Optical Free Induction Decay*†

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A simple application of the Stark-pulse technique, developed by Brewer and Shoemaker, demonstrates optical free induction decay—the optical analog of free induction decay in NMR. A molecular sample which is coherently prepared by a cw laser beam exhibits such a decay when it is suddenly switched out of resonance by a Stark field. Observations are presented for a nondegenerate Doppler-broadened infrared transition of NH_2D, where the sample is optically thin, and the decay behavior can be compared quantitatively with a solution of the Bloch equations. When the molecular sample is prepared under steady-state conditions, the solutions are analytic; for pulse excitation, a numerical solution is required. The treatment invokes a hard-collision relaxation model. Such characteristics as the abrupt termination of the decay and the related edge echo, which result from Doppler dephasing, can be examined for Stark pulses of finite extent.

I. INTRODUCTION

This article reports the observation of optical free induction decay (FID)—the optical analog of FID in nuclear magnetic resonance.[1] A molecular sample which is coherently prepared by a cw laser beam exhibits such a decay when it is suddenly switched out of resonance by a Stark field. Results are given here for a nondegenerate Doppler-broadened infrared transition of NH_2D, where the sample is optically thin, and the decay behavior can be compared quantitatively with a solution of the Bloch equations. Such characteristics as the abrupt termination of the decay and the related edge echo, which are a result of the inhomogeneous Doppler dephasing, can be examined in detail. The Stark-pulse technique has also led recently to the observation of photon echoes,[2] optical nutation,[2] and two-photon superradiance.[3]

Free induction decay in nuclear magnetic resonance, predicted by Bloch[4] and observed by Hahn,[1] occurs when a group of coherently excited spins are allowed to precess freely in a magnetic field. The spin sample thus emits magnetic dipole radiation and induces an rf current in a pickup coil. In the presence of an external rf field, this signal is detected as a beat note which decays because of relaxation and interference processes.

In the optical region, FID arises when a group of coherently excited molecules spontaneously emit electric dipole radiation in the absence of the exciting field. For laser beam excitation, the FID emission is coherent, intense, and directional. These properties follow from the coherent preparation of the sample which contains molecules emitting in a cooperative manner with an enhanced spontaneious-emission rate. The behavior resembles Dicke's superradiance,[5] with the distinction that the system's quantum states (field plus molecules) are a superposition of the Dicke states. The semiclassical description, on the other hand, states that the sample is a set of N oscillating dipoles which are excited in phase by coherent light. The coherent preparation thus induces a macroscopic dipole moment which can radiate with an intensity proportional to N^2. For an optically thin sample, where propagation effects can be neglected, this description is the same as in nuclear resonance.

II. TECHNIQUE

The method used to observe optical FID is based on the realization that optical transient effects can be observed simply by pulsing the optical-molecular interaction. Our approach is to switch the transition frequency of the absorber in or out of resonance with a cw laser source.[2] In a low-pressure gas or possibly in some solids at low temper-

ature, switching may be accomplished by the Stark effect.

A schematic of our experimental arrangement is shown in Fig. 1 and the switching principle is illustrated in Fig. 2. A gaseous molecular sample which is Stark tunable is excited by a cw laser beam, and transient optical signals are observed in transmission by electronically gating the optical absorption with a pulsed electric field.

Consider now what happens in a nondegenerate two-level system when a step-function Stark field is applied. We assume that initially the laser frequency ω_L falls within the Doppler linewidth of ~80 MHz and excites in steady state a narrow velocity group v whose homogeneous linewidth is ~100 kHz. Referring to Fig. 2, this group will spontaneously radiate the FID signal at frequency ω when it is switched out of resonance by the Stark field. Simultaneously, a second velocity group v' will be suddenly switched into resonance and will exhibit an optical ringing or nutation effect. Both of these are shown in Fig. 3 for the molecule NH_2D. The nutation appears as a slowly varying background and the FID as a high frequency $(\omega_L - \omega)$ heterodyne beat signal since its emission is collinear with the laser beam and has the same polarization. Because the FID is short-lived, only one-half of a nutation period is shown. (Compare the nutation signal for CH_3F, Fig. 1 of Ref. 2, which possesses many periods of oscillation because the observation time is longer; however, FID is not evident in this degenerate transition since there are 18 different beat frequencies which interfere.)

It is evident that this technique possesses several unique advantages over the pulsed laser method. First, with a cw source the only time-dependent behavior is the desired transient effect itself. In contrast, a pulsed laser contributes a large background signal. Second, the Stark-pulse shape and duration as well as the pulse sequence and repetition rate can be tailored to the particular experiment since the pulses are generated electronically. Thus, transient signals may be easily stored in a computer for signal averaging or other data han-
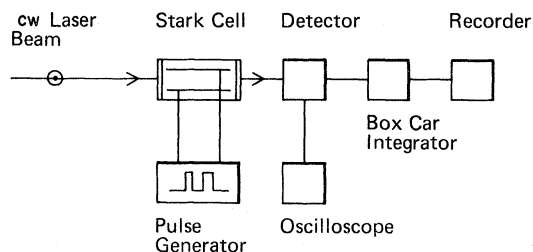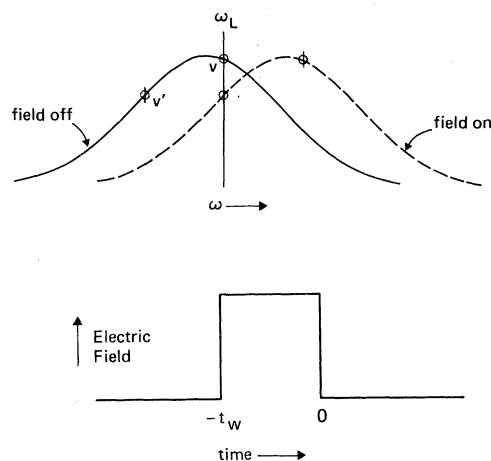

FIG. 2. Optical switching behavior of a nondegenerate Doppler-broadened transition produced by a Stark pulse of duration t_w. The laser frequency is ω_L.

dling. Third, heterodyne detection is possible, as in nuclear resonance, so that the sensitivity is enhanced a thousandfold.

III. APPARATUS

Returning to Fig. 1, we note that FID beat signals, monitored by a gold-doped germanium detector (40-nsec risetime), may be observed directly on an oscilloscope due to the high detection sensitivity. However, the noise level may be greatly suppressed as in Fig. 3 by the use of a boxcar integrator with 10-nsec resolution. This averages repetitive FID decays and the result can be conveniently displayed on an X-Y recorder in a period of about 5 min. In addition, traces of this kind may be stored digitally on line in an IBM 1800 computer and further averaged with some improvement.

For these studies, the molecule NH_2D is ideal since it possesses several nondegenerate transitions which are in near coincidence with CO_2 laser lines. The nondegeneracy property ensures a simple FID signal with a single beat. Furthermore, since the transition assignments and matrix elements are known, the results can be compared readily with theory. The principal transition examined was the $(v_2, J, M) = (1, 5, 5) \rightarrow (0, 4, 4)$ which was Stark tuned ~2000 MHz using a 3660-V/cm bias field (first-order Stark effect), into resonance with the $P(20)$ CO_2 laser line at 944.1948 cm^{-1}.[6] The transition $(1, 5, 3) \rightarrow (0, 4, 4)$ also occurs, but since it is 90 times weaker in its intensity, it can be neglected.

Repetitive Stark fields in the form of a step function or a square pulse are derived from pulse-forming circuits which consist of digital logic elements. This provides 0–40-V pulses of arbitrary length
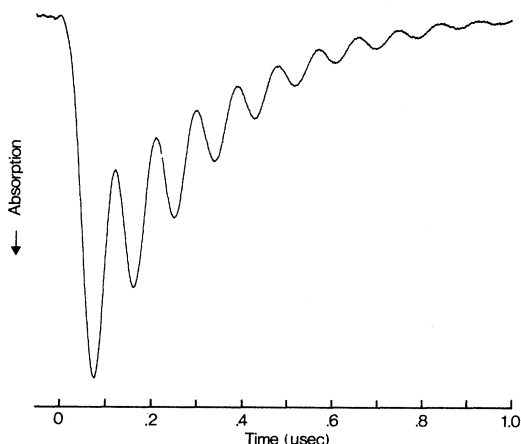

FIG. 1. Monitoring technique for observing optical transient signals following one or more Stark pulses.

FIG. 3. Optical FID in NH_2D at 10.6 μm following a step-function Stark field. The transition is (v_2, J, M) $= (1, 5, 4) \rightarrow (0, 4, 3)$. The signal appears as a heterodyne beat where the slowly varying background is the result of a second velocity group which undergoes optical nutation.

(80–2000 nsec), having a 40-nsec risetime.

The Stark cell is made of components with optical tolerances and includes two fused quartz disks which are 4 in. in diameter by $\frac{3}{4}$ in. thick, flat to $\pm 10^{-5}$ cm, and coated on the inner surfaces with vacuum-deposited aluminum. Separating the flats are fused quartz spacers whose thickness as determined by gauge blocks is 0.30531 ± 0.00003 cm. Even though the cell's optical path length is only 10 cm, it is quite adequate for obtaining signal-to-noise ratios in excess of 100 at sample pressures of a few mTorr. This is a consequence of NH_2D having a large vibrational transition matrix element of 0.3 D.[7] Nevertheless, the absorption is 1% or less, corresponding to ~10^{10} molecules, and satisfies the requirement for an optically thin sample.

Measurements were made using a stable free-running cw CO_2 laser which is described elsewhere.[8] It is sealed off and operates at a single-frequency (TEM_{00q} mode). Since the FID signal lasts no more than a few μsec, frequency jitter of the order of 20 kHz in a 1-sec interval is of no consequence in a single decay. Nevertheless, when signal averaging is employed, stability against drift is essential for reproducibility. Laser output is about 6 W/cm^2 in a 2.7-mm beam diameter for the $P(20)$ 10.6-μm line which is selected by a rotatable grating at one end of the laser cavity. A piezoelectric at the other end provides fine tuning of the optical cavity length (75 cm) for maximum output. The laser polarization is linear and perpendicular to the Stark field so that $\Delta M = \pm 1$ selection rules apply.

IV. THEORY

In this section a semiclassical treatment of optical FID is developed which can be compared quantitatively with our experimental results. The sample, which is prepared in a superposition state by a cw laser beam, freely radiates once it is switched out of resonance with the laser frequency by a Stark field. Our task is to obtain the electric field emitted for a preparative stage of arbitrary duration.

The polarization for an ensemble of two-level molecules is first obtained from a solution of the Bloch equations assuming an electric-dipole-allowed optical transition. The emitted electric field amplitude is then calculated from the Maxwell wave equation with this polarization as a source term. In a similar treatment, Shea, Hopf, and Scully have derived an expression for FID following an infinitely long Stark pulse.[9] Results are obtained here for Stark pulses of arbitrary length.

In the interest of simplicity, we ignore the fact that molecules are spread out over many wavelengths, and assume instead that they all see the same optical field $E = E_0 \cos\omega_L t$. Although the directionality properties of the emission are lost by such a treatment, the comparison between theory and experiment is not affected. For all molecules to see the same optical field the sample also must be optically thin, which is certainly true in our experiments. We also assume that hard collisions are the dominant relaxation mechanism, i.e., that $T_1 = T_2$. This is equivalent to the assumption that molecular collisions terminate coherent-emission processes, as for example by a change in rotational state. Soft collisions, which do not change the rotational state but only the molecular velocity, require a different treatment; in such a case, the emission frequency can actually shift because of a diffusion in the inhomogeneous line shape, a problem which has been handled in spin resonance[10] using the Fokker–Planck equation.

Another mechanism which is neglected is the cooperative or superradiant burst predicted by Dicke.[5] For an initially inverted population, this emission would appear as a hyperbolic secant pulse of width $\tau_P = \kappa/[g^2(N+1)]$ if the following inequalities[11] are satisfied:

$$1/T_2 \ll 1/\tau_P \ll \kappa \quad .$$

Here, $\kappa = c/2L$, where L is the sample length; N is the number of molecules; and $g = \mu_{ab}E_0/\hbar$. When the sample is initially in a superposition state, because of a $\frac{1}{2}\pi$ pulse, the same inequalities apply, but now the burst is replaced by a hyperbolic secant decay, i.e., only one-half of the pulse would occur. While it would be of considerable

interest to verify these theoretical expectations, the left-hand inequality is not met under our experimental conditions of low density ($\sim 10^9$ molecules/cm^3) and short path length (10 cm).

We begin by assuming that the laser frequency ω_L overlaps some Doppler-broadened transition of the sample as shown in Fig. 2. At some time $t = -t_w$, a Stark field suddenly shifts the center frequency of the transition Ω_0 to a new value Ω_0'. This causes molecules of velocity v to emit a FID signal while those of velocity v' are coherently excited. At $t = 0$, the Stark field returns to its original value, and now the group v' emits a FID while the group v is coherently excited. Let us focus our attention on the group v' for the purpose of this discussion. To describe this excitation and subsequent emission, we first solve the undamped Bloch equations for a single molecule, and then average over all transition frequencies ω_0 and all collision times t_0 for an ensemble of molecules.

In a coordinate frame rotating at ω_L, the undamped Bloch equations can be written

$$\dot{r}_{\text{I}} = - (\omega_0 - \omega_L) r_{\text{II}} \ ,$$

$$\dot{r}_{\text{II}} = (\omega_0 - \omega_L) r_{\text{I}} - 2y r_{\text{III}} \ , \tag{1}$$

$$\dot{r}_{\text{III}} = 2y r_{\text{II}} \ .$$

r_{I}, r_{II}, and r_{III} are components of a vector[12] $\vec{r}$ which describes the state of the molecule, ω_0 is the molecular transition frequency, and $y = \mu_{ab} E_0/2\hbar$. The optical field $E = E_0 \cos\omega_L t$ is assumed to be linearly polarized and μ_{ab} is the transition dipole matrix element.

For a molecule which entered the ground state of the transition via a collision at a time t_0 during the Stark pulse, Eqs. (1) give

$$r_{\text{I}}(t) = - [y(\omega_0 - \omega_L)/2\gamma^2]\{1 - \cos[(2\gamma)(t - t_0)]\} \ ,$$

$$r_{\text{II}}(t) = (y/\gamma) \sin[(2\gamma)(t - t_0)] \ , \tag{2}$$

$$r_{\text{III}}(t) = (y^2/\gamma^2)\{1 - \cos[(2\gamma)(t - t_0)]\} - 1 \ ,$$
where
$$\gamma = \tfrac{1}{2}[(\omega_0 - \omega_L)^2 + 4y^2]^{1/2} \ .$$

For a molecule entering the ground state *before* the Stark pulse, one has the same solutions as Eqs. (2) but with t_0 replaced by $-t_w$, since no excitation occurs until the Stark pulse begins.

At $t = 0$, the excited molecules are shifted out of resonance by turning off the Stark pulse. We assume that the frequency shift $\Delta\omega$ is large enough that every molecule excited during the pulse is now far off resonance, i.e., that $(\omega_0 + \Delta\omega) - \omega_L \gg 2y$ for each excited molecule. The minimum $\Delta\omega$ necessary to fulfill this condition will depend on the pulse

length and the laser intensity. For a long pulse and low laser intensity, $\Delta\omega$ need only be larger than the homogeneous width.

Since the molecules are far out of resonance for times $t > 0$, their behavior is very simple. The Bloch equations (1) now reduce to

$$\dot{r}_{\text{I}} = - (\omega_0 + \Delta\omega - \omega_L) r_{\text{II}} \ ,$$

$$\dot{r}_{\text{II}} \simeq (\omega_0 + \Delta\omega - \omega_L) r_{\text{I}} \ , \tag{3}$$

$$\dot{r}_{\text{III}} \simeq 0 \ ,$$

and hence $\vec{r}$ just precesses about the III axis. It is convenient to solve Eqs. (3) in a new coordinate frame rotating at $\omega_L + \Delta\omega$ since the emission will occur at this frequency. The solutions are given by

$$r_{\text{I}}(t) = - r_{\text{II}}(0) \sin(\omega_0 - \omega_L)t + r_{\text{I}}(0) \cos(\omega_0 - \omega_L)t \ ,$$

$$r_{\text{II}}(t) = r_{\text{II}}(0) \cos(\omega_0 - \omega_L)t + r_{\text{I}}(0) \sin(\omega_0 - \omega_L)t \ , \tag{4}$$

$$r_{\text{III}}(t) = r_{\text{III}}(0) \ .$$

These solutions hold for all times $t > 0$ with $r_{\text{I}}(0)$, $r_{\text{II}}(0)$, and $r_{\text{III}}(0)$ given by Eqs. (2) evaluated at $t = 0$. Equations (4) describe the behavior of a single molecule. It now remains to average over an ensemble of molecules, assuming random hard collisions with τ the mean time between collisions. At any time $t > t_0$, the number of molecules which entered the ground state via a collision between t_0 and $t_0 + dt_0$ and which have a transition frequency between ω_0 and $\omega_0 + d\omega_0$ is

$$N(\omega_0, t_0) = \frac{N}{\pi^{1/2}\Delta\omega_D \tau} e^{-(\omega_0 - \Omega_0)^2/\Delta\omega_D^2} e^{-(t-t_0)/\tau} dt_0 d\omega_0 \ , \tag{5}$$

where N is the equilibrium Boltzmann population of the ground state, $\Delta\omega_D = (\Omega_0/c)(2kT/m)^{1/2}$ is the Doppler width, and Ω_0 is the center frequency of the Doppler-broadened transition. Since the transition is assumed to be in the infrared or optical region, the number of molecules which enter the excited state via a collision is very small and will be ignored.

Because all the molecules in the group discussed above have identical transition frequencies and collision times, they also have identical solutions to the Bloch equations. Furthermore, one can show that the vector component r_{II} is proportional to the induced polarization with μ_{ab} the proportionality constant. Thus the polarization for the group of molecules is just

$$p(t, t_0, \omega_0) = N(\omega_0, t_0) \mu_{ab} r_{\text{II}}(t) \ , \tag{6}$$

where $r_{\text{II}}(t)$ is given by Eq. (4).

The induced polarization for the entire sample can be calculated by integrating Eq. (6) over all possible collision times t_0 and transition frequencies ω_0:

$$P(t) = \frac{N\mu_{ab}}{\Delta\omega_D \pi^{1/2}\tau} \int_{-\infty}^{\infty} d\omega_0 \exp\left[\frac{-(\omega_0 - \Omega_0)^2}{\Delta\omega_D^2}\right]$$

$$\times \left\{ \int \int_{-\infty}^{0} dt_0\, e^{-(t-t_0)/\tau} \gamma_{11}(t) \right\} \quad . \quad (7)$$

The integral in curly brackets can be done analyt-

ically. To simplify the resulting expressions we let $\theta = 2\gamma t_w$, $s = 2\gamma\tau$, $\Omega = \omega_0 - \omega_L$, and find that

$$P(t) = \frac{N\mu_{ab}y}{\Delta\omega_D \pi^{1/2}}\, e^{-t/\tau} \int_{-\infty}^{\infty} \exp\left[\frac{-(\omega_0 - \Omega_0)^2}{\Delta\omega_D^2}\right]$$

$$\times [p_1(t, \omega_0) + p_2(t, \omega_0)] d\omega_0 \quad , \quad (8)$$

where

$$p_1(t, \omega_0) = \frac{1}{\gamma}\, e^{-t_w/\tau}\left(\cos\Omega t \sin\theta - \frac{\Omega}{2\gamma}\sin(\Omega t)(1 - \cos\theta)\right) , \quad (9)$$

$$p_2(t, \omega_0) = \frac{2\tau}{1 + s^2}\left\{\cos\Omega t\left[1 - e^{-t_w/\tau}\left(\cos\theta + \frac{1}{s}\sin\theta\right)\right] - \tau\Omega\sin(\Omega t)\left[1 - e^{-t_w/\tau}\left(1 + \frac{1}{s}\sin\theta + \frac{1}{s^2}(1 - \cos\theta)\right)\right]\right\}. \quad (10)$$

In general the integral in Eq. (8) must be evaluated numerically, although one case for which analytic results can be obtained will be discussed below. The emitted electric field amplitude ϵ can be obtained from $P(t)$ by using the linearized form of the wave equation:

$$\left(\frac{1}{c}\frac{\partial}{\partial t} + \frac{\partial}{\partial z}\right)\epsilon = -\frac{2\pi i\omega_0}{c} P(t) \quad . \quad (11)$$

In our experiments, ϵ builds up over a sample length of only 10 cm while it decays away in a time on the order of τ, which is typically 1 μsec. Thus $\partial\epsilon/\partial z \gg 1/c \cdot \partial\epsilon/\partial t$ and Eq. (11) has the simple solution

$$\epsilon \cong -(2\pi i\omega_0 L/c) P(t) , \quad (12)$$

where L is the length of the sample, and we have assumed the polarization to be uniform throughout the sample.

It is useful to consider two limiting cases for the emission signal. First, if the Stark pulse is short compared to the relaxation time τ, $p_2(t, \omega_0)$ approaches zero since it is the polarization due to molecules which enter the ground state *during* the Stark pulse. Thus the entire polarization arises from $p_1(t, \omega_0)$, which is the contribution from molecules which were present in the ground state at the beginning of the Stark pulse. The phenomenon of edge echoes, which will be discussed below, also arises entirely from $p_1(t, \omega_0)$. Second, if the Stark pulse is long compared to the collisional relaxation time, $p_1(t, \omega_0)$ approaches zero, and $p_2(t, \omega_0)$ reduces to

$$p_2(t, \omega_0) = \frac{2\tau}{1 + s^2}(\cos\Omega t - \tau\Omega\sin\Omega t) \quad . \quad (13)$$

Since Eq. (13) has a frequency response which is very narrow compared to the Doppler width, the factor $e^{-(\omega_0 - \Omega_0)^2/\Delta\omega_D^2}$ can be pulled out of the integral in Eq. (8) and an analytic expression for $P(t)$ obtained:

$$P(t) = \exp\left(\frac{-(\omega_0 - \Omega_0)^2}{\Delta\omega_D^2}\right)$$

$$\times \left(\frac{2\mu_{ab}y N\pi^{1/2}}{\Delta\omega_D}\right)\left(\frac{1}{\tau(1/\tau^2 + 4y^2)^{1/2}} - 1\right)$$

$$\times \exp\left(\frac{-t}{\tau}\right)\exp\left[-\left(\frac{1}{\tau^2} + 4y^2\right)^{1/2}t\right]. \quad (14)$$

This result, which describes the polarization induced by an infinitely long Stark pulse, is identical to the result obtained by Shea, Hopf, and Scully.[9]

According to Eq. (14), the polarization and hence the induction signal, decay as $e^{-t/\tau}\, e^{-[1/\tau^2 + 4y^2]^{1/2}t}$. This has the following simple interpretation: (a) The first factor $e^{-t/\tau}$ is determined by collisional relaxation processes which determine the homogeneous linewidth of the freely radiating sample, and (b) the second factor $e^{-[1/\tau^2 + 4y^2]^{1/2}t}$ expresses the dephasing or the interference of transition dipoles due to the inhomogeneous Doppler broadening. The band width $(1/\tau^2 + 4y^2)^{1/2}$ reflects the homo-
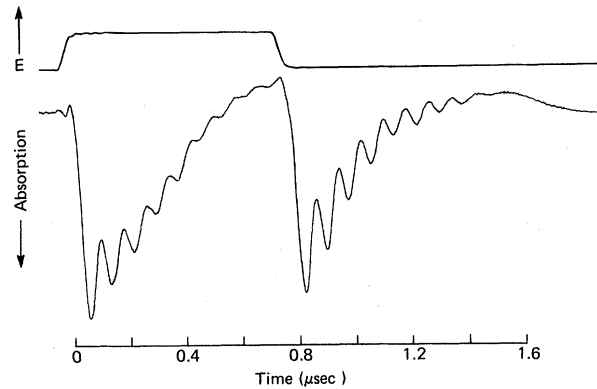

FIG. 4. Two optical FID signals in NH_2D at 10.6 μm associated with a Stark pulse ($\Delta E \sim 22$ V/cm). The transition is $(v_2, J, M) = (1, 5, 5) \rightarrow (0, 4, 4)$, and the sample pressure is 3.1 mTorr.

geneous width during the steady-state preparative stage and includes collisions and power broadening. Since the homogeneous line shape is burned into the Doppler profile, it leads to a rapid dephasing after the Stark field is applied. The freely radiating sample, which now exhibits no power broadening, will decay only by collisions and Doppler dephasing.

V. RESULTS AND DISCUSSION

Figure 3 shows the optical FID signal which is observed for NH_2D when the sample is prepared by a step-function Stark field. This result is the first clear observation of optical FID.[13] Because of the Stark shift, the FID appears as a beat with the laser, and this signal is superimposed on an optical nutation background. Using the Stark-pulse technique, we have now observed the optical analogs of all three basic NMR transient effects: optical nutation,[2] photon echoes,[2] and optical FID. In addition, two-photon superradiance[3] which is unknown in NMR has been seen with this method.

For the case of a step-function Stark field, Eq. (14) gives an analytical description for the decay which may now be compared with our observations. For evaluation, the parameter $\tau = 1.2$ μsec is obtained from the photon echo decay envelope and $2y = 8.7$ MHz is derived from the period of optical nutation. This yields an effective decay constant $\tau_{eff} = 0.1$ μsec where $1/\tau_{eff} = 1/\tau + (1/\tau^2 + 4y^2)^{1/2}$. By comparison, the measured FID value under the same experimental conditions is 0.12 μsec. Note that this decay constant is ten times faster than the echo result because of rapid dephasing. This reflects the power-broadened linewidth which was burned into the Doppler profile during the preparation ($4y^2 \gg 1/\tau^2$). The decay behavior of Eq. (14), therefore, is in quantitative agreement with our experimental findings.

When a Stark field pulse is applied rather than a step function, new effects appear, such as the abrupt termination of FID and the formation of edge echoes. The termination behavior is illustrated in the second FID signal of Fig. 4. The beat suddenly disappears after a time equal to the pulse width (0.75 μsec), i.e., at $t = 1.5$ μsec. This type of behavior has been discussed theoretically by Hopf and Scully.[14] Qualitatively, the effect results from the fact that a pulse of width t_w excites a frequency band of $\sim (\Omega \pm 2\pi/t_w)$. The dipoles then dephase completely in a time which is just the Fourier
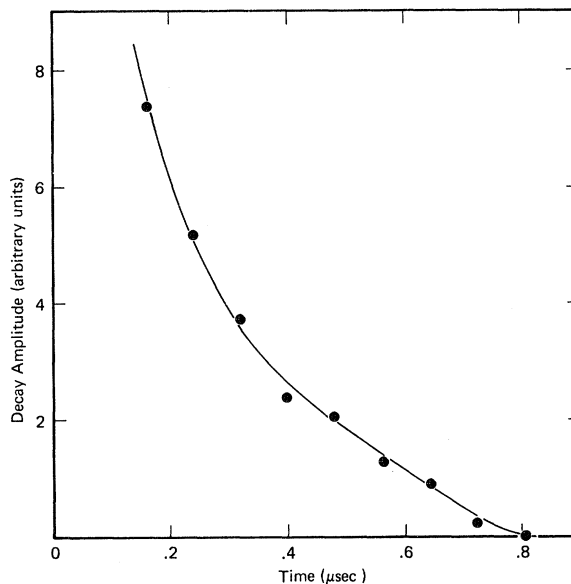

FIG. 5. Free induction decay amplitude in NH_2D vs time for the second FID of Fig. 4. Closed circles: experimental; solid line: numerical evaluation of Eq. (8).

transform of this bandwidth, i.e., in a time t_w.

The decay amplitude for the second FID signal of Fig. 4 is plotted in Fig. 5 (closed circles). The solid line is a theoretical calculation using a numerical integration of Eq. (8) with the parameters $2y = 6$ MHz, $\tau = 1.4$ μsec, and a pulse length of 0.8 μsec. Here also the agreement between theory and experiment is quite satisfactory. The curve shown in Fig. 5 is the response to a pulse of $\sim 1.5\pi$. Numerical calculations show that for pulses of 2π or greater the decay curve begins to show an oscillatory behavior just before it disappears. This is the edge echo which was first observed by Bloom in NMR.[15] In the present experiments the laser intensity was not high enough to see this phenomenon clearly, although a flattening out of the decay curve near its termination was observed.

ACKNOWLEDGMENTS

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Infrared and Raman Spectra of Inert Solutions of Diatomic Molecules. II. Stochastic Theory of Band Moments

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The spectral moments of ir and Raman bands of diatomic molecules in inert solutions are calculated by the help of recent stochastic theories of ir- and Raman-band profiles. Both vibrational and rotational motions are considered. It is found that for ir and rotational Raman bands, the stochastic theories produce expressions for the band moments which closely parallel the corresponding thermodynamic expressions. New expressions are proposed for the moments of isotropic and of vibrational-rotational anisotropic Raman bands.

I. INTRODUCTION

Spectral moments $(\omega_n)_\omega$, of ir and rotational Raman (R) bands of liquids formed by linear molecules have been calculated, for low n, by the help of full thermodynamic theories implying the totality of $3N$ degrees of freedom of the liquid state.[1-4] The purpose of this communication is to show that, using widely different mathematical techniques, the stochastic theories[5,6] produce expressions for $(\omega_n)_\omega$, which closely parallel the corresponding thermodynamic expressions. The simplicity of the procedure makes it easy to determine the spectral moments of isotropic and of vibrational-rotational anisotropic R bands which have not yet been calculated in any other way.

II. THEORY

The system being investigated is formed by an active molecule and a large number of nonactive solvent molecules. The following four basic hypotheses are introduced: (a) The active molecule executes anharmonic vibrations modulated by a stochastic potential $V_s(r, t)$ because of the solvent. (b) The active molecule executes stochastic reorientations describable by means of the variable $\theta(t)$; this variable represents the angle between two successive directions $\vec{u}(0)$, $\vec{u}(t)$ of the molecular axis. (c) The correlation between vibrations and rotations is taken to be small and is neglected. (d) The vibrations are describable by the help of

quantum mechanics; the rotations are describable by means of classical mechanics. The conditions of validity of semiclassical theories have been discussed, e.g., in the Ref. 7.

The spectral moments $(\omega_n)_\omega$, and the correlation function $G(t)$ of the band under study are simply related. Putting

$$\omega^n e^{i\omega t} = (-i)^n \frac{d^n}{dt^n} (e^{i\omega t})$$

and integrating by parts gives

$$(\omega_n)_0 \equiv \frac{\int I(\omega)\omega^n d\omega}{\int I(\omega) d\omega} = \frac{\int d\omega\, \omega^n [\int_{-\infty}^{\infty} G(t) e^{i\omega t} dt]}{\int d\omega [\int_{-\infty}^{\infty} G(t) e^{i\omega t} dt]}$$

$$= i^n \frac{G^{(n)}(0)}{G(0)} , \tag{1a}$$

$$(\omega_n)_{\omega'} \equiv \frac{\int I(\omega)(\omega - \omega')^n d\omega}{\int I(\omega) d\omega}$$

$$= \sum_{p=0}^{n} (-1)^p C_n^p (\omega_{n-p})_0 \omega'^p , \tag{1b}$$

where $I(\omega)$ is the band intensity at the frequency ω and C_n^p are the binomial coefficients. Thus calculating band moments essentially reduces to the differentiation of correlation functions.[8,4,6] The results are most simply expressible by introducing unique symbol γ to designate either M, α, or β. where M is the length of the dipole moment vector $\vec{M}$ of the active molecule, α its mean polarizability, and β its magnitude of anisotropy. The calculation is indicated in Secs. III–V.