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Two-Photon Superradiance*

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A transient two-photon process is observed in the infrared which exhibits all the co-operative properties associated with superradiant two-level systems. It arises when a cw laser beam excites a molecular sample whose *level degeneracy* is suddenly removed by a Stark field. The resulting emission, which heterodynes with the laser, gives precise ground- and excited-state Stark splittings, and decays with a homogeneous relaxation time since Doppler dephasing effects are absent in forward scattering.

Superradiance[1] in the past has been associated exclusively with a one-photon process which produces coherent spontaneous emission in an ensemble of two-level systems. In this Letter, we extend the concept of superradiance to three levels which are connected by a two-photon transition and report a new coherent transient effect of this type. The effect arises when a molecular sample is excited by a cw laser beam and its level degeneracy is suddenly removed by a Stark field. The Stark-pulse technique also has led recently to the observation of photon echoes,[2] optical nutation,[2] and free-induction decay.[3]

As a point of reference, consider first a nondegenerate Doppler-broadened transition. We assume that initially the degeneracy is lifted by a constant Stark field and that under steady-state conditions only two of its levels are in resonance with a cw laser beam. Sudden application of a step-function Stark field switches these molecules out of resonance, and they emit an optical free-induction decay signal.[3] This superradiant emission propagates in the forward direction, is collinear with the laser beam, and produces a heterodyne beat signal at a detector monitoring the transmitted light. The beat appears as a damped oscillation whose frequency is the Stark shift. We note that the decay of this signal is due to (1) relaxation processes which determine the homogeneous linewidth, and (2) dephasing of the transition dipoles due to the inhomogeneous Doppler broadening. During the steady-state preparation, the homogeneous linewidth, which can be dominated by power broadening, is burned into the Doppler profile. This determines the molecular velocity bandwidth and thus the importance of dephasing in the decay rate. During the decay, power broadening will obviously be absent and cannot contribute to (1) whereas molecular collisions will. These ideas are contained in a solution of the coupled Maxwell-Schrödinger equations which yield a decay of the form $\exp(-t/T) \times \exp\{-[(\mu_{ij}\epsilon/\hbar)^2 + 1/T^2]^{1/2} t\}$, where T is the homogeneous relaxation time and $\mu_{ij}\epsilon/\hbar$ is the saturation parameter.[4] In contrast, photon echoes are described by a decay envelope of $\exp(-t/T)$ which is independent of inhomogeneous broadening. We will report[3] subsequently, in more detail, that these expectations are verified quantitatively in experiments with NH_2D where the free-induction

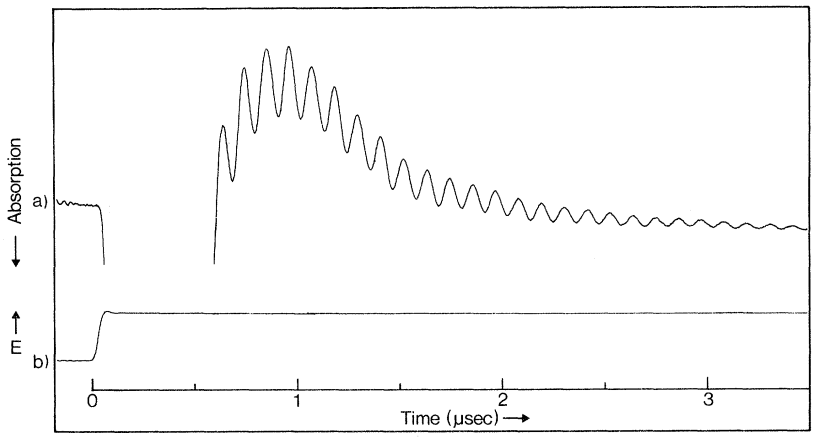

FIG. 1. (a) Superradiance beat signal in $C^{13}H_3F$ at 3.25 mTorr pressure following (b) a step-function Stark pulse (0–46.58 V/cm). Two beats are actually present whose intensity ratio (~ 10 here) depends on the laser intensity. The strong downward spike and background is an optical-nutation signal. The optical path length is 10 cm.

decay constant is typically 3 times faster ($T/3$) than the echo decay constant (T) for the same experimental conditions.

Consider next the degenerate case which produces effects having a different origin. The molecular system is again prepared in steady state by coherent excitation, but the levels are degenerate in the absence of a bias Stark field. The beat signal which is now observed following a step-function Stark field is shown in Fig. 1 for the ν_3 band transition ($J,K = 4,3 \leftarrow 5,3$) of $C^{13}H_3F$. The background signal is due to optical nutation.[2,3] As in the two-level case, this emission is coherent, propagates forward, and is collinear with the laser beam. Excitation is by a linearly polarized 1-W cw CO_2 laser oscillating on the $P(32)$ line at 1035.474 cm^{-1} which falls within the absorber's 66-MHz Doppler width. The selection rules are $\Delta M = \pm 1$. See Ref. 2 for other experimental details.

The simplicity of the beat pattern in Fig. 1 is an unexpected result. Actually, eighteen different frequencies for the $\Delta M = \pm 1$ transitions can occur, because the upper and lower states Stark tune at different rates, and each of these should produce a free-induction decay beat. However, these beats are not easily identified because they all overlap with one another and with the first nutation spike as their decay is short lived (< 1 μsec) because of dephasing. The signal which does survive is evidently not a free-induction decay.

Other characteristics of the observed emission are as follows: (1) The beat signal appears only for $\Delta M = \pm 1$ selection rules and completely vanishes for $\Delta M = 0$ excitation. (2) The beat signal contains two frequencies, shown in Fig. 2, and is readily obtained from a spectrum analyzer which monitors the detector output. They are given by the first-order Stark shift $2\mu EK/J(J+1)$ for a $\Delta M = 2$ interval in the upper ($J,K = 5,3$) and the lower ($J,K = 4,3$) levels, respectively. (3) The beat amplitude decreases rapidly as the initial Stark bias field departs from zero, the response being that of the homogeneous line shape (~ 170 kHz half-width at half-maximum). (4) The beat amplitude varies linearly with the number of

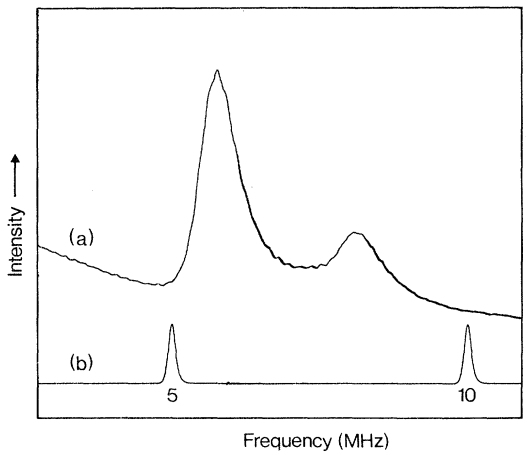

FIG. 2. (a) Superradiance beat spectrum of $C^{13}H_3F$ at 4.4 mTorr pressure. The low-frequency component is ω_{31} and the other ω_{42}. (b) Frequency calibration (Stark voltage, 0–28.23 V/cm). The transient decay signals are detected with an HP8552-3B spectrum analyzer having 100 kHz bandwidth, and its output is displayed on an X-Y recorder. The nutation frequency of ~ 1 MHz can also be observed but is not shown here.

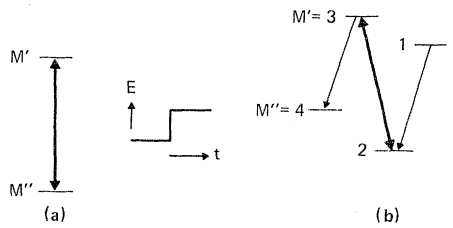

FIG. 3. Energy-level diagram for a degenerate two-level system (a) before and (b) after a step-function Stark field. Laser radiation is in resonance with all the levels in (a) but only the 2-3 transition in (b). This applies to the ν_3 band line $(J'', K''=4,3) \rightarrow (J', K'=5,3)$ of $C^{13}H_3F$. The other M states are not shown, nor are the negative M levels which behave similarly.

molecules N. (5) Finally, the beat signal decays as $\exp(-t/T)$ and gives the same relaxation time T, to within 5%, as that obtained from photon echoes, for the same experimental conditions.

We propose that the beat phenomenon in Figs. 1 and 2 is a superradiant two-photon process. The relevant energy levels following a step-function Stark field E are shown in Fig. 3. Two resonant or near-resonant processes can occur. For example, a molecule initially in the excited $M'=1$ level can transit to $M'=3$ by the emission of a photon and by the absorption of a laser photon. Similarly, the transition $M''=2 \rightarrow 4$ can occur. The transitions of Fig. 3(b) and the corresponding negative-M transitions have the highest transition probability because the laser frequency remains in resonance, to within the homogeneous width, with the $M''=\pm 2 \rightarrow M'=\pm 3$ interval. This is a consequence of the Stark shifts being approximately equal for only these M levels. Of course, two-photon transitions involving other M states, which are further out of resonance with the intermediate level, will contribute to a small degree (Raman effect). In fact, the $Q(12, 2)$ ν_3 transition of $C^{12}H_3F$ shows the same beat behavior of Fig. 1 even though all M transitions are shifted out of resonance by several homogeneous linewidths.

These processes can occur co-operatively because of the coherent preparation of the sample. Off-diagonal elements in the density matrix for the ensemble are thereby produced. These persist even after the Stark field is applied, and, in fact, give rise to the observed emission. Molecules which enter these levels at subsequent times, following the application of the Stark field, do not possess these off-diagonal terms and therefore cannot contribute to the emission.

In an ensemble of two-level systems, a superradiant state is defined as one in which an off-diagonal element of the density matrix exists in the absence of a driving field.[5] Since the analogous situation occurs in the two-photon process described above, it also can be called superradiant.

The specific form of the polarization for the two-photon transition $2 \rightarrow 4$ of Fig. 3(b) is

$$P_{24}(t) = 2N \operatorname{Re}[\mu_{24} \int \langle a_2(t) a_4^*(t) \times \exp(-i\omega_{24} t) \rangle G(\omega_{24})\, d\omega_{24}]. \quad (1)$$

Here, $\langle a_2 a_4^* \exp(-i\omega_{24} t) \rangle$ is the ensemble-averaged off-diagonal density-matrix element, the integral denotes a Doppler average over the line-shape function $G(\omega)$, and the level splitting is ω_{24}. The off-diagonal element is determined initially by the steady-state preparation and decays towards zero as $\exp(-t/T)$ once the Stark field is applied. The transition dipole μ_{24} is, of course, zero for the direct transition but does exist for the two-quantum process.[6] Therefore, the system does not radiate at ω_{24} but does produce a beat of this frequency, resulting from the laser and the emitted field.

We wish to emphasize that the Doppler averaging yields an interesting result in this three-level problem. Whereas the Doppler line shape increases the decay rate in a two-level free induction decay, this effect is completely absent in two-photon forward scattering. This is because the Doppler shift for two-photon forward scattering is $(v/c)(\nu_1 - \nu_2)$, which is ~10 Hz in this problem, while for a single-photon emission it is $(v/c)\nu \sim 60$ MHz. Hence, $G(\omega)$ is a δ function and the polarization does not dephase as a result of inhomogeneous broadening. This has the practical consequence that the decay of the two-photon beat signal (Fig. 1) is the pure homogeneous component, given by $\exp(-t/T)$, and thus can be observed long after free-induction decay.

The observed beat signal according to Eq. (1) will thus vary directly with the number of molecules N, it will decay away in time as $\exp(-t/T)$, and its frequency will be ω_{24}. Similarly, a beat at ω_{31} will also occur as a result of the other three-level configuration (1-2-3). As we have seen, these two beats are clearly displayed in Fig. 2 with the aid of a spectrum analyzer.

It is now possible to understand the several observations (1)–(5) listed above, particularly the selection rules and the beat frequencies. The coherent preparation of the sample, point (3), deserves further attention, however. To understand this, assume that the levels of Fig. 3(a) are ini-

tially split by a bias Stark field and by an amount greater than the homogeneous width. Then the amplitude a_4* will be virtually zero for the particular velocity group which is excited in the 3-2 transition. On the other hand, for another velocity group, a_4* will be nonzero but the 3-2 transition will not be excited. Thus, coupled transitions will not occur. Arguments of a similar nature apply to the (1-2-3) levels.

The coherent preparation may also be achieved in other ways and with interesting effects. The step-function Stark field can be replaced by a pulse which has a zero field value during the on time but is biased in the off time. By varying the pulse duration, or the laser intensity, one can control the initial amplitudes of the levels in Fig. 3(b) and thus the relative intensity of the two beat signals (Fig. 2). This occurs because the matrix elements for these transitions are all different, and what is a 2π pulse for the 1-2 transition is a 0.8π pulse for the 3-4, for example.

We note that this superradiant effect yields the same spectral information as an optical double-resonance experiment,[7] but has the distinct advantage of requiring only one laser. The technique thus provides a new kind of Fourier-transform spectroscopy. One may hope to measure homogeneous relaxation times and narrow Stark splittings with ease and precision in a variety of molecular transitions, especially with a tunable laser. The principal requirement of a coupled three-level system which is Stark tunable is not especially restrictive, and furthermore, the technique is not limited to the linear Stark effect as shifts of only a few homogeneous linewidths are needed. In addition, it opens the way for examining the superradiance aspects of these processes.[8]

Numerous conversations on this subject have added to our understanding, and we acknowledge with pleasure those with H. Morawitz, M. Scully, R. Shea, J. Eberly, E. Hahn, G. Herrmann, A. Schawlow, and F. Hopf. As usual K. Foster and D. Horne expedited all technical problems.

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Measurement of the Differential Cross Section for H($n = 2$) Direct Excitation in H^+-on-H Collisions

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We have determined experimental differential cross sections for elastic scattering and the $n=2$ excitation in H^+-on-H collisions at an impact energy of 1 keV and compared the results with previous theoretical calculations.

The collision H^+ on H is of special interest because of its relative simplicity (one-electron system). Consequently, it is considered as a very good test for the theoretical approach to the heavy-particle scattering problem. From the experimental point of view, the situation is of course very different, the difficulty of handling an H-atom target being the main reason for the small amount of available data. In this field the pioneering measurements of Everhart and co-workers[1] have stimulated extensive theoretical investigations. Bates and Williams[2] predicted that, in the keV energy range, inelastic processes should be induced by a rotational coupling between the $2p$