Coherent Optical Transient Effects of the Spin-Rotation Interaction in $^{13}CH_3F$

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Photon-echo interference damping and anomalous coherent Raman beats are observed due to the spin-rotation interaction from laser-excited vibration-rotation transitions in $^{13}CH_3F$ at 9.6 μm. Pulsed Stark fields superimposed upon a constant magnetic field control the intrinsic mixture of spin-rotation states. The spin-rotation interaction for spin $I = \frac{1}{2}$ is confirmed from photon-echo measurement and theory.

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We report overdamped photon-echo envelope modulation and Doppler-free coherent Raman beats caused by the spin-rotation interaction $\mathcal{H} = C\,\vec{I}\cdot\vec{J}$, where C is the interaction constant and I and J are spin and molecular rotation quantum numbers, respectively. The effects are observed from CO_2-laser–excited two-level vibration-rotation transitions in gaseous $^{13}CH_3F$. Small values of C are difficult to detect by conventional spectroscopy methods, but can nonetheless cause large spin-rotation state mixing. Our transient measurements show surprisingly large anomalous signal behavior due to the mixing, which is controlled by a novel variable quenching effect of applied Stark fields. Although this investigation does not resolve the small value of C in $^{13}CH_3F$ (~ 20 kHz) because of short photon-echo signal damping times $T_2 < 2\pi/\hbar C$, photon-echo measurements of C should be possible in both ground and excited vibrational states with an increase in apparatus resolution.

The optical Stark switching technique of Brewer and Shoemaker[1] is applied where we now take into account abrupt changes in admixtures of rotational states accompanied by abrupt changes in Stark electric field. The dc Stark field $\hat{z}E_S$ is oriented parallel or perpendicular to the laser field modulus $\mathcal{E}_l$ ($\vec{E}_S \| \vec{\mathcal{E}}_l$ or $\vec{E}_S \perp \vec{\mathcal{E}}_l$). In addition we apply a steady magnetic field $B\hat{z}$ to the sample for the purpose of superimposing nuclear-spin Zeeman splitting upon the electric Stark splitting of the rotational levels. As described in previous investigations[2] of $^{13}CH_3F$, the freely radiating dipoles produce heterodyne beats and photon echoes at the Stark shift frequency after the dipoles are shifted in and out of resonance with the cw incident CO_2-laser beam by Stark pulses. The signal is detected, digitized, averaged, and Fourier analyzed by an on-line microcomputer so that specific level transitions may be studied in the presence of Doppler broadening.

In $^{13}CH_3F$ the $(J,K) = (4,3) \leftrightarrow (5,3)$ transition of the ν_3 vibrational mode is excited at 9.66 μm, where K is the component of rotational angular momentum J along the molecular symmetry axis. We make the simplifying approximation that the molecule contains only a single on-axis nuclear moment μ_I with spin $I = \frac{1}{2}$, and the sublevels of each vibrational state are given by $|M_I\rangle \otimes |M_J\rangle$. Here $M_I = \pm\frac{1}{2}$ and $M_J = -J, -J+1, \ldots, +J$ are the components of I and J, respectively, along the z axis. The level eigenvalues are given[3] by

$$W_{IJ} = -p_{JK}E_S M_J - 2\mu_I B M_I + C M_I M_J, \qquad (1)$$

where $p_{JK} = \mu_e K/(J^2+J)$ and μ_e is the permanent electric dipole moment of the molecule. For $|\hbar\delta| = |p_{JK}E_S - 2\mu_I B| \gg C$, the Stark split $|M_I\rangle \otimes |M_J\rangle$ levels are pure states as shown in Fig. 1(a). When $\hbar\delta = 0$ (as, for example, when $E_S = B = 0$),

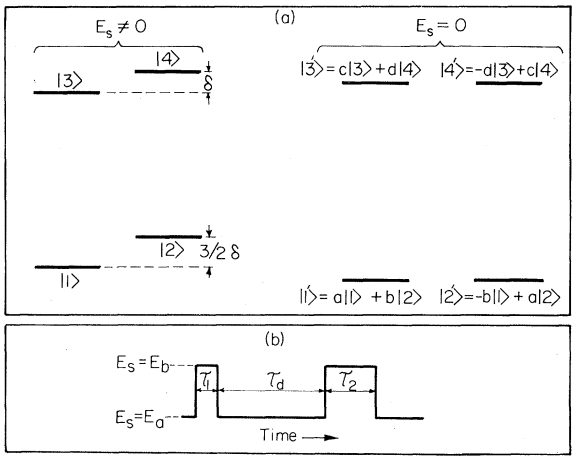

FIG. 1. (a) Mixing of eigenstates for $B = 0$ as levels become nearly degenerate ($E_S = 0$). Pure states $|1\rangle$, $|2\rangle$, $|3\rangle$, and $|4\rangle$ are defined for strong Stark field $E_S = \hbar\delta/p_{JK} \gg C/p_{JK}$. For $E_S = 0$ or $\delta \lesssim C/\hbar$, pure states convert to mixed states $|1'\rangle$, $|2'\rangle$, $|3'\rangle$, and $|4'\rangle$, where a, b, c, and d are mixing coefficients and $a^2 + b^2 = c^2 + d^2 = 1$. In the limit of pure states $a^2 = c^2 = 1$ and $b^2 = 0$. (b) Two Stark pulse sequences for obtaining photon echo at time τ_d after the second pulse.

Stark and Zeeman shifts cancel and nearly degenerate levels $|M_I=\frac{1}{2}\rangle\otimes|M_J\rangle$ and $|M_I=-\frac{1}{2}\rangle\otimes|M_J+1\rangle$ are mixed by raising and lowering operators of the off-diagonal component of $\mathcal{H}$, expressed by $\frac{1}{2}C[I_+J_-+I_-J_+]$. The small diagonal splitting CM_IM_J is not shown.

The effect of state mixing upon the photon-echo intensity maximum may be calculated[4] and compared to experiment if the condition $|p_{JK}E_b - 2\mu_I B| \gg C$ applies during application of two Stark pulses [peak value $E_S = E_b$, Fig. 1(b)] in the presence of a magnetic field. The inequality assures that the laser never drives more than a single pair of pure states (i.e., $|1\rangle \nrightarrow |2\rangle$) in a given molecule. After the pulses are switched off to the bias value $E_S = E_a$, the condition $|p_{JK}E_a - 2\mu_I B| \lesssim C$ permits the formerly driven level pair, now in superposition, to mix with neighboring undriven levels through the spin-rotation interaction. The level mixing scheme is shown in Fig. 2, with external spin Zeeman interaction included, where only a quartet of states shown need be considered in the calculation. Neighboring quartets of states behave similarly but independently.

For a two-pulse echo sequence, the photon-echo intensity at time τ_d after the second pulse is given by

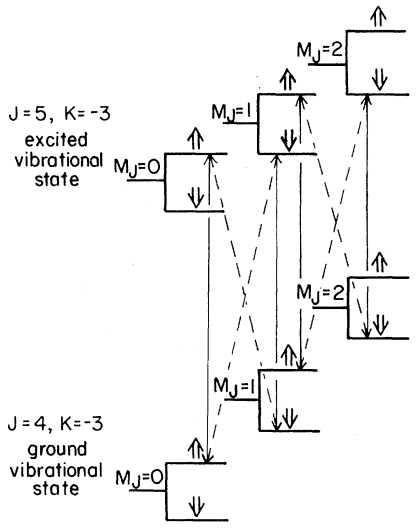

FIG. 2. Eigenstates in antiparallel Stark and Zeeman fields. ↑ and ↓ represent spin-up and spin-down states. Solid arrows are allowed transitions $\Delta M_J=0$, $\Delta M_I=0$ for $\vec{\delta}_1 \| \vec{E}_S$. Dashed arrows are forbidden transitions for $\Delta M_J = \pm 1$, $\Delta M_I = \mp 1$, now allowed because of state mixing among degenerate levels in the excited vibrational state. For the Stark field chosen none of the ground states are degenerate and do not mix significantly. Notice how the analysis breaks up into quartets of states.

$$S = S_0\Big([a^4+b^4+2a^2b^2\cos(\omega_{21}'\tau_d)][c^4+d^4+2c^2d^2\cos(\omega_{43}'\tau_d)] + abcd\,(\mu_{42}/\mu_{31})\{(a^2-b^2)(c^2-d^2)[1-\cos(\omega_{21}'\tau_d)][1-\cos(\omega_{43}'\tau_d)]+\sin(\omega_{21}'\tau_d)\sin(\omega_{43}'\tau_d)\}\Big)\,. \quad (2)$$

The echo intensity in the absence of state mixing is given[5] by S_0, and the state-mixing coefficients are defined from mixed states given in Fig. 1(a). Dipole transition matrix elements μ_{42} and μ_{31} are defined for the pure $\Delta M_J=0$ transitions, and ω_{21}' and ω_{43}' are the splittings of the nearly degenerate mixed states that provide a measure of C.

A plot of Eq. (2) and corresponding data is shown in Fig. 3. The results depend upon pulse areas only through S_0. As E_a or B is adjusted, variation of the state admixture parameters (a, b, c, and d) occur which determine the echo intensity at fixed time τ_d after the second pulse. Here we have assumed that the only spin present is fluorine, with $C=21$ kHz in the ground ($J=4$) state, and $C=12$ kHz in the excited ($J=5$) state.[6] For $B=0$, the maximum mixing occurs near $E_a=0$. For $B=140$ G, maximum mixing occurs when the degeneracy condition $p_{JK}E_a = 2\mu_I B$ is satisfied and maximum interference causes a minimum in the echo intensity. This condition occurs for two values of E_a: one for the ground and one for the excited vibrational states. In the ground states cancellation occurs at $E_a = 4$ V/cm; cancellation in the excited states (shown by the example of Fig. 2) occurs at $E_a = 6$ V/cm.

The extra structure in the $B=140$ G data (solid points) near $E_a=1.5$ V/cm is caused by the spin-rotation state mixing of the ^{13}C nucleus, which is not included in the theory plot of Eq. (2). Also not included is the mixing effect of the three protons, very near that of the fluorine. Since proton and fluorine magnetic moments differ by about 6%, we do not resolve the proton from the fluorine structure. Resolution would require a field of nearly 1000 G.

Although our measurements are consistent with the previously reported[6] value of $C \sim 20$ kHz, they do not resolve frequencies $\omega_{21}', \omega_{43}' \ll T_2^{-1} \simeq 0.2$ μsec^{-1} (at 1 mTorr gas pressure) sufficiently to fit C with any precision to the data. The effect of

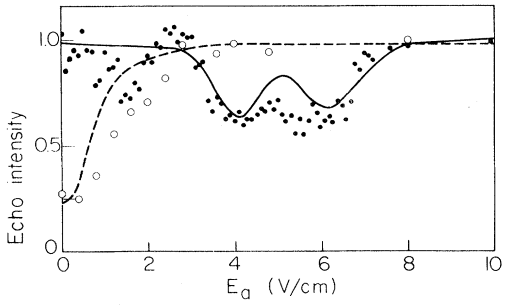

FIG. 3. Photon-echo intensity change S/S_0 as a function of Stark field E_a at fixed τ_d, laser power ~0.12 W/cm^2, gas pressure 0.6 mTorr, gas-cell path length 8 m, $\tau_1 = 0.6\,\mu$sec, and $\tau_2 = 1.8\,\mu$sec. Transition $M_J = 1 \leftrightarrow M_J = 1$ is displayed, with Stark pulse excitation amplitude fixed at $E_b - E_a = 38.4$ V/cm. The dashed line and open circles denote theory and experimental data for $B = 0$ G and $\tau_d = 6\,\mu$sec. Solid line and closed circles pertain to data for $B = 140$ G and $\tau_d = 5\,\mu$sec.

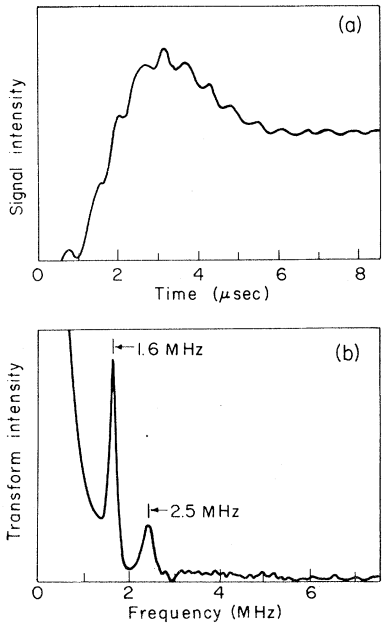

FIG. 4. Anomalous Raman beats from $^{13}CH_3F$ for $\vec{\mathcal{E}}_l \parallel \vec{E}_S$, laser power ≃0.05 W/cm^2, gas pressure 1 mTorr. (a) Beats in time after an applied Stark field switches degenerate mixed states, prepared in superposition, out of laser resonance. Beat lifetime T_2 is not limited by inhomogeneous Doppler broadening. (b) Fourier spectrum of beats in (a) of excited-state (δ) and ground-state ($\frac{3}{2}\delta$) Stark field (18.4 V/cm) splittings.

echo envelope T_2 damping constraints Eq. (2) to a resolution in time τ_d less than a quarter of an oscillation period caused by the interaction C. Resolution should be achieved by lowering the gas pressure to increase T_2, by increasing the magnetic field strength B, and by increasing the gas-cell optical path length to compensate for loss of signal intensity.

The clue to the existence of spin-rotation mixing in our work was provided by the observation of forbidden Doppler-free Raman beats. These beats appear in the free-induction-decay signal after the degenerate mixed levels [for $E_S = 0$, Fig. 1(a)] are first placed into superposition at laser resonance, and then switched out of resonance when the Stark field $E_S \neq 0$ is switched on (either for $\vec{\mathcal{E}}_l \perp \vec{E}_S$ or $\vec{\mathcal{E}}_l \parallel \vec{E}_S$). The nonadiabatic switching converts the final levels to pure M_J states, which results in a second contribution to coherent superposition among neighboring M_J states separated by $\Delta M_J = \pm 1$. As a result of these two superposition contributions the anomalous beats correspond to splittings δ and $\frac{3}{2}\delta$ [see Fig. 1(a)], as measured in Fig. 4. The allowed beats, first observed by Brewer and Shoemaker[7] in $^{13}CH_3F$ for $\vec{\mathcal{E}}_l \perp \vec{E}_S$ only, correspond to splittings twice as large (2δ and 3δ). Allowed beats result from superposition among rotational states separated by $\Delta M_J = \pm 2$, prepared in superposition only by laser resonance among pure states, and do not depend upon hyperfine mixing of rotational states.

In conclusion, we have calculated and observed coherent transient effects arising from the molecular spin-rotation interaction which can be controlled by external electric and magnetic fields. The pulse transient technique indicates clearly the effects of a small interaction off-diagonal coupling term in the Hamiltonian, even if the exact size of the interaction is unresolved. Increase in resolution should allow measurement of spin-rotation constants in ground and excited states for each nucleus separately. Investigations concerning the effect of collisional electric fields upon mixed states as a function of gas pressure should be possible, since random fluctuations of the state-mixing coefficients will induce photon-echo envelope decay.

We are grateful for the opportunity to learn by private communication from S. B. Grossman and R. G. Brewer of their observation of anomalous echo beats, different from the type reported here. Their observation stimulated the research which is presented here. We thank Dr. Sun Tao-Heng for his assistance in making measurements. This work was supported in part by the Division of Materials Research, National Science Foundation. One of us (J.A.K.) also thanks IBM for pre-

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[4]The calculation (J. A. Kash, E. L. Hahn, and Sun Tao-Heng, to be published) is related to calculations by E. L. Hahn and D. E. Maxwell, Phys. Rev. 84, 1246 (1951), and L. Q. Lambert, A. Campaan, and I. D. Abella, Phys. Rev. A 4, 2022 (1971).

[5]The measured value of S_0 accounts for T_2 damping in the limit where rotational degeneracy is removed, and random collisional Stark electric fields are less likely to cause fluctuating level degeneracy and mix the states. This pressure-dependent effect is operative mainly when the states are nearly degenerate (to be treated in a later paper). It contributes a small amount of extra damping which is not included in the derivation of Eq. (2).

[6]This value has been measured for the ground state of $^{12}CH_3F$, and is assumed to apply also for the ground and excited states of $^{13}CH_3F$ [S. C. Wofsy, J. S. Muenter, and W. Klemperer, J. Chem. Phys. 55, 2014 (1971)].

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