Laser-induced collisional energy transfer: Experimental study of the spectral profile

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We report a measurement of the excitation spectrum of the laser-induced collisional energy transfer process for the Eu-Sr system in the weak-field regime. The measurement has been performed in a detuning range extending up to 85 cm^{-1} in the static wing, providing a wider check of existing theoretical models. The frequency resolution of the measurement (0.1 cm^{-1}) was suitable for a quantitative study of the core of the line spectrum, where a comparison with the results of numerical calculations based on an effective three-level model gives complete evidence for a cooperative decay from the $Sr(5p^2)^1D_2$ final level.

I. INTRODUCTION

In an atomic collision the transfer of excitation energy between nonresonant levels of different atoms can be switched on by a laser field of appropriate frequency. The process, usually referred to as laser-induced collisional energy transfer (LICET), is described by the reaction

$$A^*+B+\hbar\omega \rightarrow A+B^* ,$$

where A^* and B^* denote electronic excited states of atoms A and B, respectively, and ω is the laser frequency, nearly resonant with the interatomic transition frequency $\omega_0=[E(B^*)-E(A^*)]/\hbar$. The reaction can be viewed as a radiative transition of the transient molecule (quasimolecule) formed by the atoms during the collision.

The importance of the study of this effect for the understanding of the basic mechanisms underlying the selective control of chemical reactions by laser radiation has been stressed by several authors.[1,2] The process, first proposed by Gudzenko and Yakovlenko[3] in 1972 and observed by Harris and co-workers[4] in 1977, has been extensively studied in the last decade both theoretically and experimentally.[5–11] However, only recently, progress in the measurement accuracy as well as in the model development has led to an interpretation of the experimental results.[12–16]

Most of the effort has been devoted so far to the study of the excitation spectrum as a function of the laser frequency ω. The LICET cross section is characterized by a strongly asymmetric shape, peaked at the interatomic transition frequency ω_0, and showing an extended wing (quasistatic wing) in the frequency region where the energy defect of the laser photon can be compensated by the collisional shift of the atomic levels.

Up to the more recent theoretical models, it appears that the basic approximations introduced by Gudzenko and Yakovlenko are still the same: (i) the atomic trajectories are assumed classical and rectilinear; (ii) the collisional interaction is described by a dipole-dipole potential; (iii) the magnetic degeneracy is neglected; and (iv) the laser field, assumed constant during the collision, is described classically.

Following these approximations, the Schrödinger equation reduces to a set of coupled differential equations for the probability amplitudes of the three relevant product states of the uncoupled atoms $|i\rangle$ (initial), $|x\rangle$ (intermediate), and $|f\rangle$ (final) (see Fig. 1 for the Eu-Sr pair).

The main differences among subsequent treatments are related to the approximations introduced in the solution of the equations of motion, in order to simplify the calculation of the line shape and gain more insight into the problem. Neglecting the transient population of the intermediate level, the system can be reduced to a set of only two coupled equations, whose solution leads to a power law for the cross section behavior in the quasistatic wing:[17]

$$\sigma(\omega) \propto |\omega-\omega_0|^{-1/2} .$$

However, the first high-resolution measurement for the Eu-Sr pair[9] showed a deviation from this simple law predicted on the basis of a two-level model.

The discrepancy between theory and experiment was overcome by an effective three-level model providing, at the first order in the laser field amplitude, the following law for the quasistatic wing profile:[13]

$$\sigma(\omega) \propto |\omega-\omega_0|^{-1/2}(\Delta+|\omega-\omega_0|)^{-3/2} , \quad (1)$$

where Δ is the energy difference between initial and intermediate states. A quantitative comparison between (1) and measured values has been recently provided in a detuning range of 50 cm^{-1} for the Eu-Sr system by Matera *et al.*[14] This result can be considered as a good demonstration of the validity of the approximations of the model in the weak-field regime.

However, further investigation is still required in order to compare the experimental results to the theoretical predictions over the whole detuning range, including the

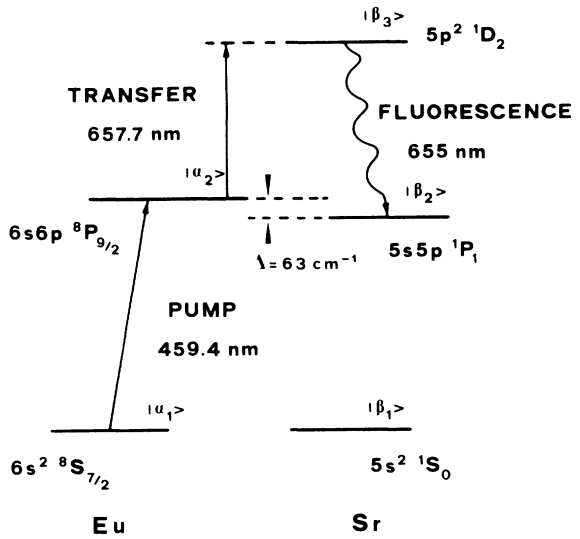

FIG. 1. Diagram of the energy levels relevant to the Eu-Sr laser-induced process. Product state basis: $|i\rangle=|\alpha_2\rangle|\beta_1\rangle$; $|x\rangle=|\alpha_1\rangle|\beta_2\rangle$; $|f\rangle=|\alpha_1\rangle|\beta_3\rangle$.

core and the side wing of the spectrum.

Up to now measured line profiles have been compared to theory separately in the core region or in the static wing due to the fact that in these regions (i) different approximations are conveniently used in theoretical treatments and (ii) different background processes can affect the measurement.

Furthermore, calculations of the LICET cross section under conditions of strong laser field have shown that the whole spectral shape can be affected by intensity effects.[8,12] It is, therefore, of increasing importance to make careful measurements of the spectral profile over the widest detuning range.

We report here a new measurement of the excitation spectrum of the LICET process between europium and strontium atoms in the weak-field regime. The measurement has been performed with a frequency resolution suitable for a detailed analysis of the core region and good accuracy up to large detunings in the static wing, leading to wider and more detailed checks of existing theoretical models and to the identification of background processes limiting the accuracy of the measurement.

II. EXPERIMENTAL SETUP AND RESULTS

We have studied the reaction

$$\mathrm{Eu}(6s6p)^8P_{9/2}+\mathrm{Sr}(5s^2)^1S_0+\hbar\omega \rightarrow \mathrm{Eu}(6s^2)^8S_{7/2}+\mathrm{Sr}(5p^2)^1D_2 ,$$

involving the atomic levels shown in Fig. 1. The setup of the experiment is similar to the one used in previous experiments.[14] Two dye lasers were pumped by a XeCl excimer laser equipped with an unstable optical cavity, providing pulses of 50 mJ energy, 20 ns duration, and 0.5 mrad divergence. For the oscillators of both dye lasers the grazing incidence configuration with four-prism beam expanders was used. The pump laser, consisting of the oscillator alone, was set to provide pulses of 50–100 μJ energy with a bandwidth of 1 cm^{-1}. The transfer laser, consisting of an oscillator-amplifier combination, provided pulses up to 1 mJ energy with a bandwidth of 0.1 cm^{-1}. The frequency resolution and resettability of the tuning system was comparable to the emission bandwidth.

A cross heat-pipe oven allowed an easy mixing of the laser beams without using dychroic mirrors. Using a counterpropagating geometry, it was possible to focus the beams separately without affecting the collection efficiency of the emitted fluorescence. Furthermore, the observation at 90° with respect to the laser axis led to a much lower contribution to the collected signal from diffusion of the laser beams on the windows.

The time delay between pump and transfer laser pulses, needed to avoid (or at least reduce) the direct two-photon excitation of Sr, could be easily changed in the 20–40-ns range by using the White design for the optical delay line.[18]

The fluorescence emitted at $\lambda=658$ nm in the Sr $(5p^2)^1D_2\rightarrow\mathrm{Sr}(5s5p)^1P_1$ transition, filtered by a 0.85-m double monochromator and detected by a high gain photomultiplier with an S-11 photocathode, was measured by using synchronous integration with a 50-ns gate duration.

An IBM-XT personal computer was used to control the dye lasers and the spectrometer and make data acquisition. At a repetition rate of 10 pulses/s and averaging over 20 pulses/point, a typical acquisition time was about 10 min for a detuning interval of 100 cm^{-1}.

The measured excitation spectrum is shown in Fig. 2 [curve (a)]. In order to show in more detail the core profile, a logarithmic compression of the frequency scale has been made. The measurement was performed at a temperature of 750 °C with 10 mbar of Ar buffer gas. The

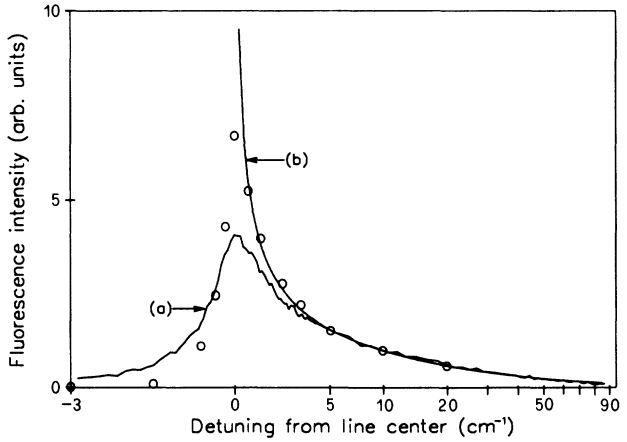

FIG. 2. (a) Spectral profile of the Eu-Sr LICET process vs detuning of the transfer laser from the interatomic transition $\omega_0-\omega$. Notice the logarithmic compression of the frequency scale. (b) Analytical expression (1). (○), numerical calculation performed following Ref. 13.

heat-pipe oven was temperature stabilized within a few tenths of degree. The corresponding europium and strontium densities, obtained by vapor pressure curves, were, respectively, of the order of 10^{13} and 10^{14} atoms/cm^3. With an optical delay of about 40 ns between the transfer and the pump laser pulses, the direct two-photon excitation to the final Sr$(5p^2)^1D_2$ level was reduced to a negligible amount. The peak power of the transfer laser in the interaction region was estimated to be of the order of 10 MW/cm^2, resulting from 20-ns laser pulses with 0.1 mJ energy focused to a 200-μm-diam focal spot. In order to have high resolution in the core spectrum, while keeping the measure time reasonably short compared to the drift time of the experimental setup, the increment of the frequency scanning was 0.1 cm^{-1} in the region -3 cm^{-1} $<\omega_0-\omega<14$ cm^{-1} and 1.7 cm^{-1} in the region $\omega_0-\omega>14$ cm^{-1}. During the measurement the energy of the laser pulses as well as the base-line level of the electronics were continuously monitored.

III. DISCUSSION

A. Background processes

The measured spectrum showed a residual signal for $\omega_0-\omega<-8$ cm^{-1} in the antistatic region, where the LICET cross section is expected to vanish. This signal makes manifest that other physical processes are concomitant to the LICET reaction, contributing to some extent to the population of the final Sr$(5p^2)^1D_2$ level.

A careful investigation carried out on the binary vapor mixture as well as on each atomic species separately showed that the main background process affecting the accuracy of the measurement was a two-step radiative excitation of the Sr atom via the $5s5p$ level due to (i) nonresonant absorption in the collision-induced wing and (ii) resonant absorption of the residual broad-band emission of the dye lasers.

Since this process, requiring the presence of both lasers, is dependent on the frequency of the transfer laser, the corresponding background signal cannot be easily subtracted, but must be minimized. The optimization of the signal to background ratio was then accomplished by optimizing the narrow-band to broad-band emission ratio of the dye lasers even at expenses of the total output energy. Furthermore, since the main agent responsible for the absorption in the wing of strontium atoms was found to be the argon buffer gas, the measurement was performed at the minimum argon pressure (10 mbar), still preventing atomic vapor deposition on the heat-pipe windows.

Other processes, like, for instance, energy pooling reactions between excited europium atoms followed by collisional transfer to strontium atoms, are likely to be dependent on the pump laser only, whose frequency does not change during the measurement. The corresponding background signal does not depend on the emission frequency of the transfer laser and can therefore be easily subtracted.

As a result the background signal, measured for large detunings in the antistatic region of the spectrum, was reduced to about 1% of the peak signal, corresponding to less than 30% of the full signal detected at the maximum detuning in the static wing (85 cm^{-1}). This residual background signal is subtracted in the spectrum of Fig. 2.

B. Comparison with theoretical predictions

The experimental results have been compared to the theoretical predictions of Ref. 13. This model, besides providing the analytical expression (1) for the cross-section behavior in the static wing, allows the evaluation of the whole spectral profile by a straightforward numerical integration.[19] In Fig. 2, the solid line (b) represents Eq. (1) and the circles represent the results of the numerical calculations. As expected, the two sets of values, derived by the same three-level model, follow the same behavior in the wing, while showing a departure in the core region, where the approximate analytical expression (1) fails.

The comparison of the experimental results to the theoretical spectral profile over the whole detuning range show a very good agreement in the static wing up to the maximum detuning of 85 cm^{-1}, making significant the normalization of the data in this region. As a result, a marked discrepancy between experimental and theoretical results in the core region is evident.

In order to obtain more insight into the origin of this discrepancy, measurements at various heat-pipe temperatures and laser intensities (up to $\sim$10 MW/cm^2) have been performed. From these measurements, the static wing profile was found independent of these parameters, while the core width was found to increase with either temperature and intensity. This result is in contrast with the predictions of LICET models, even taking into account strong-field effects, which would eventually lead to a line narrowing.[8,12]

The discrepancy was then ascribed to collective effects, namely, stimulated emission in the Sr$(5p^2)^1D_2$ $\rightarrow$Sr$(5s5p)^1P_1$ transition, causing an anisotropy of the

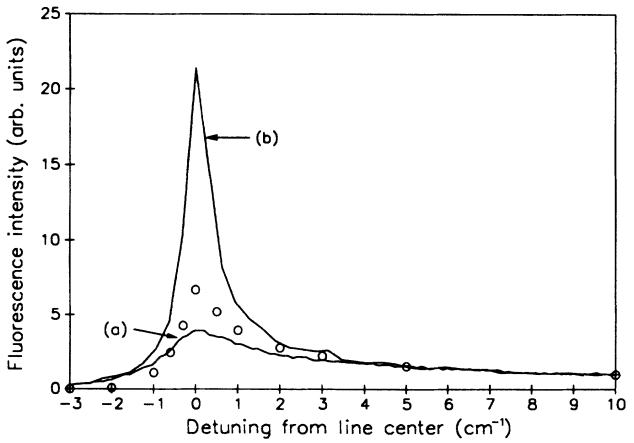

FIG. 3. Comparison between theoretical and experimental line profiles in the core region: (○) numerical results; (a) this experiment (90°, fluorescence collection); (b) Ref. 14 (backward fluorescence collection).

emitted fluorescence. In the collinear geometry used in our experiment, the transition gain is maximum along the laser direction, inducing an enhancement of the signal detected in this direction and a reduction of the signal detected at 90°. This effect is expected to increase with the population of the final $Sr(5p^2)^1D_2$ level, depending on temperature, laser intensity, and detuning. This interpretation is consistent with the results of previous measurements,[14] where, as shown in Fig. 3, the observation of the fluorescence in the backward direction provided an enhancement of the peak.

IV. CONCLUSION

We have reported a study of the LICET spectrum for the Eu-Sr system in the weak-field regime. A careful analysis of concomitant processes has allowed a reduction of the background signal to a level of about 1% of the peak signal. The measurement has been performed in a detuning range extending up to 85 cm^{-1} in the static wing, providing a wider check of the Bambini and Berman model for the cross-section behavior in the far wing.[13]

Furthermore, the frequency resolution of the measurement (0.1 cm^{-1}) has allowed a quantitative study of the core profile of the line spectrum. A comparison of the experimental results with the predictions of an effective three-level model has given complete evidence for a stimulated emission from the $Sr(5p^2)^1D_2$ final level. This effect should be carefully taken into account for the study of the process in the strong-field regime, since it might easily hide the saturation properties of the interatomic radiative transition.

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