Observation of Light-Induced Collisional Energy Transfer

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We have observed light-induced energy transfer in collisions of Eu atoms in three excited levels with Sr ground-state atoms and compared its spectra with the results of calculations. A four-photon parametric process in the transient Eu-Sr molecule was also observed.

Remarkable efforts have recently been devoted to the theoretical clarification of an elementary interaction process of atoms and radiation, which is variously labeled as "light-induced inelastic collisions" or "light-assisted collisional energy transfer."[1-11] In this kind of process, an atom A excited to level 2 passes along its excitation energy, in the course of a collision, to an off-resonant atom B, while the energy balance is preserved by the emission or absorption of a light quantum: $A(2)+B(1')+\hbar\omega \rightarrow A(1)+B(3')$. It is obvious that this type of process offers a vast potential for the deliberate selective transfer of excitation energy and, ultimately, for the control of chemical processes by light. One experiment, by Harris and collaborators,[12] has been reported so far, where the tuning spectrum of the light-induced collisional excitation of ground-state calcium atoms by excited strontium atoms was observed.

We have performed an experiment on light-induced collisions making use of a binary mixture of europium and strontium vapor. The beneficial features of this system (see Fig. 1) are (1) the close proximity of *three* excited Eu states, $^8P_{9/2,7/2,5/2}$, above and below the intermediate Sr $^1P_1$ level by 63, −93, and −253 cm^{-1}, and (2) the compatibility of the vapor pressures in the useful temperature range of 800–1000 C. The experimental arrangement includes a wide-bore heat-pipe oven, which contains the metals, and an 800-kW-peak-power N_2 laser of 4-nsec pulse duration, whose emission excites a dye laser (rhodamine 6G and cresyl violet) continously tunable in the red from approximately 640 through 660 nm and a stepwise tunable dye laser (coumarine 1) in the blue around $\lambda_1 = 460$ nm, both with a peak power of the order of 1 kW and a bandwidth of ca. 0.06 nm. The 2-nsec output pulses, which can be mutually delayed, propagate coaxially and in the same direction along the axis of the heat pipe. Excitation of the Sr $^1D_2$ level is detected by the backward fluorescence of the $(5p^2\,^1D_2)$-$(5p\,^1P_1)$ transition at 655.0 nm with the help of a monochromator and a photomultiplier. The fluorescence signal is monitored by gated synchronous detection and an X-Y recorder. The signal is recorded versus the tuning of the red light whose frequency approximately corresponds to the energy gap of the interatomic transition $EU(^8P)$-$Sr(^1D_2)$, while the light of the blue laser first excites the europium atoms into one of their ^8P levels:

$$\mathrm{Eu}(^8P_J)+\mathrm{Sr}(^1S_0)+\hbar\omega_2(\lambda_2\simeq 658\ \mathrm{nm}) \rightarrow \mathrm{Eu}(^8S_{7/2})+\mathrm{Sr}(^1D_2).$$

In order not to confuse the LICET signal with the 400 times more intense two-photon excitation in Sr $(^1S_0 \rightarrow {}^1D_2)$, the red-light pulse is delayed by

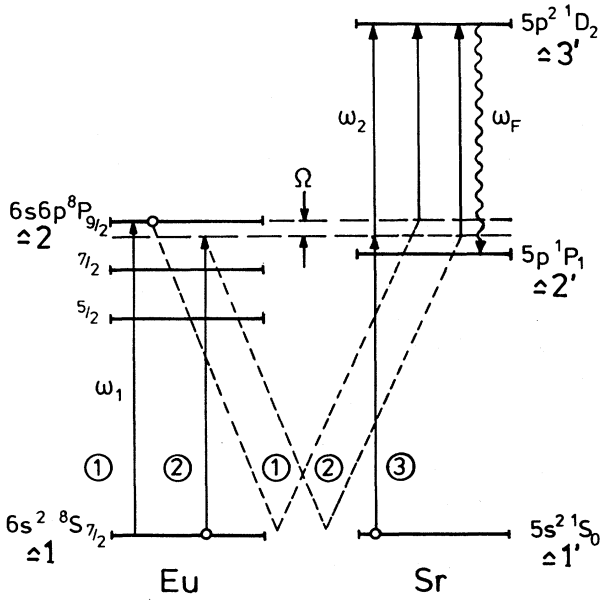

FIG. 1. Simplified energy-level diagram of europium and strontium. Process 1, light-induced collisional energy transfer (LICET); process 2, external two-photon process; and process 3, internal two-photon process.

5–6 nsec compared to the blue-light pulse. This lapse of time between the two light pulses is sufficient for all excited optically coherent states to relax, and no two-photon signal occurs under this condition.

Figure 2 shows spectra obtained for resonant excitation of each of the three Eu ^8P levels; their vertical scales relate to each other approximately as 1:2:10. The curve at the top of Fig. 2 is a spectrum which was calculated by the semiclassical method of coupled equations of motion.[11,13] The usual approximations of a straight collisional path and neglect of level degeneracy have been made. The amplitude of the final state Sr $^1D_2$ was numerically calculated with a Runge-Kutta algorithm. From its asymptotic value, the cross section was derived as a function of the wavelength of the process-inducing red light by phase-space integration. The agreement with the shape of the experimental spectrum substantiates the interpretation of the results.

The conspicuous asymmetry of the LICET spectrum is understood through the concept of a transient quasimolecule which exists during the atomic encounter.[12,13] The interaction with the light field results in a *crossing* of the potential curves at a finite internuclear separation. It appears as an extended wing on one side of the line, determined by the relative slope of the potential curves and by the relative energy of level 2 as compared with the intermediate level 2′.[3] The latter is demonstrated in Fig. 2.

The fluorescence signal turned out to depend linearly on the power of the red light. Therefore the conditions of the experiment correspond to the low-intensity limit, and no drastic change of the spectral shape is expected when the laser power is varied.

The cross section for the LICET process per unit light intensity, as derived from the observation of the fluorescence from the levels Eu $^8P_{9/2}$ and Sr $^1D_2$, is $\sigma_{\mathrm{expt}}/P = 120$ Å^2/(MW/cm^2). This value should be compared with $\sigma_{\mathrm{theor}}/P = 450$ Å^2/(MW/cm^2) which was calculated from a previously derived expression[13] which neglects the degeneracy of the involved levels.

It was recently stressed that the LICET process is analogous to two-photon absorption by the atom B to be excited.[10,11] However, in the framework of light interaction with a diatomic molecule AB, the LICET process represents the second step in a "stepwise" excitation. In this context, the LICET process is energy transfer plus a single-photon process (2′-3′), in contrast with

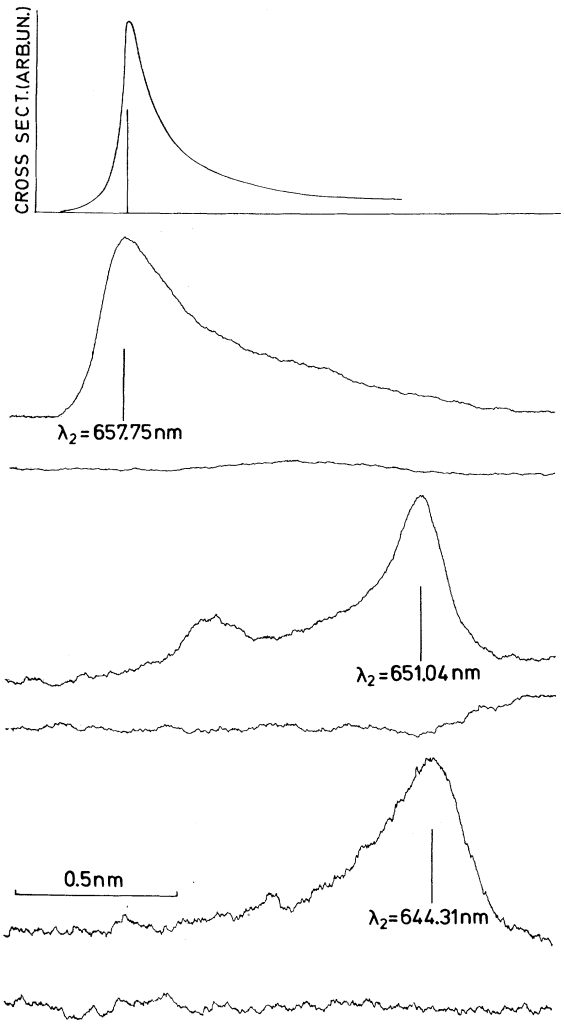

FIG. 2. LICET spectra (λ_2 increasing to the right) for the excitation of the ^8P ($J = \frac{9}{2}, \frac{7}{2}, \frac{5}{2}$) levels. Baselines were recorded with I_1 blocked. Top: calculated spectrum for laser with zero bandwidth.

the "external" two-photon process (1-3′, process 2) and the "internal" two-photon process (1′-3′, process 3) which occur—because of the rapid decay of the optical coherences—only with *simultaneous* light pulses, i.e., at zero pulse delay.

For a synopsis of the elementary processes which predominantly contribute to the interaction, we outline a perturbation expansion of the system's density matrix $c_i^* c_j$, although higher-order processes contribute on resonance *even* at small light fluxes. With the notation of perturbation

chains, these processes are written as

$$(c_1{}^*c_1 \xrightarrow{E_1} c_1{}^*c_2 \xrightarrow{E_1{}^*})c_2{}^*c_2 \xrightarrow{\text{coll}} c_2{}'^*c_2{}' \xrightarrow{E_2} c_2{}'^*c_3{}' \xrightarrow{E_2{}^*} c_3{}'^*c_3{}', \quad (1)$$

$$c_1{}^*c_1 \xrightarrow{E_1} c_1{}^*c_2 \xrightarrow{\text{coll}} c_1{}'^*c_2{}' \xrightarrow{E_2} c_1{}'^*c_3{}' \xrightarrow{E_1{}^*} c_2{}'^*c_3{}' \xrightarrow{E_2{}^*} c_3{}'^*c_3{}', \quad (2)$$

$$c_1{}'^*c_1{}' \xrightarrow{E_1} c_1{}'^*c_2{}' \xrightarrow{E_2} c_1{}'^*c_3{}' \xrightarrow{E_1{}^*} c_2{}'^*c_3{}' \xrightarrow{E_2{}^*} c_3{}'^*c_3{}'. \quad (3)$$

The dominant two-photon process 3 is characterized by a symmetric spectrum, which is narrower than that of LICET. In a spectral range of λ_1 which includes the Eu $^8S_{7/2}$-$^8P_{9/2}$ and the Sr $^1S_0$-$^1P_1$ resonance transitions, we have plotted the peak values of such spectra (Fig. 3), along with the wavelength settings of the blue laser (vertical lines). Because of two-photon resonance condition, there is a corresponding scale for λ_2 which includes the interatomic transition Eu($^8P_{9/2}$)-Sr($^1D_2$). The resulting spectrum is characterized by complete extinction at the wavelength of the Sr resonance transition. At the center of this resonance, single-photon excitation of the Sr $^1P_1$ level and successive decay dominate to such a degree that two-photon excitation in the observed volume element and the concomitant fluorescence signal are quenched. A second resonance occurs at the wavelength of the interatomic transition. Its spectral shape includes *negative lobes* which reduce the peak of the two-photon signal. The magnitude of the signal is large compared to the pure LICET signal and, on the other hand, is a considerable fraction of the two-photon signal. These observations support the surmise that the additional contribution is generated by *interference* of a Sr two-photon amplitude (process 3) with an external two-photon amplitude (process 2) and/or a LICET amplitude (process 1).[2] The probability of this contribution is, in a perturbation calculation,

$$c_3{}'^{(3)*}c_3{}'^{(1)} = \frac{1}{32\hbar^5} \frac{\mu_{1'2'}\mu_{2'3'}E_1{}^*(\omega_1)E_2{}^*(\omega_2)}{\Delta_{1'2'}{}^*\Delta_{1'3'}{}^*} \frac{\mu_{12}\mu_{21}\mu_{1'2'}\mu_{2'3'}E_1(\omega_1)E_2(\omega_2)}{\Delta_{12}\Delta_{1'2'}\Delta_{23'}} g(\omega_2). \quad (4)$$

Here, the superscripts refer to the processes; $\Delta_{ij} = \omega_{ij} - \omega + i\gamma_{ij} = \Omega_{ij} + i\gamma_{ij}$; ω is the quasiresonant light frequency ω_1, ω_2, or $\omega_1+\omega_2$; ω_{ij}, γ_{ij}, and μ_{ij} are the frequency, phase relaxation rate, and moment of the transition i-j, respectively; and E_1 and E_2 are field amplitudes of the two light fields.

We have made use of

$$\int_0^\infty (b^2+v^2t^2)^{-3/2}\exp(i\Delta_{23'}t)dt = (i/\Delta_{23'})[b^2+v^2t_0{}^2(\omega_2, b, v)]^{-3/2},$$

where b is the distance of closest approach and v is the relative velocity of the atoms. Averaging the second factor over b and v gives $g(\omega_2)$, which varies only slowly, and without zeros, across the resonance.[14]

With application of the two-photon resonance condition

$$\hbar^{-1}[W(3') - W(1')] = \omega_{1'3'} = \omega_1 + \omega_2, \quad (5)$$

the excitation rate of level 3′ due to the interference is

$$(\mathrm{Im}\, c_3{}'^{(3)*}c_3{}'^{(1)})_{\omega_1+\omega_2} = \frac{\mu I_1 I_2}{32\hbar^5(\Omega_{1'2'}{}^2+\gamma_{1'2'}{}^2)} \frac{\Omega^2 - \gamma_{12}\gamma_{23'}}{(\Omega^2+\gamma_{12}{}^2)(\Omega^2+\gamma_{23'}{}^2)} g(\omega_2), \quad (6)$$

where μ is the product of six transition moments, $\Omega = \Omega_{12} = \Omega_{23'}$, and the second factor provides for a non-Lorentzian line shape with negative side lobes and two zeros in qualitative agreement with the observed envelope in Fig. 3. The spectral width is, however, determined by the bandwidth of the laser emissions, and the distance between the zeros is much larger than $2(\gamma_{12}\gamma_{23'})^{1/2}$. In addition to the above terms, the interference term $c_3{}'^{(3)*}c_3{}'^{(2)}$ contributes to the excitation of level 3′ as well, but does not generate negative lobes in the spectrum. These two interference contributions are analogous to the two "nonlinear interference effects" in cross saturation (or optical double resonance) due to (i) pure two-photon processes and (ii) an interaction of a two-photon amplitude with a single-photon amplitude.[15,16]

The two-photon peaks show, in general, a shift as compared with the theoretical two-photon resonance condition (5); this is indicated in Fig. 3 by comparison with the wavelength values of the vertical lines. The shift is also shown as a function of the tuning in the upper part of the same figure. There is dispersion from the Sr $^1P_1$ resonance level, and also some indication of a dispersive effect at the interatomic transition wavelength.

The interference effects at the interatomic

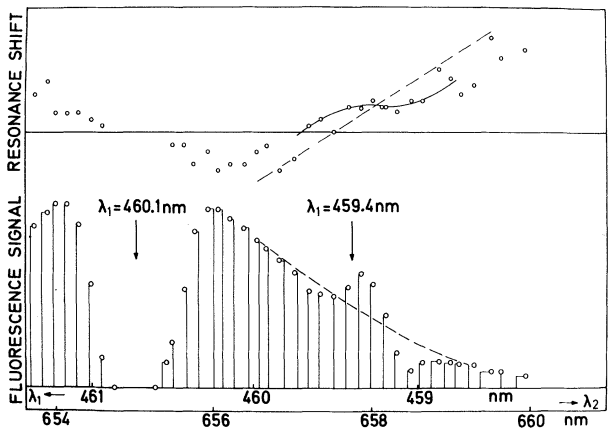

FIG. 3. Two-photon peak signals vs λ_1 (and λ_2) at zero pulse delay. Bottom: vertical lines show the wavelength settings of the blue laser (λ_1); circles are at the wavelength values of the spectral peaks. Top: shifts vs wavelengths, indicating dispersive effects.

resonance can be alternatively interpreted in the framework of a *transient molecule.*[12] In this context, the phenomenon is a parametric four-photon interaction ($\omega_{12}, \omega_{23'}, \omega_{3'2'}, \omega_{2'1'}$) where the two light fields simultaneously drive the two-photon transition 1′-3′ and the stepwise transition sequence 1-2-3′. No such effect seems to have been observed before in a transient, unstable system.

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[1]L. I. Gudzenko and S. I. Yakovlenko, Zh. Eksp. Teor. Fiz. 62, 1686 (1972) [Sov. Phys. JETP 35, 877 (1972)].

[2]S. E. Harris and D. B. Lidow, Phys. Rev. Lett. 33, 674 (1974), and 34, 172(E) (1975).

[3]V. S. Lisitsa and S. I. Yakovlenko, Zh. Eksp. Teor. Fiz. 66, 1550 (1974) [Sov. Phys. JETP 39, 759 (1974)].

[4]M. G. Payne and M. H. Nayfeh, Phys. Rev. A 13, 595 (1976); M. G. Payne, C. W. Choi, and M. H. Nayfeh, in *Proceedings of the International Conference on Multiphoton Processes, Rochester, New York, 1977* (Wiley, New York, 1977).

[5]L. I. Gudzenko and S. I. Yakovlenko, Phys. Lett. 46A, 475 (1974).

[6]S. Geltman, J. Phys. B 9, L569 (1976).

[7]T. F. George, Jian-Min Yuan, I. H. Zimmermann, and J. R. Laing, Disc. Faraday Soc. 62, 246 (1977); Jian-Min Yuan, John R. Laing, and T. F. George, J. Chem. Phys. 66, 1107 (1977).

[8]N. M. Kroll and K. M. Watson, Phys. Rev. A 13, 1018 (1976).

[9]A. M. F. Lau, Phys. Rev. A 14, 279 (1976).

[10]P. L. Knight, J. Phys. B 10, L195 (1977).

[11]P. W. Milonni, J. Chem. Phys. 66, 3715 (1977).

[12]S. E. Harris, R. W. Falcone, W. R. Green, D. B. Lidow, J. C. White, and J. F. Young, in *Tunable Lasers and Applications*, edited by A. Mooradian, T. Jaeger, and P. Stokseth (Springer, Berlin, 1976), p. 193; R. W. Falcone, W. R. Green, J. C. White, J. F. Young, and S. E. Harris, Phys. Rev. A 15, 1333 (1977).

[13]S. E. Harris and J. C. White, J. Quant. Electron. 13, 972 (1977).

[14]This is because $g(\omega_2)$ is the ratio of the approximately bell-shaped LICET amplitude spectrum and the Lorentzian $\Delta_{23'}^{-1}$.

[15]Th. Hänsch and P. E. Toschek, Z. Phys. 236, 213 (1970).

[16]P. E. Toschek, in *Frontiers in Laser Spectroscopy*, edited by S. Haroche and S. Liberman (North-Holland, Amsterdam, 1977), p. 323.