Transition from Second- to First-Order Dipole-Dipole Interaction in the Excited EuSr Molecule

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For the first time a transition from a second- to first-order dipole-dipole interaction (van der Waals to resonance interaction) has been observed in a study of the excited EuSr molecule which dissociates into europium $4f^7 5s6p \, ^8P_{9/2}$ and strontium $5s^2 \, ^1P_1$ atoms. The transition was verified by measurement of the wavelength dependence in the quasistatic wings of the cw-laser–excited 4595.3-Å line in Eu broadened by Sr ground-state atoms.

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If the wave functions of two dissimilar atoms are not overlapping, the molecular interaction between the two can be calculated accurately by means of a second-order perturbation theory applying the multipole expansion. If one atom is, e.g., in its resonance and the other in its ground state it is often sufficient to include only the dipole-dipole term. But it should be noted that there are also cases[1,2] where higher-order terms have to be taken into account. If the dipole-dipole term is the leading term, the long-range potential is a van der Waals interaction potential $\Delta E = hC_6/R^6$, where the coefficient C_6 is given by

$$C_6 = \sum_i a_i \rho_i. \tag{1}$$

a_i are the angular integrals and ρ_i are

$$\rho_i = e^4 \sum_{A:n} \sum_{B:m} \frac{\mu_{1n}^2 \mu_{0m}^2}{\Delta E_{1n} + \Delta E_{0m}}. \tag{2}$$

$\mu_{1n} = e \langle 1|r^A|n \rangle$ and $\mu_{0m} = e \langle 0|r^B|m \rangle$ are the dipole matrix elements connecting the resonance level 1 with the levels n in atom A and the ground state 0 in B with the levels m. ΔE_{1n} and ΔE_{0m} are the energy differences of the levels in A and B, respectively.

If the resonance level of atom A is very close to the resonance level in atom B the dominating term in Eq. (2) arises from the resonance transitions in A (1 → ground state) and B (ground state 0 → resonance state) because (i) the matrix elements are large, and (ii) the energy denominator is small.

A system where these conditions are perfectly fulfilled is Eu-Sr which was also the subject of recent laser-induced collisional energy transfer (LICET) studies.[3] The energy differences between the fine-structure components of the Eu resonance levels $4f^7 6s6p \, ^8P_J$ and the Sr resonance level $5s5p \, ^1P_1$ are $+62.8$ $(J=\frac{9}{2})$, -93.3 $(J=\frac{7}{2})$, and -253.9 cm^{-1} $(J=\frac{5}{2})$.[4,5] If Eu is excited to the $J=\frac{7}{2}$ or $\frac{5}{2}$ fine-structure level and perturbed by Sr in its ground state the van der Waals forces are large and attractive. But if the Eu atom is in the $J=\frac{9}{2}$ fine-structure resonance

level the van der Waals forces are repulsive (because of the negative energy denominator) and even larger. Repulsive van der Waals interactions have been studied recently in other systems.[1,2,6] If we take into account the oscillator strengths[7] of the Eu and Sr resonance lines, the relevant matrix elements can be calculated. When we neglect all other contributions and estimate the sum of the angular integral to be of unity order of magnitude,[1,2] the following effective C_6 constants (in s^{-1} cm^6) are found: $+8.3 \times 10^{-29}$ $(J=\frac{9}{2})$, -6.7×10^{-29} $(J=\frac{7}{2})$, and -3.3×10^{-29} $(J=\frac{5}{2})$. Note that these constants are about four orders of magnitude larger than in a case where the Sr atom is replaced by a noble gas atom. On the other hand, if Sr is in the resonance and Eu in the ground state the contributions from the different resonance transitions in europium cancel strongly. The van der Waals interaction is attractive and weak.

If the interaction energy of Eu*-Sr is of the order of the energy difference of both resonance levels there is no longer a nondegeneracy of the Eu*$(J=\frac{9}{2})$-Sr and Eu-Sr* states. We have to treat the system of dissimilar atoms like a system of identical atoms in the first-order approximation. The interaction energy now varies as R^{-3} (resonance interaction). The problem of a transition from second- to first-order dipole-dipole interaction has been treated for dissimilar alkali atoms theoretically by Nikitin.[8] The effective resonance-interaction potential for Eu*$(J=\frac{9}{2})$-Sr is given by $\Delta E = +hC_3/R^3$, where $C_3 = \sum_i a_i \mu_{1n} \mu_{0m} = 1.3 \times 10^{-8}$ s^{-1} cm^3. Because they are small, remaining second-order contributions from Eq. (2) can still be neglected in the interatomic region of resonance interaction. Figure 1 shows the effective long-range potentials. Note that the ground-state van der Waals potential is almost flat. The C_6 constant is more than two orders of magnitude smaller compared to the excited states. As can be seen in Fig. 1, the transition from the van der Waals to the resonance region occurs when the Eu* and Sr atoms are still very far apart, at about 19 Å. Here the exchange forces can still be regarded as
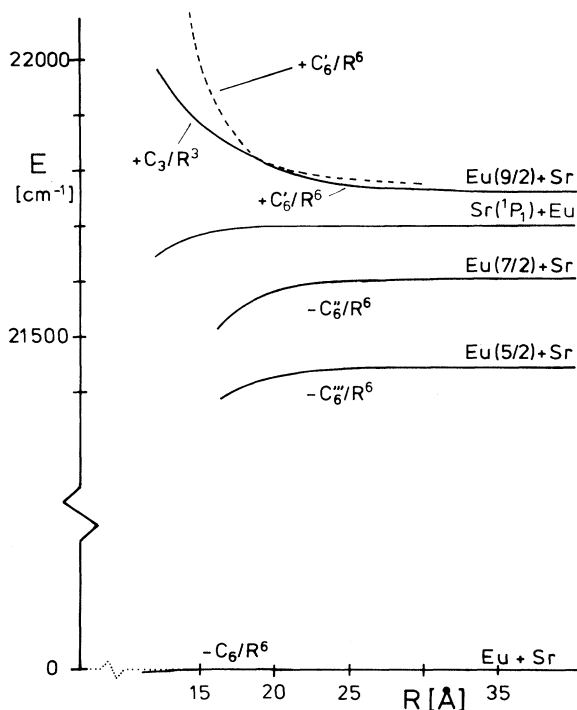
FIG. 1. The effective (averaged) long-range potentials of the Eu-Sr system.

small.

As in our recent papers[1,2,6] the long-range interaction potentials were investigated by looking at the wavelength dependence of pressure-broadened line wings. Traces of Eu evaporated together with Sr in a stainless-steel heat-pipe cross were excited by the light of a frequency-stabilized dye ring laser (dye: Stilben 3). While the laser was locked to the center of the Eu line, the fluorescence was detected at right angles by scanning of a 1.5-m monochromator across the Sr-broadened line. The light at the exit slit was recorded photoelectrically with a photon-counting system. The spectra were recorded by a strip-chart recorder. At fixed particle densities the far wings were measured first with large slit widths (bandwidth about 1 Å),

which were then reduced step by step down to 10 μm (bandwidth about 0.05 Å) to study the near-line wings. The temperature of the heat pipe was varied between 1000 and 1150 K generating Sr vapor pressures of 1 to 3 Torr. The corresponding partial vapor pressures of Eu were 5 to 6 orders of magnitude smaller. Under these conditions resonance broadening of the Eu resonance lines could be neglected. Neon was used as a buffer gas. If the line center is free of scattered light the absolute line wing intensities $I(\lambda)/N_{Sr}\int I(\lambda)d\lambda$ can be measured. Such conditions could not be totally achieved with our setup. Moreover, in part the line centers were optically thick. Therefore only the relative wing intensities are given.

Figure 2 displays a typical scan over the wavelength region of the Eu resonance lines when the 4595.3 Å line was excited. The Sr resonance line as well as the two other Eu resonance lines are excited by collisional redistribution or transfer. The respective blue and red asymmetries of the Sr-broadened 4595.3- and of the 4628.5- and 4663.2-Å Eu lines is eye-catching. The Sr line, which is optically thick, is mainly broadened by Sr atoms in the ground state (resonance broadening). It is symmetrical and of Lorentzian shape, which was checked separately by tuning and locking the dye ring laser to the Sr resonance line. The dashed curves in Fig. 2 show the extrapolations of the Lorentzian wings of the self-broadened Sr line. In evaluation of the Eu spectra the intensities of the Sr line wings have to be subtracted. In Fig. 3, we give the results of our measurements for the Eu 4595.3-Å line. The open and filled circles, the crosses, and filled squares represent the data from successive scans with different resolutions at fixed particle densities. Even in the far wings the uncertainty of the data is not larger than about 7%. Instead of plotting $I(\lambda)/N_{Sr}\int I(\lambda)d\lambda$, we give the relative reduced absorption coefficient $k(\lambda)_{rel}/N_{Eu}N_{Sr}$, where the Boltzmann factor $\exp(-hc\Delta\lambda/\lambda^2 kT)$ with $T = 1000-1150$ K was taken into account. The strong blue asymmetry as well as the antistatic behavior of the red wing can be seen. Between 1 and about 10 Å the slope of the quasistatic blue wing is -1.5. This is known to be the slope of a pure van der Waals wing.[9]
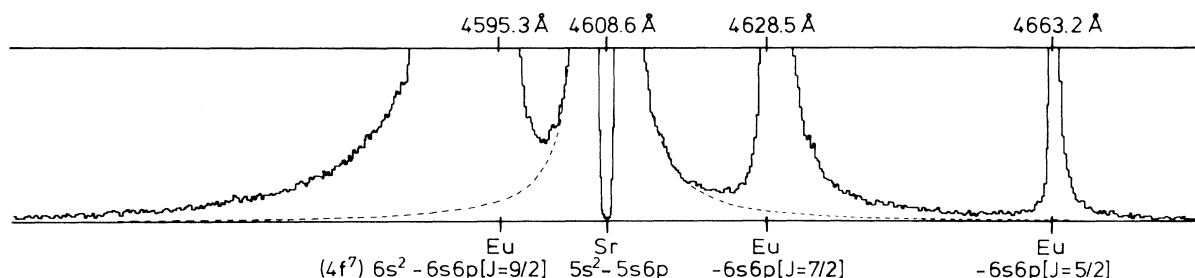

FIG. 2. Directly reproduced fluorescence spectrum from excitation of the Sr-broadened Eu line 4595.3 Å ($^8S_{7/2}$-$^8P_{9/2}$).
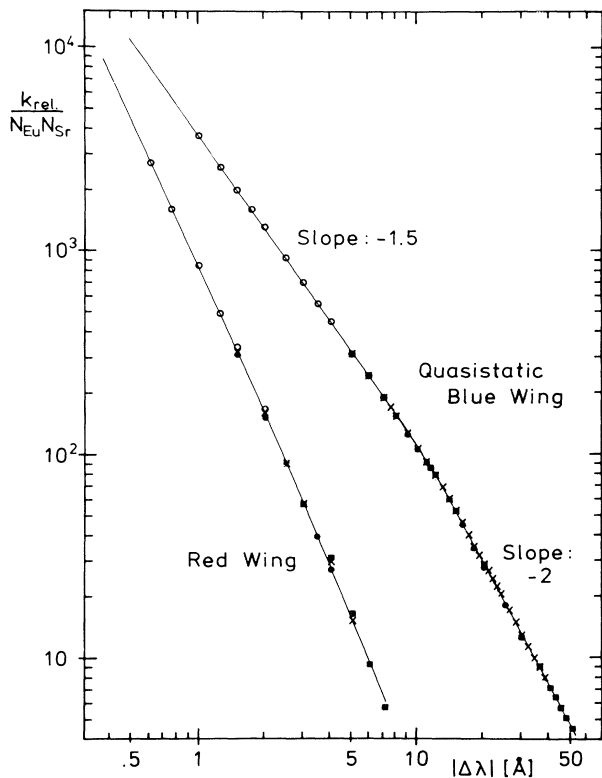
FIG. 3. Relative reduced absorption coefficient $k_{rel}/N_{Eu}N_{Sr}$ of the Sr-broadened Eu line 4595.3 Å against the wavelength difference from the line center $|\Delta\lambda|$. Monochromator bandwidth: 0.05 Å (open circles), 0.2 Å (crosses), 0.3 Å (filled circles), and 1.0 Å (filled squares).

Beyond the wavelength difference of 10 Å from the line center, the slope of the blue wing changes toward -2, a Lorentzian shape, an evidence of a transition from van der Waals to resonance interaction in the Eu*-Sr molecular system. Because the molecule is still in the long-range interaction region, only a change

from R^{-6} to R^{-3} dependence can be responsible for the observed change in the slope. It can be excluded that the finding is due to a satellite structure. There is no nearby Sr level above the Eu level which could induce a maximum in the long-range interaction potential. Because the interesting region is masked by the 4663.2-Å line of Eu, the change from van der Waals to Lorentzian shape could not be studied in the red wing of the 4628.5-Å line [Eu*$(J = \frac{7}{2})$-Sr].

The transition from second- to first-order dipole-dipole interaction has been discussed before,[8] in particular for the resonance levels of dissimilar alkali atoms (e.g., K-Rb or ^{6}Li-^{7}Li). But because of tremendous experimental problems caused by the overlapping dimer spectra at higher densities it could not be measured in these systems by line-broadening techniques.

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