PHYSICAL REVIEW
LETTERS

VOLUME 33 | 23 DECEMBER 1974 | NUMBER 26

Observation of Quantum Beats in Photon Echoes and Optical Nutation*

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(Received 7 September 1974)

We extend the technique of quantum-beat spectroscopy to the infrared region by utilizing the strong, directional absorption and emission which occurs in photon echoes and optical nutation. Using a vibrational transition of NH_2D, we have made the first observations of infrared quantum beats in these phenomena. The hyperfine splitting which produces the quantum beats has not been observed in Lamb-dip spectroscopy but is clearly resolved in these time domain studies.

Recently there has been considerable interest in a type of quantum-beat spectroscopy in which a laser pulse prepares the atoms or molecules in a coherent superposition of states.[1] The resulting fluorescence is monitored with a photodetector and can exhibit modulations (quantum beats) in its emission due to a quantum mechanical interference between the levels. This technique is limited to the visible and uv regions, however, because in the infrared, fluorescence from a single state is generally too weak to be observable. In the Letter we demonstrate how quantum-beat spectroscopy can be done in the infrared region by using transient effects such as the photon echo where *coherent emission from a phased array of dipoles is observed in the forward direction.* Using a vibrational transition in NH_2D, we have made the first observations of infrared quantum beats in photon echoes and optical nutation. Photon echoes can be produced using two laser pulses.[2] The sample emits following excitation by the first pulse, but the emission quickly dies out because of Doppler dephasing of the radiating dipoles. A second pulse of specified energy and delayed by a time τ reverses the dephasing so that at time 2τ the sample again radiates strongly in the forward direction. The echo amplitude as a function of pulse delay τ is the observable of interest. Optical nutation can be produced by a step-function laser pulse and appears as a damped ringing signal which occurs as the system is coherently driven back and forth between the ground and excited states.[3] We note that there has been one previous observation of a modulated photon-echo decay in the visible region (ruby at 6943 Å),[4] while quantum mechanical interference in an optical nutation signal has not been seen previously.

A most interesting feature of the work described here is that the quantum beats we observe are due to an excited-state splitting which was unobserved in a previous Lamb-dip study of this transition.[5] This demonstrates that there can be real advantages to doing high-resolution optical spectroscopy in the time domain rather than in the frequency domain.

Our experiments were performed on a deuterated ammonia, NH_2D, using the Stark-switching technique of Brewer and Shoemaker.[6] In this method a cw laser beam passes through a sample whose resonance frequency can be shifted by an electric field. Electric field pulses thus can shift molecules in and out of resonance and they react as if they were excited by a pulsed laser.

The first set of experiments involved photon-echo measurements on two NH_2D transitions which can be Stark shifted into resonance with a CO_2 laser by a strong dc electric field.[5,7] The field removes the M_J degeneracy so that we can pick whatever $M_J \rightarrow M_{J'}$ component we wish using the appropriate bias field and selection rules. The sample cell contains a few milliTorr of NH_2D, and pulsed electric fields are applied across a pair of plates in the cell 30 cm long and separated by 0.45 cm. Because of collisional relaxation, the echo amplitude as a function of delay time is expected to die away as $\exp[-at^3]$ for short delay times and as $\exp[-bt]$ for longer times.[8] Our experimental results are shown in Fig. 1. The upper trace shows the expected dependence and is for the $M_J = \pm 4 \rightarrow \pm 5$ component of a $(\nu_2, J) = (0, 4) \rightarrow (1, 5)$ transition which overlaps the $P(14)$ laser line at 10.6 μm. The lower trace is also an $M_J = \pm 4 \rightarrow \pm 5$, $(\nu_2, J) = (0, 4) \rightarrow (1, 5)$ transition overlapping with the $P(20)$ laser line.[9] It shows a 17% modulation in addition to the decay. We note immediately that this modulation cannot be simply due to a beat between the echoes from two independent transitions, since the echoes here are very weak and can only be seen as a heterodyne beat signal with the laser, i.e., as a signal proportional to $E(\text{laser}) \cdot E(\text{echo})$. The term $E(\text{echo}) \cdot E(\text{echo})$ will be smaller than $E(\text{laser}) \cdot E(\text{echo})$ by about 10^6. Since no modulation is observed for the $P(14)$ overlap and both transitions involve the same lower state, we are left with the possibility that a true quantum beat is occurring in which two (or more) upper levels are excited from a common lower level. We have investigated this hypothesis and found that it matches our observations in all respects.

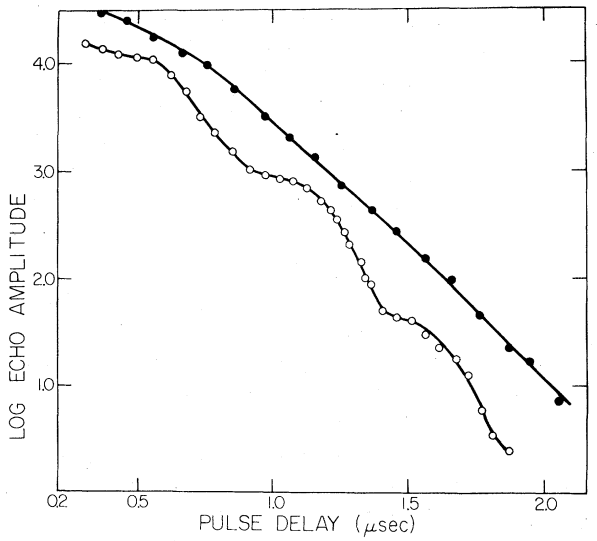

FIG. 1. Logarithm of the photon echo amplitude in NH_2D as a function of the delay between excitation pulses. The upper trace is for the $P(14)$ overlap, while the lower trace, which shows quantum beats, is for the $P(20)$ overlap.

The theory of the three-level echo problem has been worked out in considerable detail.[10] The echo amplitude as a function of pulse delay τ was shown to be proportional to $\alpha_1^4 + 2\alpha_1^2\alpha_2^2 \cos 2\pi \Delta F \tau + \alpha_2^4$, where ΔF is the upper-state level splitting, and the coefficients α_1 and α_2 are complicated functions of the dipole matrix elements $\mathcal{P}_1$ and $\mathcal{P}_2$, the field amplitude, and the pulse width. Using this expression we can fit the data of Fig. 1, and we find an upper-state level splitting of $\Delta F = 2.4 \pm 0.1$ MHz. The theory in Ref. 10 assumes pulse widths much less than the Doppler dephasing time T_2^*, which is not the case in the present experiment. We have tested the effect of a finite pulse width using a third-order perturbation treatment in the electric-dipole–field interaction, but found no new effects. If we take $\alpha_2 > \alpha_1$ (the designation of 1 and 2 is arbitrary), then our experiment shows $\alpha_1/\alpha_2 \sim 0.3$. Note that we find $\alpha_1/\alpha_2 = \mathcal{P}_1/\mathcal{P}_2$ in the case of our third-order calculation, so one might take 0.3 as a preliminary estimate of the ratio of the two dipole matrix elements. A more precise determination is given below.

The optical nutation signal in this transition provides a further test of the quantum-beat hypothesis. Figure 2 shows optical nutation signals for the $P(14)$ overlap and the $P(20)$ overlap. The $P(14)$ transition (lower trace), which showed a normal echo decay, also shows the expected nutation behavior, namely, a single-frequency oscillation which dies away exponentially because of collisions. The $P(20)$ overlap (upper trace), on the other hand, has a nutation signal in which the initial 3.1-MHz oscillation frequency suddenly decreases at about 1.2 μsec and then reappears weakly near 1.6 μsec before dying out. Since 1.2 μsec corresponds exactly to the time at which the first maximum in the echo appears (the echo occurs at twice the pulse delay), it seems plausible that the effect has the same origin as the echo modulation. This is confirmed by a straightforward density matrix calculation of the optical nutation behavior for a three-level system.

We assume that the decay times are the same for all three levels and neglect repopulation of

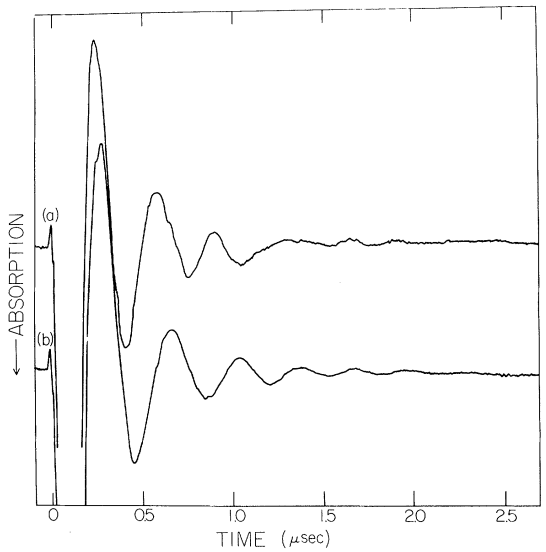

FIG. 2. Optical nutation in NH_2D. The upper trace a, which shows destructive interference, is for the $P(20)$ overlap. The lower trace b is for the $P(14)$ overlap.

the lower level. The decay and oscillations factor in the usual manner, the resulting three equations are solved in the rotating frame, and the integral over frequencies is then performed numerically.[3] Since the splitting is given from the echo data and the initial oscillation frequency by the nutation data, the only free parameter is the ratio of the dipole matrix elements. The nutation signal is rather complex since it contains simultaneously the quantum beat and the superposition of the two nutations. We are able to obtain qualitative agreement with experiment only for dipole matrix element ratios in the interval 0.2 to 0.25 and a near-exact fit is given by $\mathcal{P}_1/\mathcal{P}_2 = 0.23$. This number is consistent with the estimate given earlier from the echo data. Note that although the fit is very precise, we have neglected the transverse variation of laser intensity across the beam. Thus, the number may not be as accurate as we have indicated.

The fact that two independent experiments can be quantitatively matched by assuming a three-level system is very strong evidence in its favor. The two questions which still remain to be answered concern the origin of the splitting, and the reason it was not observed in a previous Lamb-dip study of the transition. Assuming the assignments $(\nu_2, J) = (0_a, 4_{04}) \rightarrow (1_a, 5_{05})$ for the $P(20)$ overlap and $(0_a, 4_{04}) \rightarrow (1_s, 5_{14})$ for the $P(14)$ overlap,[9] we have calculated theoretical spectra including the hyperfine structure due to the Stark effect and nuclear quadrupole coupling.[11] When the Stark coefficients and the rotationally averaged field gradient, $q_J = \langle \partial^2 V/\partial Z^2 \rangle_{av}$, are calculated for the 5_{05} and 5_{14} states, one finds that while the Stark splittings are a few MHz for both states the quadrupole coupling constants are $eQq_J = -2.183$ MHz for 5_{05} and -0.459 MHz for 5_{14}. The small value of eQq_J compared to the Stark splitting for the 5_{14} state implies that the nuclear spin is effectively uncoupled from the molecular rotation and one then has rigorous selection rules $\Delta M_I = 0$, $\Delta M_J = 0, \pm 1$.[12] For the $M_J = \pm 4 \rightarrow \pm 5$ component of the $4_{04} \rightarrow 5_{14}$ transition, then, each of the three lower-state levels corresponding to $M_I = 0, \pm 1$ is connected to only one upper-state level (while $M_J = \pm 4 \rightarrow \pm 3$ can occur, its intensity is only $\sim 2\%$ of the $M_J = \pm 4 \rightarrow \pm 5$, so we will ignore it). Thus, no quantum beats are expected for the $4_{04} \rightarrow 5_{14}$, $M_J = \pm 4 \rightarrow \pm 5$ transition in agreement with our observations for the $P(14)$ overlap.

For the $4_{04} \rightarrow 5_{05}$ transition, on the other hand, eQq_J is comparable to the Stark splitting. This causes a mixing of the uncoupled IJM_IM_J wave functions and a breakdown of the selection rules.[12] An exact diagonalization of the energy matrix shows that here the $|J, M_I, M_J\rangle = |5_{05}, \mp 1, \pm 5\rangle$ and $|5_{05}, 0, \pm 4\rangle$ states are mixed, so that both states are coupled to the $|4_{04}, \mp 1, \pm 4\rangle$ lower state. The splitting between the two excited states is 2.39 MHz, and the mixing is such that the calculated ratio of dipole matrix elements is $\mathcal{P}_1/\mathcal{P}_2 = 0.215$. These numbers are in almost exact agreement with the experimental results given earlier. Thus, we have a positive confirmation of the upper-state assignments of Kelly, Francke, and Feld[7] and of the explanation for our experimental results. We also note that the excellent agreement between experiment and our calculated values indicates that the excited-state quadrupole coupling constants are not appreciably different from ground-state values.

One can now understand why the splitting we have observed was not seen in the previous Lamb-dip study. We recall that the intensity of a Lamb dip varies as $\mathcal{P}^4$ where $\mathcal{P}$ is the transition dipole matrix element.[13] Thus, for a matrix element ratio $\mathcal{P}_1/\mathcal{P}_2 = 0.215$, the weaker transition has a Lamb dip which is only 1/500 the intensity of the main line. This is too weak to be observable. However, one might expect that the so-called "crossover resonance" which varies as $\mathcal{P}_1^2\mathcal{P}_2^2$ could be seen.[5,13] The difficulty is that this resonance is now separated from the main line by

about 1.2 MHz, instead of 2.4 MHz. Also, there are actually three strong Lamb dips (one for each allowed value of M_I) and the one having an associated crossover resonance has one of the other strong components situated *between* the two. The net result is that only a single broad Lamb dip will be observed unless extremely high resolution and sensitivity are available.[14]

It is clear that the type of quantum-beat spectroscopy reported here can be very useful in probing infrared hyperfine structure and in identifying molecular transitions. Since many molecular constants may be obtained from only a few accurately measured lines, positive identification of those transitions is very important. As we have seen, this can sometimes best be done by looking for the quantum beats arising from the hyperfine structure of the transition. Weak transitions can easily be seen in these time-resolved experiments, and, in addition, the effective resolution in an echo experiment can be higher than in steady-state experiments because the echo decay contains no contribution from power broadening.

We are grateful to R. G. Brewer and I. D. Abella for helpful discussions, to D. W. Anderson for experimental assistance, and to M. Sargent, III, for his assistance with the computer calculations.

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*Work sponsored in part by U. S. Air Force Contract No. F04695-67-C-0197 and in part by the National Science Foundation, Grant No. GH-42024.

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[9]The assignment given in Ref. 5 is $(\nu_2, J) = (0_a, 4_{04}) \rightarrow (1_s, 5_{14})$ for the $P(20)$ overlap. Kelly, Francke, and Feld (Ref. 7) later reassigned the upper state to give $(0_a, 4_{04}) \rightarrow (1_a, 5_{05})$ for the $P(20)$ overlap and gave $(0_a, 4_{04}) \rightarrow (1_s, 5_{14})$ as the assignment for the $P(14)$ overlap.

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[14]While the $M_J = \pm 3 \rightarrow \pm 4$ component was the one actually studied in Ref. 5, the hyperfine structure and Lamb-dip spectrum of this component is essentially the same as for $M_J = \pm 4 \rightarrow \pm 5$.