \begin{Bmatrix} J'_A & 1 & J_A \\ M'_A & -\alpha & -M_A \end{Bmatrix} \begin{Bmatrix} J'_B & 1 & J_B \\ M'_B & \alpha & -M_B \end{Bmatrix} \frac{2}{(1-\alpha)!(1+\alpha)!}. \tag{9}
\end{aligned}$$

Considering the sign, note that the absolute values of reduced matrix elements are given for straightforward substitution of square roots of oscillator strengths.

On the other hand, the matrix elements of the dispersive potential V_{dis} are of the form

$$\begin{aligned}
\langle \Psi | V_{\text{dis}} | \Psi'' \rangle &= \sum_{\substack{n'_A, L'_A, J'_A \\ n'_B, L'_B, J'_B}} \sum_{\substack{a, a', \alpha \\ b, b', \alpha'}} \delta_{S_A S'_A} \delta_{S_B S'_B} (-)^{J_A+J'_A+L_A+L'_A-M_A-M'_A+J_B+J'_B+L_B+L'_B-M_B-M'_B} \frac{16\pi^2}{R^{a+b+a'+b'+2}} \\
& \times \frac{(a+b)!(a'+b')![(2J_A+1)(2J'_A+1)(2J_B+1)(2J'_B+1)]^{1/2}(2J'_A+1)(2J'_B+1)}{\{(2a+1)(2b+1)(2a'+1)(2b'+1)[(a-\alpha)!(a+\alpha)!(b-\alpha)!(b+\alpha)!(a'-\alpha)!(a'+\alpha)!(b'-\alpha)!(b'+\alpha)!]\}^{1/2}} \\
& \times \begin{Bmatrix} J_A & L_A & S_A \\ L'_A & J'_A & a \end{Bmatrix} \begin{Bmatrix} J_B & L_B & S_B \\ L'_B & J'_B & b \end{Bmatrix} \begin{Bmatrix} J'_A & L'_A & S_A \\ L''_A & J''_A & a' \end{Bmatrix} \begin{Bmatrix} J'_B & L'_B & S_B \\ L''_B & J''_B & b' \end{Bmatrix} \\
& \times \begin{Bmatrix} J_A & a & J'_A \\ -M_A & -\alpha & M'_A \end{Bmatrix} \begin{Bmatrix} J_B & b & J'_B \\ -M_B & \alpha & M'_B \end{Bmatrix} \begin{Bmatrix} J'_A & a' & J''_A \\ -M'_A & -\alpha' & M''_A \end{Bmatrix} \begin{Bmatrix} J'_B & b' & J''_B \\ -M'_B & \alpha' & M''_B \end{Bmatrix} \\
& \times \frac{\langle nL(S) || \mathcal{M}_a || n'L'(S) \rangle_A \langle n'L'(S) || \mathcal{M}_{a'} || n''L''(S) \rangle_A \langle nL(S) || \mathcal{M}_b || n'L'(S) \rangle_B \langle n'L'(S) || \mathcal{M}_{b'} || n''L''(S) \rangle_B}{(E_{(nSLJ)}^A - E_{(n'SL'J')}^A + E_{(nSLJ)}^B - E_{(n'SL'J')}^B)}. \tag{10}
\end{aligned}$$

To get further simplification of (10) one should specify the order of multipoles in the interaction. Also, the approximation $E_{(nLSJ)} \approx E_{(nL)}$ is made in the cases where the differences of weighted energies of the multiplets [under the summation sign in (10)] are much larger than the energy differences between the components of fine structure for each atom. In our case, this approximation brought in an error of at most 5%. Because of the summation over J this is actually a much better approximation. Also, let atom B be in its ground state such that $L_B=0$, $J_B=S_B$, then we can write

$$\begin{aligned} & \langle \Psi | V_{\text{dis}} | \Psi'' \rangle \\ &= \delta_{S_A S_A''} \delta_{S_B S_B''} \delta_{M_A M_A''} \delta_{M_B M_B''} [(2J_A+1)(2J_A''+1)]^{1/2} \frac{1}{R^6} \\ & \times \sum_{\substack{n'_A \neq n_A \\ L'_A}} \sum_{\substack{n'_B \neq n_B \\ L'_B=1}} \frac{1}{(2L'_B+1)} \left[\frac{\delta_{L_A L'_A} \delta_{J_A J'_A}}{(2L_A+1)(2J_A+1)} + 3 \sum_{M_{L_A}} \begin{Bmatrix} L_A & S_A & J_A \\ M_{L_A} & (-M_{L_A}+M_{J_A}) & -M_{J_A} \end{Bmatrix} \right. \\ & \quad \times \begin{Bmatrix} L''_A & S_A & J''_A \\ M_{L_A} & (-M_{L_A}+M_{J_A}) & -M_{J_A} \end{Bmatrix} \left. \begin{Bmatrix} L'_A & L_A & 1 \\ -M_{L_A} & M_{L_A} & 0 \end{Bmatrix} \begin{Bmatrix} L'_A & L'_A & 1 \\ -M_{L_A} & M_{L_A} & 0 \end{Bmatrix} \right] \\ & \times \frac{\langle nL(S) \| D_A \| n'L'(S) \rangle_A \langle n'L'(S) \| D_A \| n''L''(S) \rangle_A \langle nL(S) \| D_B \| n'L'(S) \rangle_B \langle n'L'(S) \| D_B \| n''L''(S) \rangle_B}{(E_{(nSL)}^A - E_{(n'SL')}^A + E_{(nSL)}^B - E_{(n'SL')}^B)}. \quad (11) \end{aligned}$$

The angular parts of the matrix elements of the effective Hamiltonian can now be calculated up to the second order of perturbation by substitution of wave functions in the formulas (8) [(9)] and (10) [(11)] for general (dipole-dipole) interaction, respectively. For the case of the quasimolecule Eu-Sr the set of basis functions is presented in Table I.

Let us now denote the product of reduced matrix elements of dipole moment by

$$| \langle nL(S) \| D_A \| n'L'(S) \rangle_A \langle nL(S) \| D_B \| n'L'(S) \rangle_B | = \mathcal{C}_3 \quad (12)$$

and the sums of the products in (11) by

$$\sum_{\substack{n'_A \neq n_A \\ n'_B \neq n_B}} \frac{|\langle nL(S) \| D_A \| n'L'(S) \rangle_A|^2 |\langle n0(S) \| D_B \| n'1(S) \rangle_B|^2}{(E_{(nSL)}^A - E_{(n'SL')}^A + E_{(nSL)}^B - E_{(n'SL')}^B)} = \begin{cases} \mathcal{S}^A; & L_A=1, L'_A=0 \\ \mathcal{D}^A; & L_A=1, L'_A=2 \\ \mathcal{P}; & L_A=0, L'_A=L'_B=1 \end{cases} \quad (A, B = \text{Eu, Sr}). \quad (13)$$

Formula (13) is written for atom B initially being in its ground state ($L_B=0$, $L'_B=1$). For the sums \mathcal{S} the additional condition exists: the resonance transitions in atoms must be excluded, i.e., $n'_A \neq n_A^0$ and $n'_B \neq n_B^*$ in formula (13). \mathcal{P} stands for the case where both atoms are initially and finally in the ground state, and it describes the interaction potential of the ground state of a quasimolecule. The values of reduced matrix elements defined in (12) and (13) can be calculated by means of atomic oscillator strengths, which are presented in the Appendix for Eu and Sr atoms. For the Eu-Sr quasimolecule, the results of radial parts are presented in Table II. The figures quoted there were obtained by prior use of experi-

mentally measured oscillator strengths (when available). The uncertainties were estimated by comparing the values calculated via experimental and theoretical oscillator strengths and/or the values obtained by the use of different possible coupling schemes for Eu terms (see Appendix).

Now we shall present the symmetric matrices of the effective Hamiltonian or, in other words, the C_3 and C_6 constants for the Eu-Sr system. The matrix element $M_{ii'}(\Omega)$ means the transition among different states of Ω symmetry, distinguished by indices i and i' , the selection rule for the quantum number Ω being $\Delta\Omega=0$ [see formulas (8)–(11)]. The submatrices are as follows.

$\Omega = \frac{3}{2}$:

$$\left[\begin{array}{c}
 \frac{5}{18} \delta^{\text{Eu}} + \frac{41}{180} \mathcal{D}^{\text{Eu}} \\
 E_{J=3/2}^{\text{Eu}} + \frac{\quad}{R^6} \\
 \\
 -\frac{1}{3\sqrt{14}} \delta^{\text{Eu}} - \frac{1}{30\sqrt{14}} \mathcal{D}^{\text{Eu}} \\
 \\
 E_{J=7/2}^{\text{Eu}} + \frac{\frac{10}{63} \delta^{\text{Eu}} + \frac{68}{315} \mathcal{D}^{\text{Eu}}}{R^6} \\
 \\
 -\frac{1}{6} \sqrt{5/7} \delta^{\text{Eu}} - \frac{1}{60} \sqrt{5/7} \mathcal{D}^{\text{Eu}} \\
 \\
 E_{J=5/2}^{\text{Eu}} + \frac{\frac{29}{126} \delta^{\text{Eu}} + \frac{281}{1260} \mathcal{D}^{\text{Eu}}}{R^6} \\
 \\
 E_{J=5/2}^{\text{Sr}} + \frac{\frac{1}{9} \delta^{\text{Sr}} + \frac{19}{90} \mathcal{D}^{\text{Sr}}}{R^6} \\
 \\
 E_{J=5/2}^{\text{Sr}} + \frac{\frac{4}{9} \delta^{\text{Sr}} + \frac{11}{45} \mathcal{D}^{\text{Sr}}}{R^6} \\
 \\
 E_{J=5/2}^{\text{Sr}} + \frac{\frac{1}{9} \delta^{\text{Sr}} + \frac{19}{90} \mathcal{D}^{\text{Sr}}}{R^6}
 \end{array} \right];$$

$\Omega = \frac{1}{2}$:

$$\left[\begin{array}{c}
 \frac{8}{27} \delta^{\text{Eu}} + \frac{31}{135} \mathcal{D}^{\text{Eu}} \\
 E_{J=9/2}^{\text{Eu}} + \frac{\quad}{R^6} \\
 \\
 -\frac{1}{27} \sqrt{5/7} - \frac{1}{270} \sqrt{5/7} \mathcal{D}^{\text{Eu}} \\
 \\
 E_{J=7/2}^{\text{Eu}} + \frac{\frac{22}{189} \delta^{\text{Eu}} + \frac{40}{189} \mathcal{D}^{\text{Eu}}}{R^6} \\
 \\
 -\frac{1}{9} \sqrt{15/7} \delta^{\text{Eu}} - \frac{1}{90} \sqrt{15/7} \mathcal{D}^{\text{Eu}} \\
 \\
 E_{J=5/2}^{\text{Eu}} + \frac{\frac{\sqrt{3}}{63} \delta^{\text{Eu}} + \frac{\sqrt{3}}{630} \mathcal{D}^{\text{Eu}}}{R^6} \\
 \\
 E_{J=5/2}^{\text{Sr}} + \frac{\frac{16}{63} \delta^{\text{Sr}} + \frac{71}{315} \mathcal{D}^{\text{Sr}}}{R^6} \\
 \\
 E_{J=5/2}^{\text{Sr}} + \frac{\frac{1}{9} \delta^{\text{Sr}} + \frac{19}{90} \mathcal{D}^{\text{Sr}}}{R^6} \\
 \\
 E_{J=5/2}^{\text{Sr}} + \frac{\frac{4}{9} \delta^{\text{Sr}} + \frac{11}{45} \mathcal{D}^{\text{Sr}}}{R^6} \\
 \\
 E_{J=5/2}^{\text{Sr}} + \frac{\frac{1}{9} \delta^{\text{Sr}} + \frac{19}{90} \mathcal{D}^{\text{Sr}}}{R^6}
 \end{array} \right].$$

TABLE I. Basis set of wave functions in the coupled approximation for the quasimolecular system Eu-Sr. The wave function (not an eigenfunction) is completely specified by Ω and index i .

| Basis set $ n, (LS)JM\rangle_{\text{Eu}}$ | $ n, (LS)JM\rangle_{\text{Sr}}$ | J | Ω | Index i |
|--|---------------------------------|---------------|---------------|-----------|
| Ground state | | | | |
| $ 6, (0, \frac{7}{2}, \frac{7}{2}, \frac{7}{2})\rangle$ | $ 5, (0,0)0,0\rangle$ | $\frac{7}{2}$ | $\frac{7}{2}$ | |
| $ 6, (0, \frac{7}{2}, \frac{7}{2}, \frac{5}{2})\rangle$ | $ 5, (0,0)0,0\rangle$ | | $\frac{5}{2}$ | |
| $ 6, (0, \frac{7}{2}, \frac{7}{2}, \frac{3}{2})\rangle$ | $ 5, (0,0)0,0\rangle$ | | $\frac{3}{2}$ | |
| $ 6, (0, \frac{7}{2}, \frac{7}{2}, \frac{1}{2})\rangle$ | $ 5, (0,0)0,0\rangle$ | | $\frac{1}{2}$ | |
| Resonant state | | | | |
| $ 6, (1, \frac{7}{2}, \frac{9}{2}, \frac{9}{2})\rangle$ | $ 5, (0,0)0,0\rangle$ | $\frac{9}{2}$ | $\frac{9}{2}$ | 1 |
| $ 6, (0, \frac{7}{2}, \frac{7}{2}, \frac{7}{2})\rangle$ | $ 5, (1,0)1,1\rangle$ | $\frac{9}{2}$ | | 2 |
| $ 6, (1, \frac{7}{2}, \frac{9}{2}, \frac{7}{2})\rangle$ | $ 5, (0,0)0,0\rangle$ | $\frac{9}{2}$ | $\frac{7}{2}$ | 1 |
| $ 6, (1, \frac{7}{2}, \frac{7}{2}, \frac{7}{2})\rangle$ | $ 5, (0,0)0,0\rangle$ | $\frac{7}{2}$ | $\frac{7}{2}$ | 2 |
| $ 6, (0, \frac{7}{2}, \frac{7}{2}, \frac{5}{2})\rangle$ | $ 5, (1,0)1,1\rangle$ | $\frac{9}{2}$ | | 3 |
| $ 6, (0, \frac{7}{2}, \frac{7}{2}, \frac{3}{2})\rangle$ | $ 5, (1,0)1,0\rangle$ | $\frac{7}{2}$ | | 4 |
| $ 6, (1, \frac{7}{2}, \frac{9}{2}, \frac{5}{2})\rangle$ | $ 5, (0,0)0,0\rangle$ | $\frac{9}{2}$ | $\frac{5}{2}$ | 1 |
| $ 6, (1, \frac{7}{2}, \frac{7}{2}, \frac{5}{2})\rangle$ | $ 5, (0,0)0,0\rangle$ | $\frac{7}{2}$ | $\frac{5}{2}$ | 2 |
| $ 6, (1, \frac{7}{2}, \frac{5}{2}, \frac{5}{2})\rangle$ | $ 5, (0,0)0,0\rangle$ | $\frac{5}{2}$ | $\frac{5}{2}$ | 3 |
| $ 6, (0, \frac{7}{2}, \frac{7}{2}, \frac{3}{2})\rangle$ | $ 5, (1,0)1,1\rangle$ | $\frac{9}{2}$ | | 4 |
| $ 6, (0, \frac{7}{2}, \frac{7}{2}, \frac{5}{2})\rangle$ | $ 5, (1,0)1,0\rangle$ | $\frac{7}{2}$ | | 5 |
| $ 6, (0, \frac{7}{2}, \frac{7}{2}, \frac{1}{2})\rangle$ | $ 5, (1,0)1, -1\rangle$ | $\frac{5}{2}$ | | 6 |
| $ 6, (1, \frac{7}{2}, \frac{9}{2}, \frac{3}{2})\rangle$ | $ 5, (0,0)0,0\rangle$ | $\frac{9}{2}$ | $\frac{3}{2}$ | 1 |
| $ 6, (1, \frac{7}{2}, \frac{7}{2}, \frac{3}{2})\rangle$ | $ 5, (0,0)0,0\rangle$ | $\frac{7}{2}$ | $\frac{3}{2}$ | 2 |
| $ 6, (1, \frac{7}{2}, \frac{5}{2}, \frac{3}{2})\rangle$ | $ 5, (0,0)0,0\rangle$ | $\frac{5}{2}$ | $\frac{3}{2}$ | 3 |
| $ 6, (0, \frac{7}{2}, \frac{7}{2}, \frac{1}{2})\rangle$ | $ 5, (1,0)1,1\rangle$ | $\frac{9}{2}$ | | 4 |
| $ 6, (0, \frac{7}{2}, \frac{7}{2}, \frac{3}{2})\rangle$ | $ 5, (1,0)1,0\rangle$ | $\frac{7}{2}$ | | 5 |
| $ 6, (0, \frac{7}{2}, \frac{7}{2}, \frac{5}{2})\rangle$ | $ 5, (1,0)1, -1\rangle$ | $\frac{5}{2}$ | | 6 |
| $ 6, (1, \frac{7}{2}, \frac{9}{2}, \frac{1}{2})\rangle$ | $ 5, (0,0)0,0\rangle$ | $\frac{9}{2}$ | $\frac{1}{2}$ | 1 |
| $ 6, (1, \frac{7}{2}, \frac{7}{2}, \frac{1}{2})\rangle$ | $ 5, (0,0)0,0\rangle$ | $\frac{7}{2}$ | $\frac{1}{2}$ | 2 |
| $ 6, (1, \frac{7}{2}, \frac{5}{2}, \frac{1}{2})\rangle$ | $ 5, (0,0)0,0\rangle$ | $\frac{5}{2}$ | $\frac{1}{2}$ | 3 |
| $ 6, (0, \frac{7}{2}, \frac{7}{2}, -\frac{1}{2})\rangle$ | $ 5, (1,0)1,1\rangle$ | $\frac{9}{2}$ | | 4 |
| $ 6, (0, \frac{7}{2}, \frac{7}{2}, \frac{1}{2})\rangle$ | $ 5, (1,0)1,0\rangle$ | $\frac{7}{2}$ | | 5 |
| $ 6, (0, \frac{7}{2}, \frac{7}{2}, \frac{3}{2})\rangle$ | $ 5, (1,0)1, -1\rangle$ | $\frac{5}{2}$ | | 6 |

TABLE II. Radial parts of the C_3 (12) and C_6 (13) constants.

| Transition and state | Constant designation | Radial integral | Δ (%) |
|----------------------|-------------------------------|---------------------------------------|--------------|
| Eu*-Sr Eu-Sr* | $C_3 \mathcal{C}_3$ | $823.9 \text{ cm}^{-1} \text{ nm}^3$ | 2 |
| Eu*-Sr | $C_6 \mathcal{D}^{\text{Eu}}$ | $-31.4 \text{ cm}^{-1} \text{ nm}^6$ | 30 |
| | $C_6 \mathcal{D}^{\text{Eu}}$ | $-46.7 \text{ cm}^{-1} \text{ nm}^6$ | 6 |
| Eu-Sr* | $C_6 \mathcal{D}^{\text{Sr}}$ | $-24.8 \text{ cm}^{-1} \text{ nm}^6$ | 10 |
| | $C_6 \mathcal{D}^{\text{Sr}}$ | $-142.4 \text{ cm}^{-1} \text{ nm}^6$ | 6 |
| Eu-Sr | $C_6 \mathcal{P}$ | $-17.9 \text{ cm}^{-1} \text{ nm}^6$ | 10 |

III. ADIABATIC POTENTIAL CURVES

When C_3 and C_6 constants are known, the adiabatic potential curves will result from a diagonalization of $H_{\text{eff}}(R)$. The quasimolecular potential curves are shown in Fig. 1. The ground state is nearly constant in the region of interest due to the relatively small value of the corresponding ground C_6 constant \mathcal{P} . As the internuclear distance R decreases, the potential curves tend to group with respect to the symmetries of the uncoupled approximation (Hund's coupling case a —the electrostatic interaction much stronger than spin-orbit coupling of the atom). These symmetries are $^8\Sigma^+$ (ground state); $^8\Sigma^+$, $^8\Pi$, $^8\Pi$, $^8\Sigma^+$ (excited states), and will show up also for the molecular oscillator strengths. Note that not all potential curves from the asymptote $\text{Eu}^*(J=\frac{9}{2})$ tend to the $^8\Sigma^+$ state. The lowest one, which corresponds to the quasimolecular state $\Omega=\frac{9}{2}$, $\gamma=2$, has different symmetry, $^8\Pi$. (Warning: do not mix the good quantum mechanical number γ with the wave function index i in Table I.) Only one more potential [$\Omega=\frac{7}{2}$, $\gamma=1$, from level $\text{Eu}^*(J=\frac{7}{2})$] changes its symmetry compared to the others from the same asymptote.

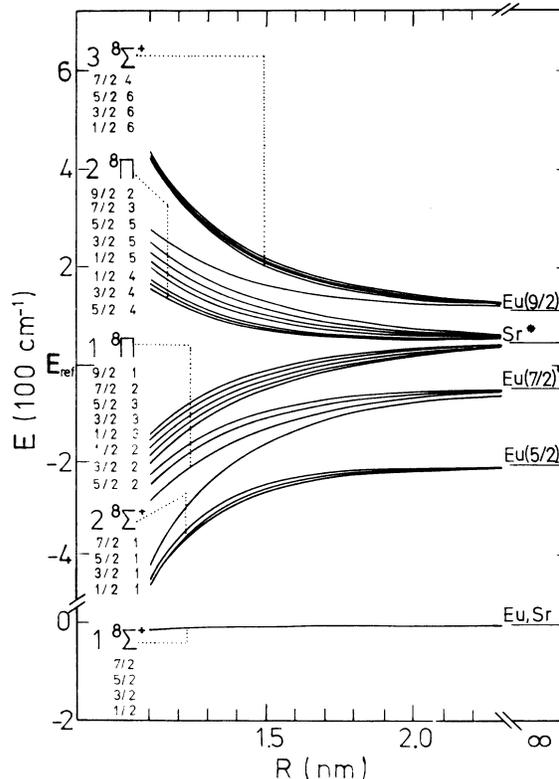


FIG. 1. Adiabatic potential curves for the quasimolecular system Eu-Sr. On the vertical axis the energy above and below the reference level ($E_{\text{ref}}=21\,651.076 \text{ cm}^{-1}$) is denoted. As R decreases, 24 potentials, obtained in the coupled representation, group in four different symmetry states according to the uncoupled representation. The quasimolecular states are denoted by quantum numbers ($\Omega\gamma$). Note how great changes occur for the resonant levels compared to the nearly constant ground state.

It is very instructive to draw the adiabatic potential curves versus R^{-3} (Fig. 2). On such plots one can inspect the character of potentials, since in the region of domination of the van der Waals interaction the potential curves are parabolic, and in the region of domination of the resonance interaction the potential curves are straight lines.

In Fig. 2 one can see that the transition from van der Waals to resonance interaction is a common property of all potentials for the quasimolecule Eu-Sr and reinforce the discussion of Niemax.¹ The region of transition moves toward smaller distances for the potentials with lower energies. For the group of potentials with symmetry ${}^3\Sigma^+$, it happens at about 1.7–2.0 nm, and for ${}^1\Sigma^+$ at about 1.2–1.4 nm (here the region of domination of the resonance interaction is very short).

For the potential curves that have the same uncoupled symmetry but originate from different asymptotes, the great mutual interaction results in a complex behavior, i.e., intensive competition of contributions of different character: repulsive versus attractive, van der Waals versus resonance. This is especially noticeable for the following states denoted as (Ω, γ) : $(\frac{9}{2}, 2)$, $(\frac{7}{2}, 3)$, $(\frac{1}{2}, 3)$, and $(\frac{3}{2}, 3)$.

One case where the type of interaction (resonance or van der Waals) that can be approximately foreseen analytically is for the 2×2 submatrices (in our case it is for $\Omega = \frac{9}{2}$). This matrix is for the heteronuclear system of the following form:

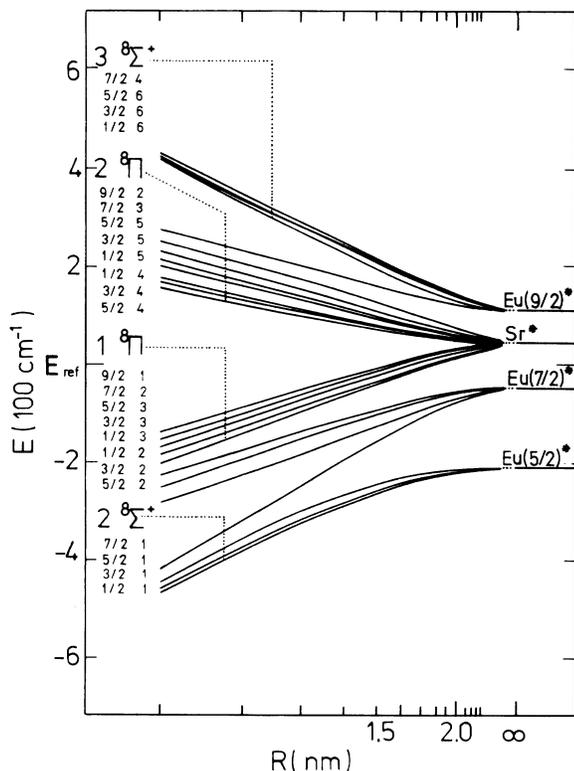


FIG. 2. Adiabatic potential curves vs R^{-3} . The resonance interaction ($\sim R^{-3}$) appears as straight lines and the van der Waals interaction ($\sim R^{-6}$) as parabolic curves (see text).

$$\begin{pmatrix} E_A + \frac{C_6^A}{R^6} & \frac{C_3}{R^3} \\ & E_B + \frac{C_6^B}{R^6} \end{pmatrix}. \quad (14)$$

We choose our quasidegenerate (reference) level to be in the middle of E_A and E_B levels and put it to be 0, i.e.,

$$(E_A + E_B)/2 = E_{\text{ref}}, \quad E_A = -E_B = \Delta E/2.$$

Thus, for eigenvalues, we get

$$V_{1,2}(R) = \frac{C_6^A + C_6^B}{2R^6} \pm \frac{1}{2} \left[\left[\frac{C_6^A - C_6^B}{R^6} + \Delta E \right]^2 + \frac{4C_3^2}{R^6} \right]^{1/2}. \quad (15)$$

If the system under consideration had been homonuclear ($A = B$), an additional term of resonance character would have appeared on the diagonal in (14) and the expression for the eigenvalues would read

$$V_{1,2}^{(A=B)}(R) = \frac{C_6}{R^6} + \frac{C_3'}{R^3} \pm \left[\frac{\Delta E}{4} + \left[\frac{C_3}{R^3} \right]^2 \right]^{1/2}. \quad (15')$$

Here it is easily seen that for great (small) interatomic distances the resonance (van der Waals) interaction will dominate.

Let us go back to the heteronuclear systems. For large distances where

$$R \gg \left| \frac{C_6^A - C_6^B}{\Delta E} \right|^{1/6} = R_0, \quad (16)$$

the first term, in parentheses under the square root in (15), can be neglected compared to the ΔE . Now by simple calculation we can get the condition for the domination of resonance interaction:

$$V \approx \pm \frac{C_3}{R^3} \quad (17a)$$

for distances

$$\left| \frac{C_6^A + C_6^B}{C_3} \right|^{1/3} = R_1 \ll R \ll R_2 = \left| \frac{C_3}{\Delta E} \right|^{1/3}, \quad (R_1, R_2 \gg R_0). \quad (17b)$$

For $R \gg R_2$ the adiabatic potential curves can be written as

$$V_{1,2}(R) \approx \frac{C_6^A + C_6^B}{2R^6} \pm \frac{C_3^2}{\Delta E R^6} \pm \frac{1}{2} \Delta E, \quad (18)$$

and competition between the attractive and repulsive potentials will occur (C_6 constants are negative in 2×2 submatrices). Here we can see how C_3 constants contribute to the potentials that behave like R^{-6} .

For $R \ll R_1$ another region of van der Waals interaction domination emerges, but now only due to the C_6 constants and, consequently, of attractive character. The

unfulfillment of the condition in (17) may cause the resonance interaction to be weak compared to the van der Waals interaction, which is, in fact, the case for a great majority of heteronuclear systems. More often than not, R_2 is smaller than R_1 , or R_2 falls in the region of exchange effects.

In the case of the Eu-Sr quasimolecule, one obtains $R_0 \approx 0.8$ nm, $R_1 \approx 0.6$ nm, and $R_2 \approx 1.6$ nm. It turns out that $R_0 > R_1$, i.e., R_1 does not fulfill the condition in the parentheses in (17), but it is quite obvious that in the region of about 1.0–1.6 nm we shall have the domination of resonance interaction. At about 2.0 nm, the intense van der Waals interaction occurs that will prolong itself up to infinity.

IV. MOLECULAR OSCILLATOR STRENGTHS

Besides the eigenvalues of H_{eff} , we are also interested in the eigenvectors, i.e., the eigenfunctions of perturbed states. After having them, we shall look at the matrix elements of the electronic dipole moment operator between certain electronic states of a quasimolecule, in order to get the absorption coefficient (see Sec. V). It is usual to define the molecular oscillator strength for a transition $|\psi\rangle \rightarrow |\psi'\rangle$ in strict analogy to the atomic oscillator strength

$$f_{(\psi \rightarrow \psi')} = \frac{2m}{3\hbar^2 e^2} \frac{(E_{\psi'} - E_{\psi})}{g_{\psi}} \sum_{\alpha, \alpha'} |\langle \Psi_{\alpha} | \mathbf{D}_{\text{mol}} | \Psi'_{\alpha'} \rangle|^2. \quad (19)$$

Here $|\psi\rangle$ and $|\psi'\rangle$ are initial- and final-state wave functions, and g_{ψ} is the multiplicity of the initial state. The sum is taken over the sublevels of initial and final states. We are interested in the molecular transitions from the ground state to the states where one of the atoms is in a resonance state. For the ground state we rewrite the ket vector simply as

$$|\Omega_0 \gamma_0\rangle = |L_A^0 S_A^0 J_A^0 M_A^0\rangle |L_B^0 S_B^0 J_B^0 M_B^0\rangle. \quad (20)$$

In an excited state of a quasimolecule, the wave functions will be certain linear combinations of basis vectors (for the Eu-Sr quasimolecule presented in Table I):

$$|\Omega \gamma\rangle = \sum_{i=1}^n \mathcal{B}_{i\gamma} |\Omega i\rangle, \quad (21)$$

where $\mathcal{B}_{i\gamma}$ is a matrix element of the $n \times n$ submatrix of eigenvectors written by columns. Now we search for the matrix elements of the molecular dipole moment that can be written in a first approximation simply as $\mathbf{D}_{\text{mol}} = \mathbf{D}_A + \mathbf{D}_B$. \mathbf{D}_{mol} is decomposed into spherical components, and the calculation gives the expression for $\langle \Omega_0 \gamma_0 | \mathbf{D}_{\text{mol}} | \Omega \gamma \rangle$ in terms of the atomic dipole momenta, i.e., the molecular oscillator strengths in terms of the atomic oscillator strengths:

$$\begin{aligned} f(\Omega_0 \gamma_0 J_0 \rightarrow \Omega \gamma) &= \frac{2(E_{(\Omega \gamma)} - E_{(\Omega_0 \gamma_0)})}{2J_0 + 1} \\ &\times \sum_i \left[(2J_A^0 + 1) \begin{Bmatrix} J_A^0 & 1 & J_A \\ L_A & S_A & L_A^0 \end{Bmatrix} \frac{(2L_A^0 + 1)}{\Delta E^A} f^A \mathcal{B}_{i\gamma}^2 \delta_{AA^*} \right. \\ &\quad \left. + (2J_B + 1) \begin{Bmatrix} J_B^0 & 1 & J_B \\ L_B & S_B & L_B^0 \end{Bmatrix} \frac{(2L_B^0 + 1)}{\Delta E^B} f^B \mathcal{B}_{i\gamma}^2 \delta_{BB^*} \right. \\ &\quad \left. + 2 \sum_{i'} \sum_{\Omega^0} (-)^{M_A^0 + M_B^0 + 2J_A^0 + 2J_B^0 + S_A + S_B + L_A^0 + L_B} [(2J_A^0 + 1)(2J_A + 1)(2J_B^0 + 1)(2J_B + 1)]^{1/2} \right. \\ &\quad \times \begin{Bmatrix} J_A^0 & L_A^0 & S_A \\ L_A & J_A & 1 \end{Bmatrix} \begin{Bmatrix} J_B & L_B & S_B \\ L_B^0 & J_B^0 & 1 \end{Bmatrix} \begin{Bmatrix} J_A^0 & 1 & J_A \\ M_A^0 & -q_A & -M_A \end{Bmatrix} \begin{Bmatrix} J_B^0 & 1 & J_B \\ M_B^0 & -q_B & -M_B \end{Bmatrix} \\ &\quad \left. \times \left[(2L_A^0 + 1)(2L_B^0 + 1) \frac{f^A f^B}{\Delta E^A \Delta E^B} \right]^{1/2} \mathcal{B}_{i\gamma} \mathcal{B}_{i'\gamma} \delta_{q_A q_B} \right]. \quad (22) \end{aligned}$$

We have denoted $\Delta E^I = E_{(\alpha SL)}^I - E_{(\alpha^0 S^0 L^0)}^I$, $f^I = f_{(\alpha^0 S^0 L^0 \rightarrow \alpha SL)}^I$, $\delta_{II^*} = 1$ when $|L_I S_I J_I\rangle$ is an excited (resonance) state, and $\delta_{II^*} = 0$ for $|L_I S_I J_I\rangle = |L_I^0 S_I^0 J_I^0\rangle$. Also, it is implicitly supposed that just one atom at a time is in the excited state.

The sign in the formula for molecular oscillator strengths must be consistent with the signs in formulas for matrix elements of H (Sec. II). It is, in fact, the choice of phase which is arbitrary but has to be the same throughout the calculation. Practically speaking, when using the Wigner-Eckart theorem and Racah algebra the kets $|nLSJ\rangle$ must not be mixed with the kets $|nSLJ\rangle$. In this paper we have used the form $|nLSJ\rangle$.

If in the ground state of a quasimolecule $l=0$ for both atoms, (21) is simplified to the form

$$\begin{aligned}
f(\Omega_0\gamma_0J_0 \rightarrow \Omega\gamma) &= \frac{2(E_{(\Omega\gamma)} - E_{(\Omega_0\gamma_0)})}{2J_0 + 1} \\
&\times \sum_i \left[\frac{f^A \mathcal{B}_{i\gamma}^2}{(2L_A + 1)\Delta E^A} \delta_{AA^*} + \frac{f^B \mathcal{B}_{i\gamma}^2}{(2L_B + 1)\Delta E^B} \delta_{BB^*} \right. \\
&\quad \left. + 2 \sum_{i'} \sum_{\Omega_0} (-)^{M_A^0 + M_B^0 + J_A + J_B + L_A + L_B} \left[\frac{(2J_A + 1)(2J_B + 1)}{(2L_A + 1)(2L_B + 1)} \right]^{1/2} \right. \\
&\quad \left. \times \begin{bmatrix} J_A^0 & 1 & J_A \\ M_A^0 & -q_A & -M_A \end{bmatrix} \begin{bmatrix} J_B^0 & 1 & J_B \\ M_B^0 & -q_B & -M_B \end{bmatrix} \left[\frac{f^A f^B}{\Delta E^A \Delta E^B} \right]^{1/2} \mathcal{B}_{i\gamma} \mathcal{B}_{i'\gamma} \delta_{q_A q_B} \right]. \tag{23}
\end{aligned}$$

Here it is obvious that $q_A + q_B = 2(\Omega_0 - \Omega)$.

In accordance with the approximation of the basis set of wave functions as a finite set (Table I), we can neglect the R dependence of the energy difference $E_{(\Omega\gamma)} - E_{(\Omega_0\gamma_0)}$ because it is just 1–5% (depending on the particular transition) of the energy of resonance levels. So we write

$$E_{(\Omega\gamma)} - E_{(\Omega_0\gamma_0)} \approx \text{const} \approx \Delta E_A \approx \Delta E_B. \tag{24}$$

Thus, in a first approximation, the R dependence in formulas (23) and (24) remains only in the coefficients $\mathcal{B}_{i\gamma}$ of the eigenvectors. Now, the sum of oscillator strengths of

all the states for a given submatrix Ω will stay constant, and is equal to the sum of oscillator strengths of particular atoms ($f_A + f_B$) divided by the dimension of the effective Hamiltonian (for the Eu-Sr system it is 24) and multiplied by the dimension of the specific submatrix. Consequently, the sum of all the oscillator strengths, for all existing states, is consistent and is equal to the sum of atomic oscillator strengths ($f_A + f_B$). With the abbreviation $\mathcal{B}_{i\gamma} = \langle i \rangle$, $\mathcal{B}_{i\gamma} \mathcal{B}_{i'\gamma} = \langle ii' \rangle$, we list the angular parts of the molecular oscillator strengths for the quasi-molecule Eu-Sr ($\gamma = 1, \dots, n$).

$$\Omega = \frac{n}{2}, \quad n = 2,$$

$$f_{\text{mol}}(\gamma) = \frac{1}{12} [f_A \langle 1 \rangle^2 + f_B \langle 2 \rangle^2 + 2\sqrt{f_A f_B} \langle 12 \rangle]. \tag{25a}$$

$$\Omega = \frac{7}{2}, \quad n = 4,$$

$$\begin{aligned}
f_{\text{mol}}(\gamma) &= \frac{1}{12} \left[f_A (\langle 1 \rangle^2 + \langle 2 \rangle^2) + f_B (\langle 3 \rangle^2 + \langle 4 \rangle^2) \right. \\
&\quad \left. + 2\sqrt{f_A f_B} \left[\frac{\sqrt{7}}{3} \langle 13 \rangle + \frac{\sqrt{2}}{3} \langle 14 \rangle + \frac{\sqrt{2}}{3} \langle 23 \rangle - \frac{\sqrt{7}}{3} \langle 24 \rangle \right] \right]. \tag{25b}
\end{aligned}$$

$$\Omega = \frac{5}{2}, \quad n = 6,$$

$$\begin{aligned}
f_{\text{mol}}(\gamma) &= \frac{1}{12} \left[f_A (\langle 1 \rangle^2 + \langle 2 \rangle^2 + \langle 3 \rangle^2) + f_B (\langle 4 \rangle^2 + \langle 5 \rangle^2 + \langle 6 \rangle^2) \right. \\
&\quad \left. + 2\sqrt{f_A f_B} \left[\frac{1}{2}\sqrt{7/3} \langle 14 \rangle + \frac{\sqrt{14}}{6} \langle 15 \rangle + \frac{1}{6} \langle 16 \rangle + 2\sqrt{2/21} \langle 24 \rangle - \frac{5}{3\sqrt{7}} \langle 25 \rangle - \frac{\sqrt{2}}{3} \langle 26 \rangle \right. \right. \\
&\quad \left. \left. + \frac{1}{2\sqrt{7}} \langle 34 \rangle + \frac{1}{2}\sqrt{6/7} \langle 35 \rangle + \frac{\sqrt{3}}{2} \langle 36 \rangle \right] \right]. \tag{25c}
\end{aligned}$$

$$\Omega = \frac{3}{2}, \quad n = 6,$$

$$\begin{aligned}
f_{\text{mol}}(\gamma) &= \frac{1}{12} \left[f_A (\langle 1 \rangle^2 + \langle 2 \rangle^2 + \langle 3 \rangle^2) + f_B (\langle 4 \rangle^2 + \langle 5 \rangle^2 + \langle 6 \rangle^2) \right. \\
&\quad \left. + 2\sqrt{f_A f_B} \left[\frac{1}{2}\sqrt{5/3} \langle 14 \rangle + \frac{1}{\sqrt{2}} \langle 15 \rangle + \frac{1}{2\sqrt{3}} \langle 16 \rangle + \sqrt{10/21} \langle 24 \rangle - \frac{1}{\sqrt{7}} \langle 25 \rangle - 2\sqrt{2/21} \langle 26 \rangle \right. \right. \\
&\quad \left. \left. + \frac{1}{2}\sqrt{3/7} \langle 34 \rangle - \frac{1}{2}\sqrt{10/7} \langle 35 \rangle + \frac{\sqrt{15/7}}{2} \langle 36 \rangle \right] \right]. \tag{25d}
\end{aligned}$$

$$\Omega = \frac{1}{2}, n = 6,$$

$$f_{\text{mol}}(\gamma) = \frac{1}{12} \left[f_A (\langle 1 \rangle^2 + \langle 2 \rangle^2 + \langle 3 \rangle^2) + f_B (\langle 4 \rangle^2 + \langle 5 \rangle^2 + \langle 6 \rangle^2) \right. \\ \left. + 2\sqrt{f_A f_B} \left[\frac{\sqrt{10}}{6} \langle 14 \rangle + \frac{\sqrt{5}}{3} \langle 15 \rangle + \frac{1}{2} \sqrt{2/3} \langle 16 \rangle + \frac{4}{3} \sqrt{2/7} \langle 24 \rangle - \frac{1}{3\sqrt{7}} \langle 25 \rangle \right. \right. \\ \left. \left. - \sqrt{10/21} \langle 26 \rangle + \frac{1}{2} \sqrt{6/7} \langle 34 \rangle - \sqrt{3/7} \langle 35 \rangle + \frac{1}{2} \sqrt{10/7} \langle 36 \rangle \right] \right]. \quad (25e)$$

The results for molecular oscillator strengths are presented in Figs. 3(a)–3(c). As R gets smaller, the values of the molecular oscillator strengths increase for the states of ${}^8_2\Sigma^+$ and ${}^8_2\Pi$ symmetry and decrease for the states of ${}^8_3\Sigma^+$ and ${}^8_1\Pi$ symmetry. There are two asymptotic values of molecular oscillator strengths: $f_A/12$ and $f_B/12$, which can easily be deduced from the expressions (25).

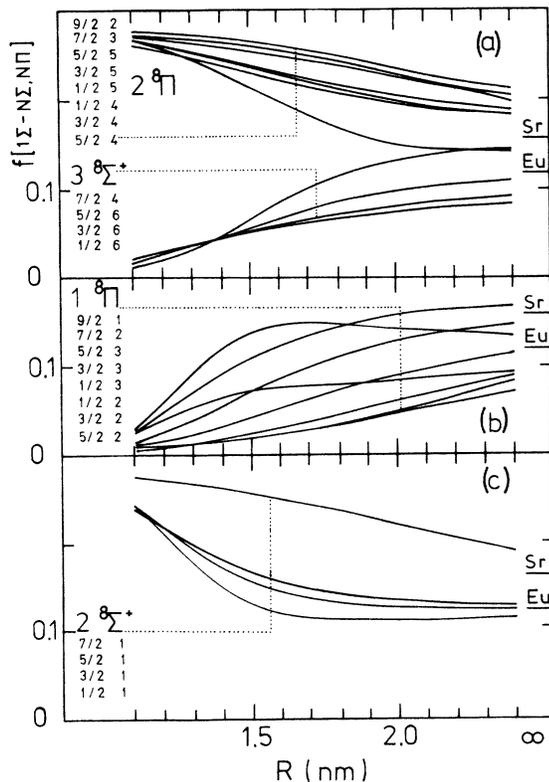


FIG. 3. Molecular oscillator strengths. The highest Σ potential (${}^8_2\Sigma^+$) and lowest Π potentials (${}^8_1\Pi$) correspond to the states which have decreasing oscillator strengths as internuclear distance decreases. In other words, the transitions to these states will be less probable for small R . The lower Σ potentials (${}^8_3\Sigma^+$) and higher Π potentials (${}^8_2\Pi$) correspond to the states with increasing molecular oscillator strengths, i.e., the molecular transitions to these states prevail at small R .

V. QUASISTATIC ABSORPTION COEFFICIENT

In order to construct the absorption line profiles we have analyzed the adiabatic approximation conditions for the relevant adiabatic molecular states. All adiabatic potential curves exhibit monotonic behavior in the region where the calculations are performed, and there is no evident anticrossing among adiabatic potential curves for the states of the same symmetry. We have checked the corresponding Massey parameters for all pairs of molecular states with the same symmetry, for temperatures near 1000 K. All values of Massey parameters are bigger than 70, i.e., the adiabatic approximation is acceptable. Moreover, for temperatures up to a few thousand kelvins, and for interatomic distances larger than 1 nm, we have arrived at the conclusion that the nonadiabatic transitions among the relevant molecular states are negligible. So one can assume that all strong nonadiabatic effects, which are important for the excitation transfer, would occur at the small interatomic distances, below the region of validity of our calculations. Consequently, these effects are of no importance for the construction of the absorption profile in the neighborhood of the Eu and Sr resonance lines.

The quasistatic approximation will be acceptable for neutral gases and vapors at temperatures up to a few thousand kelvins and pressures up to several hundred torr, and the absorption coefficient is given by a simple formula¹²

$$k_{(\Omega_0\gamma_0 \rightarrow \Omega\gamma)} = \frac{4\pi^3 e^2}{mc} N_A N_B \sum_c \frac{f_{\text{mol}}(R_c) R_c^2}{\left| \frac{1}{\hbar} \left[\frac{dV_{(\Omega\gamma - \Omega_0\gamma_0)}}{dR} \right]_{R_c} \right|} \times e^{-E_{(\Omega_0\gamma_0)}(R_c)/kT}. \quad (26)$$

$V_{(\Omega\gamma - \Omega_0\gamma_0)}$ is the differential potential and the summation is over all Condon points R_c defined by the following condition for the photon's frequency ω :

$$\hbar\omega = V_{(\Omega\gamma - \Omega_0\gamma_0)}(R_c).$$

$E_{(\Omega_0\gamma_0)}$ is the energy of initial (ground) state, f_{mol} is the molecular oscillator strength, and the other symbols are conventional.

By calculating the quasistatic absorption coefficient for

the europium line 459.53 nm ($a^8S_{7/2}-y^8P_{9/2}$) broadened by strontium (the line that is experimentally measured by Niemax¹), we can test our theoretical approach. From the behavior of the potentials we can see that only the blue wing is quasistatic, the red one being antistatic. In Fig. 4(a) one can see good relative agreement with the experiment; namely, the experimental absorption coefficient resulted in relative units due to the method of laser induced fluorescence. The experimental curve is matched to the theoretical results at the point $|\Delta\lambda| = 0.1$ nm. The contributions of particular states ($\Omega\gamma$), with the common asymptote $\text{Eu}^* y^8P_{9/2}$, are shown by thin lines. Note how the absorption coefficient, originating from the state $(\frac{9}{2}, 2)$ and having the symmetry $\frac{8}{2}\Pi$, differs from the other states with the same asymptotic energy and makes the greatest contribution to the total absorption coefficient, especially in the far-wing regions. [The same situation is repeated for the state $(\frac{7}{2}, 1)$ of the europium line 462.85 nm.]

The slope of the curve $\log_{10}k = f(\log_{10}|\Delta\lambda|)$ will give the exponent p of a dependence $k(\Delta\lambda) \sim |\Delta\lambda|^p$ and is shown in Fig. 4(b). By approximating the oscillator strengths as being constant in formula (25) one can easily

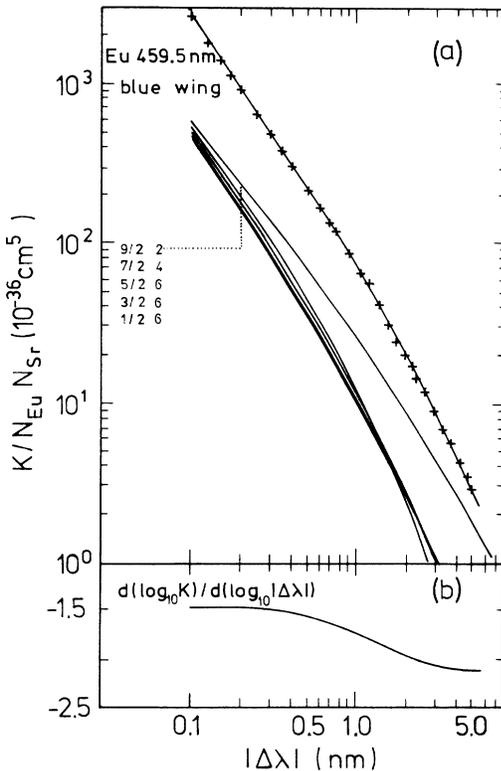


FIG. 4. Quasistatic absorption coefficient (the uppermost line) for the blue wings of the europium line 459.53 nm ($a^8S_{7/2}-y^8P_{9/2}$) broadened by strontium. The crosses denote the experimental values (Ref. 1). The contributions of the states with different Ω symmetry are shown by the five lower lines. (b) The value of the slope of the tangents on the curve in (a). For this spectral line the transition from van der Waals to resonance interaction is not masked by the influence of molecular oscillator strengths.

show that for a differential potential of the form $V \sim R^{-q}$ the quasistatic absorption coefficient is proportional to $|\Delta\lambda|^{-(1+3/2)}$. With this approximate assumption the far wings due to the van der Waals interaction should have the exponent $p \approx -1.5$, and for resonance interaction $p \approx -2$. The differences $p < -2$ for $|\Delta\lambda| > 2.0$ nm originate from the R -dependent molecular oscillator strength.

As we have seen from the analysis of the adiabatic potential curves, the transition from van der Waals to resonance interaction is a general property of the system Eu-Sr. Niemax¹ could not precisely measure the absorption coefficient of the europium line 462.85 nm ($a^8S_{7/2}-y^8P_{7/2}$), broadened by strontium, because the red quasistatic wing was masked by the blue antistatic wing of the line 466.32 nm $\text{Eu}^* (a^8S_{7/2}-y^8P_{5/2})$. For these lines the absorption coefficients are presented in Fig. 5(a). In Fig. 5(b) we can see the behavior of the cor-

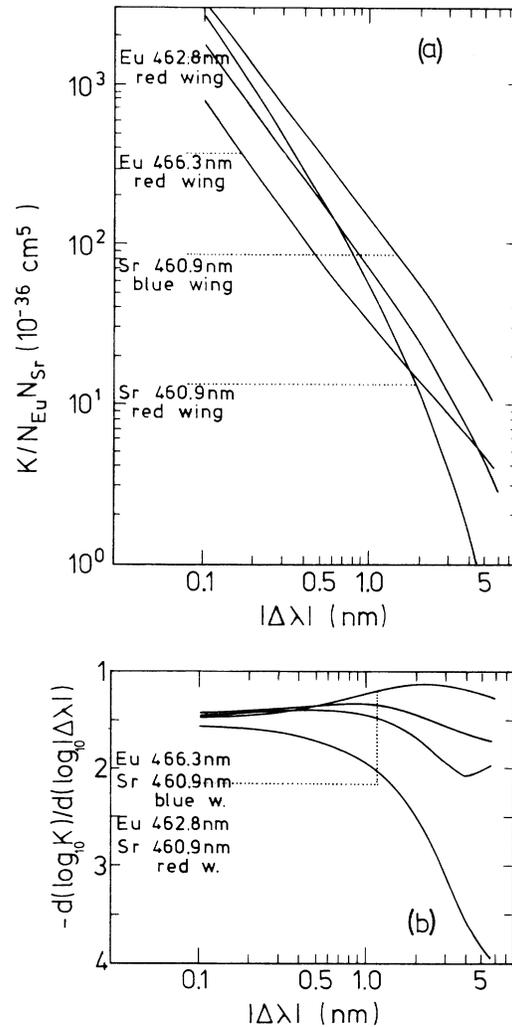


FIG. 5. (a) Quasistatic absorption coefficients and corresponding slopes p for red wings of the europium lines 462.85 nm ($a^8S_{7/2}-y^8P_{7/2}$) and 466.32 nm ($a^8S_{7/2}-y^8P_{5/2}$), broadened by strontium; and for blue and red wings of the strontium line 460.86 nm ($5s^2^1S_0-5s5p^1P_1$) broadened by europium (in mixtures where the concentration of Eu highly exceeds the concentration of Sr).

responding exponents (slopes) p . For the 462.85-nm europium line the slope $p = p(\log_{10} |\Delta\lambda|)$ reflects the character of the potentials (transition from van der Waals to resonance interaction) with a slight peculiarity at the far end. On the other hand, a rather great influence of increasing oscillator strengths can be seen for the line 466.32 nm Eu*, where a small but existing region of domination of the resonance interaction (compare to Fig. 2) cannot be predicted from the line profile alone.

Our calculations also give us the quasistatic blue and red wings of the strontium line 460.86 nm ($5s^2 1S_0 - 5s5p 1P_1$) broadened by europium (Figs. 5). Such a spectrum would be observed from mixtures where the vapor pressures of Eu highly exceed the vapor pressures of Sr (Eu atoms as predominant perturbers, i.e., the conditions just opposite those of the Niemax experiment¹). The transition from van der Waals to resonance interaction is here again masked by rising (falling) oscillator strengths for the blue (red) wing. Especially drastic absorption occurs in the far region ($|\Delta\lambda| > 1.0$ nm) of the red wing. These results still await experimental verification.

VI. DISCUSSION AND CONCLUSION

The perturbation treatment of the electrostatic interaction in a quasimolecular system yields very reliable adiabatic potential curves. The exchange effects can be easily neglected at distances much greater than the sum of atomic radii. In a first approximation the dipole-dipole interaction usually suffices. For angular parts, all that is necessary is to form a basis set for the quantum levels under consideration, and to use the formulas (8) and (9) for the first-order, and formula (11) for the second-order, perturbation calculation. The whole procedure, including the angular parts in algebraic form $a\sqrt{b}/c\sqrt{d}$, is covered by computing algorithms.

The most delicate part is the calculation of radial integrals. If possible, the experimental oscillator strengths ought to be used, at least for the dominant transitions.

The adiabatic potential curves and the molecular oscillator strengths are results of the diagonalization of the effective Hamiltonian (3), i.e., of the submatrices specified by quantum number Ω .

Concerning the quasimolecule Eu-Sr, it is a system with very close resonance levels, so that the electrostatic influence of two atoms results in a strong resonance interaction (C_3 constants are big) that goes like R^{-3} and predominates in the region of 1.0–2.0 nm.

As a general remark for the experimental approach we can say that only a rough insight into the potentials' behavior can be obtained by analyzing the absorption coefficient; namely, in strongly interacting systems with close resonance levels, besides the differential potentials, there are also the molecular oscillator strengths that can produce significant changes in line shapes.

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APPENDIX: ATOMIC OSCILLATOR STRENGTHS OF Eu AND Sr ATOMS (BY COULOMB APPROXIMATION)

To obtain the C_3 and C_6 constants it is necessary to calculate the radial integrals of the dipole moment operator for the transitions from the resonant P level to nS and nD levels for the constituents of a quasimolecular system, as well as those for the transitions from the ground S level to P levels [see Eq. (13)]. For the former transitions (from the P resonance state) there are no available experimental data for either Eu or Sr atoms, and it was an unavoidable task to calculate them. Although Eu exhibits a very complex electronic configuration, some recent papers^{7,8} showed that for lanthanides the Coulomb approximation is usually as reliable as the model-potential methods and often better than *ab initio* calculations which hardly account for atoms with complex electronic structure.

We start from the definition of an oscillator strength for the electronic transition in terms of the matrix element of the dipole moment:

$$f_{(\gamma J \rightarrow \gamma' J')} = \frac{2m}{3\hbar^2 e^2} \frac{E_{(\gamma' J')} - E_{(\gamma J)}}{(2J+1)} |\langle \gamma J || D || \gamma' J' \rangle|^2. \quad (\text{A1})$$

Further, the multiplet oscillator strength is introduced:

$$f_{(\gamma SL \rightarrow \gamma' SL')} = \frac{1}{g_i} \sum_{J, J'} (2J+1) f_{(\gamma J \rightarrow \gamma' J')}, \quad (\text{A2})$$

where g_i is the multiplicity of the initial state. The connection between the multiplet oscillator strength and reduced matrix elements, which appear in the formulas (12) and (13), can be deduced:

$$f_{(\gamma SL \rightarrow \gamma' SL')} = \frac{2m}{3\hbar^2 e^2} \frac{(E_{(\gamma' J')} - E_{(\gamma J)})}{(2L+1)} \times |\langle \gamma L(S) || D || \gamma' L'(S) \rangle|^2. \quad (\text{A3})$$

Therefore, to get the values for reduced matrix elements of dipole operator it is enough to take the multiplet oscillator strengths from the experimental data or to calculate them.

For the Coulomb approximation we have used the tables of radial integrals by Oertel and Shomo.¹³ The complex electronic configuration of lanthanides gives rise to several possible coupling schemes for ground and reso-

TABLE III. Possible coupling schemes for the electronic configuration of ground and resonant states of lanthanides with unfilled $4f$ subshell ($\nu < 14$).

| Index | Configuration (Grandparent) (parent) term | Coupling type |
|-------------------|---|------------------|
| 0 (ground state) | | |
| <i>C</i> | $f^\nu (S_0L_0)s^2 (S_{12}L_{12}) SL$ | <i>SL</i> |
| <i>D</i> | $f^\nu (S_0L_0;J_0)s^2 (S_{12}L_{12};J_{12}) J$ | <i>j-j</i> |
| 1 (excited state) | | |
| <i>A</i> | $f^\nu (S_0L_0)p (S_{02}L_{02})s SL$ | <i>SL</i> |
| <i>B</i> | $f^\nu (S_0L_0)s (S_{01}L_{01})p SL$ | <i>SL</i> |
| <i>C</i> | $f^\nu (S_0L_0)sp (S_{12}L_{12}) SL$ | <i>SL</i> |
| <i>D</i> | $f^\nu (S_0L_0;J_0)sp (S_{12}L_{12};J_{12}) J$ | <i>j-j</i> |

TABLE IV. The multiplet oscillator strengths for Eu for the transitions from ground level $4f^7 6s^2 a^8 S_{7/2}$ to $n^8 P$ multiplets, calculated by Coulomb approximation. Dashes denote nonadequacy of the Coulomb approximation. The compilation of experimental results is made from the National Bureau of Standards catalog (Ref. 11) and some recent measurements (Ref. 14), and is of an uncertainty of 15–20 %.

| Final multiplet | <i>E</i> (cm ⁻¹) | <i>B</i> | Coupling <i>C</i> (<i>D</i>) | Mix | Experiment (compilation) |
|--------------------------------|------------------------------|---------------|-----------------------------------|---------------|-----------------------------|
| <i>z</i> ⁸ <i>P</i> | 16 211.65 | 0.799 | 0 | 0(<i>C</i>) | 0.0077 |
| <i>y</i> ⁸ <i>P</i> | 21 630.0 | 1.05 | 1.86 | 1.46 | 1.45 |
| <i>y</i> ⁸ <i>P</i> | 31 255.36 | — | — | — | 0.15 |
| <i>y</i> ⁸ <i>P</i> | 34 478.8 | 0.030 | 0 | 0.015 | 0.035 |
| <i>y</i> ⁸ <i>P</i> | 36 528.98 | 0.109 | 0.194 | 0.152 | 0.015 |
| <i>y</i> ⁸ <i>P</i> | 39 064.49 | 0.0012 | 0.0022 | 0.0017 | 0.0015 |
| <i>y</i> ⁸ <i>P</i> | 40 550.35 | 0.029 | 0 | 0.015 | 0.021 |
| <i>y</i> ⁸ <i>P</i> | 41 284.5 | 0.005 | 0.0009 | 0.007 | 0.0007 |
| | | Σ 2.02 | 2.06 | 1.64 | 1.73 |

TABLE V. The multiplet oscillator strengths of Eu for transitions from the resonant level $4f^7 6s 6p y^8 P$ to $n^8 S$ and $n^8 D$ multiplets. For the resonant level, the two most probable (*B* and *C*) coupling schemes were taken.

| Final multiplet | State | <i>E</i> (cm ⁻¹) | Coupling transition | |
|---|------------|------------------------------|---------------------|------------|
| | | | <i>B-C</i> | <i>C-C</i> |
| <i>a</i> ⁸ <i>S</i> ⁰ | | 0.00 | −0.349 | −0.621 |
| <i>e</i> ⁸ <i>S</i> ⁰ | | 29 517.86 | 0.178 | 0.100 |
| <i>f</i> ⁸ <i>S</i> ⁰ | | 31 217.30 | 0.140 | 0.061 |
| <i>g</i> ⁸ <i>S</i> ⁰ | | 36 659.56 | 0.0040 | 0.027 |
| <i>i</i> ⁸ <i>S</i> ⁰ | | 39 242.56 | 0.0044 | 0.0019 |
| | <i>x</i> | | <i>B-X</i> | <i>C-X</i> |
| <i>a</i> ⁸ <i>D</i> ⁰ | <i>A</i> | 15 629.32 | −0.0007 | −0.026 |
| <i>b</i> ⁸ <i>D</i> ⁰ | <i>A</i> | 19 406.98 | −0.008 | −0.0035 |
| ⁸ <i>D</i> ⁰ | <i>A</i> ? | 35 081.42 | 0.009 | 0.305 |
| ⁸ <i>D</i> ⁰ | <i>A</i> ? | 35 505.12 | 0.413 | 0.184 |
| <i>g</i> ⁸ <i>D</i> ⁰ | <i>B</i> | 36 162.41 | 0.138 | 0.052 |
| <i>h</i> ⁸ <i>D</i> ⁰ | <i>B</i> | 36 493.38 | 0.114 | 0.050 |
| | | | Σ 0.65 | 0.12 |

TABLE VI. The (multiplet) oscillator strengths of Sr for transitions from ground state $5s^2\ ^1S_0$ to $n'\ ^1P$ levels. The uncertainty of experimental results is 20–25 %.

| Final $^1P^0$ multiplet | E (cm^{-1}) | Coulomb approx. | Experiment (Ref. 11) |
|-------------------------|--------------------------|-----------------|----------------------|
| 5s5p | 21 698.482 | 1.86 | 1.919 |
| 5s6p | 34 098.44 | 0.22 | 0.007 35 |
| 5s7p | 38 906.90 | 0.027 | 0.0157 |
| 5s8p | 41 172.15 | 0.0263 | 0.0451 |
| 5s9p | 42 462.36 | 0.0081 | 0.0449 |
| 5s10p | 43 327.94 | | 0.0287 |
| 5s11p | 43 937 | | 0.0156 |
| 5s12p | 44 365.9 | | 0.008 45 |
| 5s13p | 44 676 | | 0.005 18 |
| 5s14p | 44 903.5 | | 0.003 57 |
| 5s15p | 45 075 | | 0.002 65 |
| 5s16p | 45 208 | | 0.001 87 |
| 5s17p | 45 312 | | 0.001 44 |
| | | Σ 1.94 | 2.100 |

TABLE VII. The (multiplet) oscillator strengths of Sr for the transitions from the resonant levels $5s5p\ ^8P$ to $n'\ ^8S$ and $n'\ ^8D$ levels (multiplets).

| Final multiplet | E (cm^{-1}) | Coulomb approx. |
|-----------------------|--------------------------|-----------------|
| 5s ² 1S | 0.00 | −0.675 |
| 5s6s 1S | 30 591.8 | 0.160 |
| 5p ² 1S | 37 160.278 | 0.065 |
| 5s7s 1S | 38 444.054 | 0.015 |
| 5s8s 1S | 41 052.5 | 0.0053 |
| 5s9s 1S | 42 596.0 | 0.0025 |
| 5s10s 1S | 43 512.6 | 0.0005 |
| 5s4d 1D | 20 149.7 | −0.089 |
| 5s4d 1D | 34 727.483 | 0.675 |
| 5p ² 1D | 36 960.881 | 0.602 |
| 5s6d 1D | 39 733.114 | 0.112 |
| 5s7d 1D | 41 831.7 | 0.044 |
| 5s8d 1D | 43 020.9 | 0.022 |
| 5s9d 1D | 43 780.6 | |
| | | Σ 0.94 |

nance states,^{8,9} which are presented in Table III.

For the case of Eu, $\nu=7$ in Table III. In the resonance state the coupling types C and D are suggested, and we have performed calculations for S - P transitions just to test the method and to provide a ground for an estimation of the uncertainties (see also works^{8,9,11} on the oscillator strengths of lanthanides). For S - P transitions of Eu between the coupling types C - C and D - D one obtains the same figures. We suggest the “intermediate (BC) coupling” (in a first approximation it will be taken simply as a mean value of the results for coupling transitions C - B and C - C) because of its best agreement with the experimental data.^{11,14} (However, for the lowest $z\ ^8P$ multiplet, the C coupling scheme seems to be the best.)

We can see that the values shown in Table IV are good, considering the crudity arising when calculating the radial integrals with approximate wave functions. For transitions from the $y\ ^8P$ resonance level to S and D levels the results are presented in the Table V. Because of the lack

of experimental data the only reasonable check that we can make is to apply the sum rule for the oscillator strengths. In this case it should be 1, and we see that probably a few more P - D transitions ought to be taken into account, but either there were no data for the energies or the Coulomb approximation ceased to be valid.

A much simpler electronic configuration is that of the strontium atom. Theoretical results for oscillator strengths for S - P transitions (Table VI) are precise only for the resonance line. However, the sum rule is reproduced fairly well. The values for P - S and P - D transitions are presented in Table VII.

As a conclusion of this appendix we can say that the Coulomb approximation gives good results for the most intense (resonant) lines of europium and strontium, and nearly reproduces the trend of changes in oscillator strengths for the other lines.

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