use of one-dimensional solid-state systems in nonlinear optics. The strong dependence of $\chi^{(3)}$ on energy gap suggests that the study of small-gap compounds might uncover large nonlinearities in the infrared. In order to study separately the influence of electronic delocalization the present experiments have been conducted on centrosymmetric diacetylenes. In compounds $R-C\equiv C-C\equiv C-R'$, the two different substituent groups will produce an asymmetry of the pseudopotential and allow the existence of a second-order susceptibility $\chi^{(2)}$. This asymmetry might however reduce the delocalization. Experiments are planned to study the possible opposing influences of these two factors on $\chi^{(2)}$.

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Optical Coherent Transients by Laser Frequency Switching*

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Coherence phenomena such as photon echoes, free induction, and nutation effects are easily detected in molecular iodine using a *frequency-switched* tunable cw dye laser. This technique is generally applicable to atoms, molecules, and solids and offers unique ways for probing dynamic interactions in a selective manner. Elastic and inelastic collision mechanisms for I_2 are examined independently and compared with theory.

We present a simple and versatile laser technique which should prove useful in observing coherent optical transient phenomena in atoms, molecules, and solids. In concept, the method is analogous to pulsed nuclear-magnetic-resonance techniques,[1-3] but in practice, it more closely resembles the recently introduced Stark-switching method.[4-7]

To illustrate its use, we demonstrate photon echoes,[8] free induction decay (FID),[5] and nutation effects[4,9] in numerous lines of the visible electronic transition of I_2 (Fig. 1). Similar observations have been made also on the sodium D lines. Our work contrasts with classical optical line-broadening measurements where the various broadening mechanisms invariably remain hidden within the optical line shape. Coherent transient methods, on the other hand, allow one to distinguish individual dephasing processes. As an initial example, we inspect the collisional properties of I_2.

In the earlier Stark-switching experiments, a prescribed sequence of low-voltage Stark pulses switched a molecular sample into or out of resonance with an infrared beam from a fixed-frequency cw CO_2 laser.[4-6] Coherent emission or absorption transients were detected in the transmitted beam. A variant of this idea was later

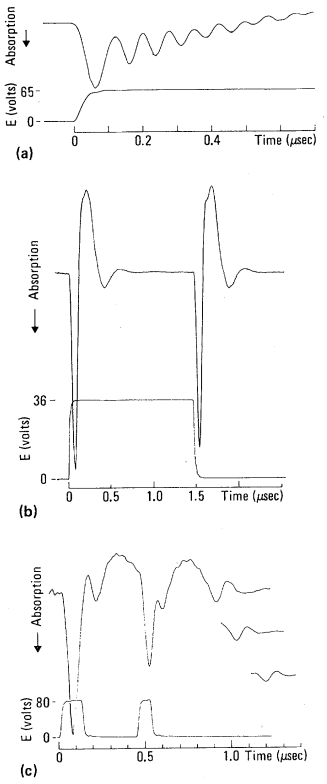

FIG. 1. Coherent optical transient phenomena in I_2 vapor: (a) free induction decay where the emission and laser produce a 13-MHz beat; (b) two optical nutation patterns; and (c) photon echoes occurring at ~1 μsec where the successive echoes decay with increasing pulse delay time. The frequency-switching pulse pattern is displayed in the lower trace of each figure.

realized by Hall[10] who *frequency switched* the laser instead of the sample. Optical transients arose for a methane sample located inside the cavity of a frequency-modulated 3.39-μm He-Ne laser.

In our configuration, Fig. 2, a stable tunable cw dye laser[11] is frequency switched while the sample's transition frequency remains constant. The sample is now external to the laser system so as to not affect its performance. Coherent transient signals again appear in the forward beam. Frequency switching is achieved with an electro-optic crystal of ammonium dihydrogen phosphate (ADP), which is inside the dye-laser cavity and is driven by a sequence of low-voltage pulses. The laser frequency follows the refractive-index variations induced in the ADP crystal. Hence, the experiment is controlled electronically and in such a way that the advantages inherent in the Stark technique are preserved here

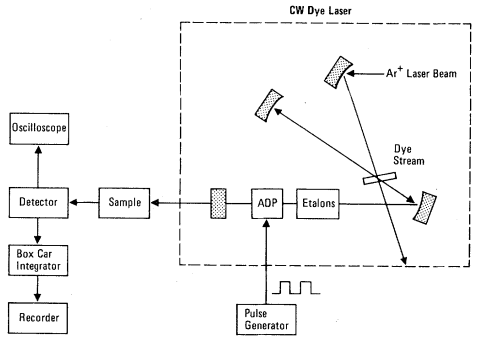

FIG. 2. Schematic of the apparatus for observing coherent optical transients using a frequency-switched cw dye laser.

as well. We find, therefore, the following: (1) The only transient observed is the desired coherent transient itself; this is not the case with pulsed-laser sources as the small coherent transient signal often rides on top of the laser pulse and the two are not easily separated. (2) Heterodyne detection is possible because the coherently radiated light propagates with the laser beam in the forward direction and is shifted from it in frequency; this increases the signal amplitude several orders of magnitude and facilitates measuring the decay of emission signals. (3) A further improvement in signal-to-noise ratio results with signal averaging, which is possible because the pulse sequence is repetitive. (4) The entire class of coherent optical transient effects can be monitored since the electronic pulse sequence can be tailored to the particular experiment of interest. *Moreover, when these features are combined with the broad tuning range available in a dye laser, it is apparent that coherent transient phenomena can now be observed with ease in a large number of optical transitions in various atomic, molecular, and solid-state systems.*

A Spectra-Physics 580A cw dye laser is utilized but modified to include the ADP modulator. The dye is Rhodamine 6G. The output beam is single mode, linearly polarized, and has a power up to 100 mW in a beam diameter of 0.5 mm. The collimated beam irradiates in single pass an evacuated and sealed-off cell, of 20 cm length, containing I_2 at a vapor pressure (3–150 mTorr) determined by a refrigerated cold finger. Laser tuning by means of an intracavity etalon allows the selection of a particular I_2 line where the overlapping Doppler-broadened I_2 hyperfine components span ~1 GHz (Doppler width, 395 MHz full width at half-maximum). Coherent transients

in I_2 are seen even at a fraction of 1 mW laser power.

The intracavity ADP crystal is driven by an HP 1900A or 214A pulse generator with a single or double pulse sequence and at a 25-kHz repetition rate. A *p-i-n* photodiode monitors the forward beam, and transients are observed with a Tektronix 7704 sampling oscilloscope or a boxcar integrator. From the observed FID beat frequency, we find that the ADP electro-optic frequency-shift parameter is 0.2 MHz/V. Hence, ~30-V pulses are adequate for nonadiabatically switching the laser frequency outside an I_2 homogeneous linewidth of ~1 MHz. On the other hand, the laser does not emit a transient signal itself, which otherwise would obscure observations in the sample, because switching occurs inside the dye's homogeneous linewidth of $\gtrsim 200$ MHz.

From the multitude of $^{127}I_2$ lines accessible, we selected in these initial studies only one line, $(v, J) = 2,59 \rightarrow 15,60$, of the electronic transition $X^1\Sigma_g^+ \rightarrow B^3\Pi_{0^+u}$. It falls at 16 956.43 cm^{-1}, 7.6 GHz to the high-frequency side of the sodium *D* line. The vibration-rotation assignment was verified from the calculated line position and the fluorescence spectrum using a 150 000×-resolving-power spectrometer.

The three coherent transient effects shown in Fig. 1 are (a) FID of an I_2 velocity group that is prepared under steady-state conditions and where the laser frequency is abruptly switched by a step-function voltage pulse; (b) optical nutation patterns arising from an I_2 velocity group that is suddenly excited at the beginning of the switching pulse and a second velocity group at the end; and (c) the photon-echo pulse which follows two short switching pulses. The theory[5,6,12] of these processes parallels the molecular infrared case for *vibration-rotation* transitions where Stark switching was employed. For *electronic* transitions, however, we must generalize these density-matrix calculations to allow the upper (level a) and lower (level b) transition levels to depopulate at different rates, $\gamma_a \neq \gamma_b$, where γ_a and γ_b are the total decay rates, radiative and nonradiative (elastic and inelastic), of the diagonal density-matrix elements.[13] Furthermore, to agree with our experiments, it will be necessary to consider that during *elastic collisions* upper and lower transition states frequency shift by significantly different amounts, so that the off-diagonal element exhibits quantum mechanical *phase interruptions* rather than classical *velocity changes*. This subtle point has emerged recently in certain line-broadening theories[14] and is consistent with the results obtained here. It follows that the normalized echo field amplitude will decay with pulse delay time τ as

$$E_c(t = 2\tau) = e^{-\gamma t}, \tag{1}$$

where $\gamma = (\gamma_a + \gamma_b)/2 + \gamma_\varphi$ is the rate[15] at which the optically induced dipole dephases and γ_φ is the elastic collision rate for phase interruptions caused by perturber-induced energy-level shifts. We note that the infrared echo results[6] represent the other limiting case where elastic collisions are dominated by velocity changes and the echo decay law is not a simple exponential. Our results, therefore, support the Berman-Lamb theory[14] for these limiting cases.

The two-pulse sequence of Fig. 1(c) also allows a measurement of the rate of population recovery, which results from *inelastic collisions* and radiative decay. The first pulse causes the upper level (a) to gain in population at the expense of the lower level (b) while the second-pulse nutation signal is a measure of the extent that the population difference of the transition levels has recovered between the two pulses. The method is described elsewhere.[6] Using the density-matrix equation of motion, we find that the normalized second nutation amplitude grows with pulse delay time τ as

$$S_\infty - S(t = \tau) = \exp(-\gamma_a t)\left(1 + \frac{\gamma_1}{\gamma_a - \gamma_b}\right) + \exp(-\gamma_b t)\left(1 - \frac{\gamma_1}{\gamma_a - \gamma_b}\right), \tag{2}$$

where S_∞ is the value at $\tau = \infty$, which we identify with the first-pulse nutation amplitude. The quantity γ_1 is the decay rate for the single channel $a \rightarrow b$; from the fluorescence intensities of the lines originating in level a, we estimate that $\gamma_1 \sim 0.1\gamma_a$. The rate γ_b is, of course, restricted to collisional processes. Equation (2) suggests that lower- and upper-state decay rates can be determined independently.

The two-pulse nutation measurements are characterized by essentially a single exponential decay in the pressure range 17–130 mTorr, indicating that $\gamma_b \sim \gamma_a$. It follows from (2) that the short-time decay rate is $(\gamma_a + \gamma_b + \gamma_1)/2$. The observed value is

$$(\gamma_a + \gamma_b + \gamma_1)/2 = (0.71 + 0.029p)\ \mu sec^{-1}, \tag{3}$$

where the I_2 pressure p is in millitorr. From the pressure-independent part, we obtain an up-

per-state radiative lifetime of about 1.4 μsec. The value is in reasonable agreement with the previous literature[16] and also agrees with our direct fluorescence-decay measurements, giving 1.32 μsec at zero pressure. The pressure-dependent part of (3) yields a total *inelastic collision cross section* $\sigma_I = 530$ Å^2. This result is about one order of magnitude larger than previous fluorescence measurements,[16] which often are insensitive to upper-state vibration-rotation quantum jumps of the emitter. In the pressure regime below 17 mTorr, the lower state seems to decay more slowly than the upper state, in accord with (2), but laser jitter and drift prevent quantitative measurements at present. Frequency locking the dye laser to the I_2 line of interest should remove this difficulty in the future.

The echo measurements reveal a different aspect of the problem, namely, the degree to which coherence is preserved following collisions. We find that the echo decays exponentially as predicted by (1), and no evidence is found for an $\exp(-Kt^3)$ decay law at short times ($\sim$100 nsec) which would be symptomatic of velocity-changing collisions.[6] The echo decay rate is

$$\gamma = (0.79 + 0.071p)\ \mu\text{sec}^{-1}, \qquad (4)$$

with p in millitorr of I_2. Utilizing the pressure-dependent parts of (3) and (4) and the relation $\gamma = (\gamma_a + \gamma_b)/2 + \gamma_\varphi$, we obtain the *elastic collision cross section* $\sigma_E = 780$ Å^2 associated with the phase interruption rate γ_φ. *We believe this to be the first optical coherence measurement of phase-interrupting collisions.* While this information is contained in the optical linewidth, it cannot generally be separated from other causes such as power, Doppler, and inelastic-collision broadening.

Although several papers[16] have dealt with the I_2 relaxation problem in the past, the measurements have been restricted almost exclusively to the upper state and to inelastic collisions, primarily those that terminate spontaneous emission such as predissociation. Some evidence for quasielastic I_2 collisions has appeared just recently also.[17]

These preliminary results may obviously be extended in several different directions—to other optically excited systems and to other coherent transient phenomena, in a manner resembling the elegant methods of pulsed NMR.

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