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Observation of Coherent Transient Birefringence in CS_2 Vapor*

J. P. Heritage, T. K. Gustafson, and C. H. Lin
Electronic Research Laboratory, University of California, Berkeley, California 94720
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We have observed short-duration birefringence in CS_2 vapor 38 and 76 psec after excitation with a mode-locked (~ 5 psec duration) 1.06-μm glass:Nd^{3+} laser pulse. These bursts are attributed to the time evolution of a coherent sum of rotational superposition states.

The refractive index of a collection of molecules prepared in a coherent superposition of several states by a pulsed excitation will in general be modulated with periods corresponding to the inverse of the transition frequencies between these states. If, as is the case for rotations, the transition frequencies display integral relationships, the refractive index exhibits short bursts separated by the fundamental periods. We have observed birefringence due to such a coherent superposition of approximately sixteen rotational states within the ground electronic and vibrational states of the linear CS_2 molecule. This has been demonstrated in the vapor at 325°K by observing ~ 10^{-11}-sec-duration birefringence centered at 38 and 76 psec subsequent to excitation with a single ultrashort (≈ 5 psec) infrared pulse. The observed 38-psec period corresponds to $1/8Bc$, where B is the rotational constant of the CS_2 molecule ($B = 0.109$ cm^{-1}).[1]

The coherent superposition of the rotational states is obtained by Raman mixing. Frequency components of the field at Stokes and anti-Stokes as well as pump frequencies are simultaneously available for ~ 35 rotational Raman transitions as a result of the overlap of the intensity spectrum of the excitation pulse with the rotational Raman transition frequencies. Each Raman process[2] (term diagram of Fig. 1) prepares a superposition state whose evolution frequency is the Raman frequency. For a linear molecule this is $\Omega_J = 4\pi Bc(2J+3)$, where J is the angular momentum quantum number associated with the lower of the two rotational states. The overall coherent superposition of states consists of a sum of these individual superposition states. In the classical limit of large J the coherent evolution can be viewed as phased rotation of a fraction of the molecules at the integrally related Raman transition frequencies Ω_J resulting in a periodic molecular alignment along the polarization direction of the excitation pulse.

The macroscopic susceptibility change associated with the polarization direction of the exciting field is described by a sum of Fourier components at the evolution frequencies Ω_J. For a linear molecule this is given by

$$\Delta\chi(t) = \frac{2\pi}{n_0} N \sum_{\substack{J=0 \\ J\,\text{even}}}^{\infty} 2\,\mathrm{Im}\left[T_J \int_0^t \exp(-i\Omega_J t')\langle \vec{E}\cdot\vec{E}\rangle\, dt' \exp(i\Omega_J t)\right]. \qquad (1)$$

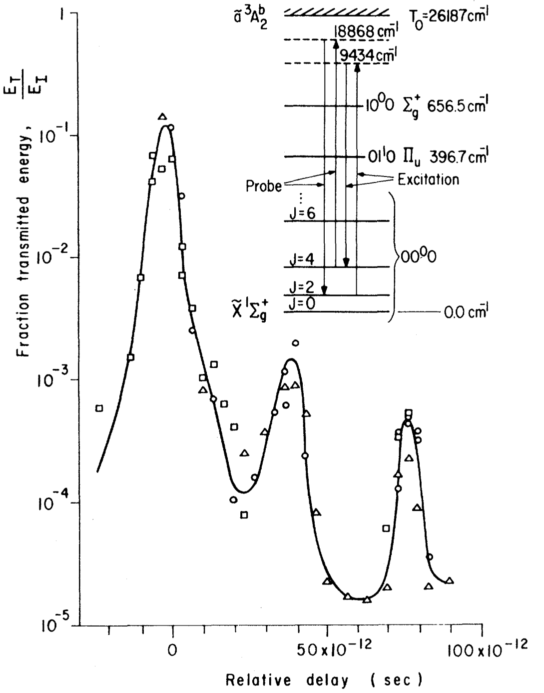

FIG. 1. The measured time dependence of the fraction of energy transmitted through the analyzing polarizer. The time origin was taken to be the observed peak in the transmitted energy. Also shown is the appropriate portion of the term diagram for the CS_2 molecule. One component of the overall Raman-mixing process is indicated (for $\Omega_J=\Omega_2$). The dashed lines indicate virtual states lying below the excited electronic states. [See G. Hertzberg, Ref. 1, p. 276, and *Electronic Spectra of Polyatomic Molecules* (Van Nostrand-Reinhold, New York, 1966), p. 601.]

T_J is the Raman coupling coefficient[3] which is dependent upon the rotational-level populations, the molecular susceptibilities, and the matrix elements. $\langle\vec{E}\cdot\vec{E}\rangle$ is the square of the optical electric field averaged over a few optical cycles.

For CS_2, the specific molecule of interest, the statistics of the identical sulfur nuclei demands the absence of all odd rotational states (J odd). As a result the period of the birefringence pulses is $1/8Bc$. Details of the refractive-index profiles are indicated in Fig. 2. Equation (1) shows that the maximum response of the coherent periodic birefringence is produced when the intensity spectrum of the excitation efficiently overlaps the rotational spectrum. This is obtained when the excitation pulse duration is of the order of the period of the transitions among the most highly populated rotational levels. For CS_2 near room temperature the optimal pulse width is approximately 0.8 psec.

The time dependence of the birefringence was detected experimentally with a modification of the Duguay and Hansen[4] high-speed optical shutter (Fig. 3). The intense beam consisted of an 8-nsec-period train of ultrashort optical pulses of wavelength 1.06 μm generated by the mode-locked glass:Nd^{+3} laser. The weak probe beam was a train of 0.53-μm pulses obtained by harmonic generation of the fundamental infrared pulses.

The birefringence induced by the 1.06-μm excitation pulse was observed by measuring the probe energy transmitted through the analyzing polarizer, as a function of the probe-pulse delay.

The energy transmitted through the analyzing polarizer consists of contributions from both the time-dependent susceptibility change induced in the gas and the spurious contributions which limit the detectability of the signal. The measured analyzing extinction ratio for nonoverlapping probe and Nd^{3+} excitation pulses was 10^{-5}. This

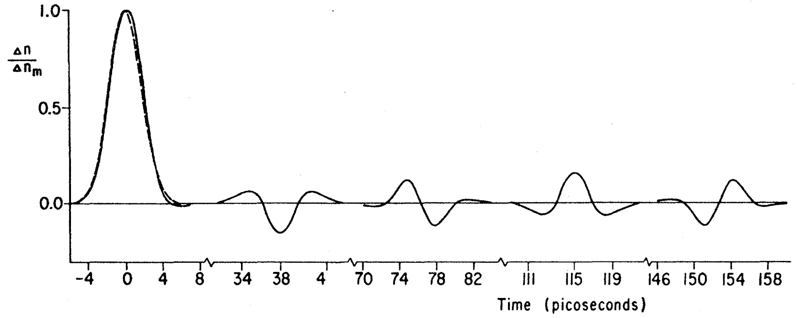

FIG. 2. Theoretically predicted time variation of the refractive-index change induced by a Gaussian-shaped optical pulse in CS_2 vapor at 296°K. The full $1/e$ intensity pulse width was taken to be 5 psec. The dashed line indicates the time-independent perturbation results. The normalization factor is

$$\Delta n_m=(2\pi N/30n_0)(\Delta\alpha)^2\langle\vec{E}\cdot\vec{E}\rangle/kT=1.74\times10^{-10}\langle\vec{E}\cdot\vec{E}\rangle\ \text{esu/mole},$$

where n_0 is the linear refractive index.

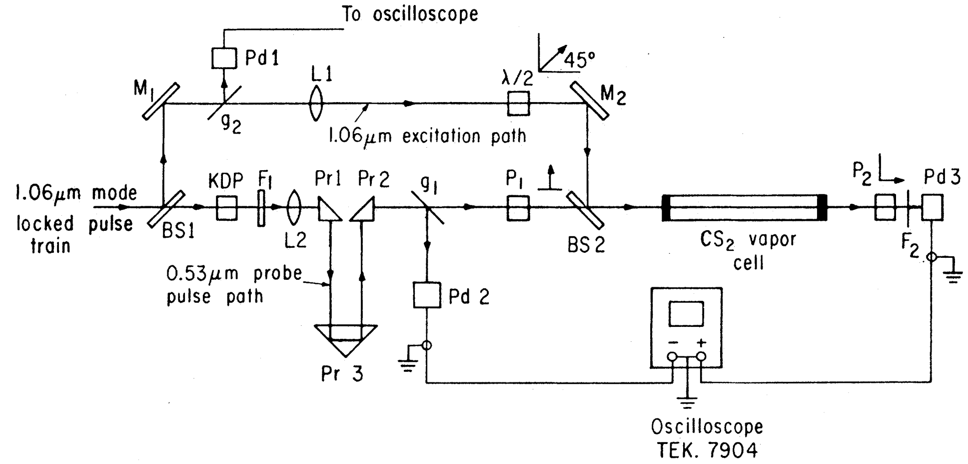

FIG. 3. Schematic of the experimental arrangement used to detect the quantum beat. BS1 and BS2 are beam splitters. M_1 and M_2 are mirrors. The potassium dihydrogen phosphate (KDP) crystal was used to generate the second harmonic of the 1.06-μm pulses. F_1 and F_2 filter out residual 1.06-μm radiation. g_1 and g_2 represent glass plates and Pd1, Pd2, and Pd3 the photodetectors. Prisms Pr1, Pr2, and Pr3 formed the adjustable delay line. P_1 and P_2 are polarizers oriented as indicated and λ/2 represents a half-wave plate. L_1 and L_2 represent 1.5-m-focal-length lenses. The CS_2 vapor cell was 1 m in length.

limited the minimum measurable refractive-index change of the vapor to 1×10^{-9} esu for the probe wavelength of 0.53 μm and the cell length of 1 m. The fraction of transmitted probe energy due to the induced birefringence in the optical components, which contribute only when the probe and excitation pulses overlapped, was estimated to be $\approx 10^{-3}$.

It was generally found that only the first few pulses out of the trains of ~ 45 pulses both were reliably mode-locked and displayed little energy between the pulses or on the wings of the pulses. Data obtained from the second pulse through 90 psec of relative delay between the probe and excitation are displayed in Fig. 1 for CS_2 vapor.

The refractive-index change detected for zero delay is associated with the developing coherence as well as with the conventional intensity-dependent Kerr effect. The width of this initial response gives an optical-excitation pulse width of approximately 5 psec. The peak response ($E_T/E_I \simeq 0.12$) at zero delay is consistent with the estimated energy of $\frac{1}{2}$ mJ/pulse as obtained from a calorimeter measurement over the entire train at the cell entrance and the 5-psec pulse width.

The birefringence burst displayed in Fig. 1 corresponding to a relative delay of 38 psec between excitation and probe pulses is attributed to the first coherent constructive superposition initiated by the 5-psec excitation pulse. The experimentally observed delay agrees with the expected delay $1/8Bc$ and corresponds to the inverse of the difference between even-J transition frequencies. This particular beat component is a direct result of the nuclear-spin statistics and would be absent if symmetry upon interchange of the nuclei (sulfur) were absent. The diminished magnitude of this birefringence burst with respect to that of the zero-delay birefringence is due to an excitation pulse of duration longer than the 0.8-psec optimum. The theoretically calculated relative strength correlates well with the experimentally measured 5-psec duration of the 1.06-μm excitation pulse.

The second burst in the birefringence corresponding to a relative delay of $1/4Bc$ (76 psec) was also observed experimentally as shown in Fig. 1. The diminished amplitude with respect to the initial coherent burst at 38 psec indicates the presence of dephasing processes. The two most important of these are anticipated to be collisions and the interference of overlapping vibrational levels[1] at 396.7 and 656.5 cm^{-1} above the ground rotational state as indicated in the term diagram of Fig. 1.

Several checks were made in order to verify that both of the delayed responses were due to the quantum interference. The most important check verified that a $\frac{1}{2}$-cm cell of liquid CS_2 displayed only extinction-limited response when it was substituted for the vapor cells at delays of 38 and 76 psec. The birefringence peaks returned upon relacing the vapor cell. This check was particularly important since satellite pulse trains or long infrared pulses could give deceptive results. In addition several complete scans over 100 psec of delay through the liquid CS_2 sample resulted in rapid monotonic decay to the extinction limit.

We note that the preparation and probing of the rotational excitations can be viewed as a superposition of two two-photon scattering processes involving the creation and destruction of coherent rotational excitations. Thus the excitations not only produce birefringence but also mix with the spectrum of the probe to produce Stokes and anti-Stokes spectral shifts. For a single, short, scattered probe pulse, superposition over all the evolution frequencies Ω_J results in a broadened frequency spectrum which would not reveal the rotational structure. Probing of the excitation with a pulse longer than $1/2Bc$ would resolve the rotational frequency components within the ground state. Resonant enhancement of the polarizability at the probe wavelength is possible when the linewidth is smaller than $2Bc$. If square-law detection were used Raman beats[5,6] at the probe transition frequencies Ω_J would then in principle be observable.

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[1] G. Hertzberg, *Infrared and Raman Spectra* (Van Nostrand–Reinhold, New York, 1966), p. 396.

[2] The effective interaction Hamiltonian is

$$H'(t) = \Delta\alpha\langle\vec{E}\cdot\vec{E}\rangle\cos^2\theta - \alpha_\perp\langle\vec{E}\cdot\vec{E}\rangle,$$

where θ is the angle between the molecular axis and the direction of the electric field vector $\vec{E}$, and $\Delta\alpha = \alpha_\parallel - \alpha_\perp$, with $\alpha_\parallel$ and $\alpha_\perp$ the polarizabilities parallel and perpendicular to the molecular axis, respectively. The nonzero matrix elements of $H'(t)$ are $H_{J,J}'$ and $H_{J,J\pm 2}'$ with the projection quantum number M unchanged.

[3] C. H. Lin, J. P. Heritage, and T. K. Gustafson, Appl. Phys. Lett. 19, 397 (1971); the value of T_J for linear molecules is

$$\frac{1}{15}\frac{(J+2)(J+1)}{(2J+3)}\frac{|D_{J+2}(0)|^2 - |D_J(0)|^2}{\hbar}(\Delta\alpha)^2,$$

where $|D_J(0)|^2$ is the occupation probability of the Jth state.

[4] M. A. Duguay and J. H. Hansen, Appl. Phys. Lett. 15, 192 (1969).

[5] R. L. Shoemaker and R. G. Brewer, Phys. Rev. Lett. 28, 1430 (1972). Other quantum-beat experiments have been reported by H. J. Andrä, Phys. Rev. Lett. 25, 325 (1970); J. N. Dodd, R. D. Kaul, and D. M. Warrington, Proc. Phys. Soc., London 84, 176 (1964); S. Haroche, M. Gross, and M. P. Silverman, Phys. Rev. Lett. 33, 1063 (1974), and references cited therein; and R. L. Shoemaker and F. A. Hopf, Phys. Rev. Lett. 33, 1527 (1974).

[6] As in Raman-beat experiments we note that the overall interaction occurs over the full Doppler line.

Molecular Quadrupoles and Atomic Shielding Factors

G. Karl, B. Nickel, J. D. Poll, and L. Wolniewicz*
Department of Physics, University of Guelph, Guelph N1G 2W1, Canada

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The electronic quadrupole moments of H_2^+ and H_2 are quadratic in the internuclear distance R at short distances and the coefficient of proportionality is the quadrupole shielding factor of the He^+ or He atom, respectively. The behavior of the quadrupole moment of H_2^+ at short and long distances can be used to approximate it at all distances.

Multipole moments are useful to describe the electromagnetic coupling of any system. For diatomic molecules the multipole moments can be computed from a (molecular) wave function which, in the Born-Oppenheimer approximation, is a function of the distance between the nuclei R. Since the wave function contains much more information than a particular multipole extracted from it, one may ask whether a specific multipole could not be obtained with less input. In this note we describe an attempt to constrain the molecular quadrupole moment, without a full computation of the molecular wave function. We discuss here the ground state of the hydrogen molecule ion H_2^+ and the hydrogen molecule H_2 whose quadrupole moments are known quite accurately.