COHERENT OPTICAL MIXING IN OPTICALLY ACTIVE LIQUIDS

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This Letter reports the observation of coherent optical sum-frequency generation in aqueous arabinose ($C_5H_{10}O_5$) solutions and other optically active liquids. The results indicate a quadratic polarizability correlated with optical activity, within one order of magnitude of the nonlinear polarizability in piezoelectric crystals. Coherent quadratic polarizability in randomly oriented molecules arises from the same structural features responsible for optical activity; the mechanisms of the two effects differ in detail, however, and their relative magnitude provides new information on molecular structure. In our experiments light beams at 6943 and 3472 Å intersected in the liquid sample to generate collimated sum-frequency emission at 2314 Å. Mirror-image solutions of the *d*- and *l*-arabinose optical isomers produced equal sum-frequency intensity; the optically inactive racemic *dl* solution showed no detectable emission.

Quadratic sum-frequency polarization $\vec{P}(\omega_1+\omega_2)$ in liquids (and gases)[1,2] is given by

$$\vec{P}(\omega_1+\omega_2)=\chi(\omega_1,\omega_2)\vec{E}(\omega_1)\times\vec{E}(\omega_2), \tag{1}$$

where χ is a pseudoscalar and $\vec{E}(\omega)$ is the optical electric field at frequency ω. Symmetry arguments show the following: (1) χ is nonvanishing only in liquids without a center of inversion; such liquids contain molecules which are not superimposable on their mirror images, and can therefore show optical rotatory power. (2) The pseudoscalar χ arises from the third-rank tensor $\chi_{ijk}-\chi_{ikj}$; optical second-harmonic generation and piezoelectricity are described by $\chi_{ijk}+\chi_{ikj}$ and vanish in liquids and gases.[3,4] Quantum and classical molecular models[1,2] indeed show that $\chi\rightarrow 0$ as $|\omega_1-\omega_2|\rightarrow 0$. These facts and the requirement of a transverse component of P dictate a crossed-beam experiment with $\omega_1\neq\omega_2$.

Our apparatus is shown in Fig. 1. A portion of the 6943-Å beam from the *Q*-switched ruby laser is converted to orthogonally polarized 3472-Å harmonic light in a crystal of potassium dihydrogen phosphate.[5,6] After separation in a thick calcite crystal the two beams pass through inverted 3× telescopes, entering the sample with angles of incidence ±24°31′. The peak incident powers at 6943 and 3472 Å were approximately 5 MW and 10 kW, and the incident beam diameters 2.0 and 1.5 mm, respectively. Analysis of Eq. (1)[1] shows the polarization indicated in Fig. 1 to be optimum.

The liquid sample was a 7°55′ prism with fused quartz windows. The prism geometry was chosen to eliminate interference between forced and free waves generated by the 2314-Å polarization wave.[6-10] The 2314-Å emission and its angular distribution were measured with a Cs_2Te cathode "solar blind" photomultiplier, through a narrow-band filter train having a transmission of 5% at 2314 Å. Pickup due to scattered 3472-Å light and other spurious radiation was less than one photoelectron per laser pulse. The angular width of the detector aperture was 0.3 deg, approximately equal to the laser beam width at the sample.

Arabinose was chosen for this work because of its high specific rotation, and availability

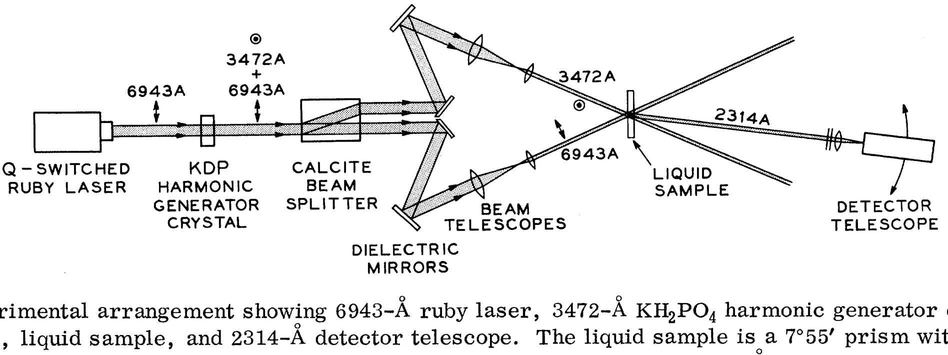

FIG. 1. Experimental arrangement showing 6943-Å ruby laser, 3472-Å KH_2PO_4 harmonic generator crystal, beam separator, liquid sample, and 2314-Å detector telescope. The liquid sample is a 7°55′ prism with refracting edge normal to and at the bottom of the figure. Due to the prism there are two 2314-Å beams but for simplicity only one is shown in the figure.

of its *d*, *l*, and *dl* isomers. Solutions were prepared at a standard concentration of 1 part arabinose to 2 parts water, molarity $M = 2.46$, and had refractive indices 1.3736, 1.3935, and 1.4347 (±0.001) at 6943, 3472, and 2314 Å, respectively. The specific optical rotatory power at 2314 Å was -9.7×10^2 and $+9.8\times10^2$ deg dm^{-1} (g cm^{-3})$^{-1}$ for the *d* and *l* isomers in $0.1M$ solution. To ensure an equilibrium distribution of the aldehydic, pyranose, and furanose isomers of arabinose introduced by mutarotation,[11] all measurements were made at least three hours after preparation of the solutions.

Figure 2 shows the measured angular distribution of 2314-Å emission from the *d*- and *l*-arabinose solutions, and from a quartz reference crystal cut as a 7°45′ prism replacing the solutions. Emission from the *dl* solution was unobservable and was <5 % of the *d* and *l* emission. The observed radiation occurs in two peaks of roughly equal intensity separated by $\Delta\psi = 50'$. For both quartz and arabinose the peak positions agree to within experimental error with the calculated angles for emission from the forced (*B*) and free (*F*) waves[7-9] associated with the 2314-Å polarization. The calculations made use of the nonlinear boundary theory of Bloembergen and Pershan[8] and Kleinman,[9] on the basis that $\vec{k}[\vec{P}(\omega_1+\omega_2)] = \vec{k}(\omega_1) + \vec{k}(\omega_2)$. The average ratio of the peak intensities from the arabinose solutions and from quartz was measured to be $(4.6\pm2.0)\times10^{-3}$.

The entrance face of the quartz prism was a (011) surface with the *x* axis in the plane of Fig. 1. For this geometry double refraction leads to four separate 2314-Å polarization components; the resulting bound-wave radiation is a quadruplet ($\Delta\theta = 3'$) and the free-wave radiation a doublet ($\Delta\theta = 3'$). The arrows in Fig. 2 show the average position of these unresolved multiplet components. On the basis of incoherent addition of the four 2314-Å polarization components, detailed calculation shows the transverse polarization component P_T in quartz to be given by

$$P_T{}^2(\omega_1+\omega_2) = 1.12 d_{111}{}^2 E^2(\omega_1)E^2(\omega_2), \tag{2}$$

where $E(\omega_1)$ and $E(\omega_2)$ are the field amplitudes at 6943 and 3472 Å, and d_{111} is a measured[12] second-order polarization coefficient. The constant d_{123} is assumed negligible.[12] Coherent addition of the four polarization components with arbitrary phase leads to numerical constants between 0.73 and 1.59 in Eq. (2). The coherence length l_c for the quartz experiment is defined[9] by $l_c = \lambda_0/(n-n')$, where $\lambda_0 = 2.34\times10^{-5}$ cm and n and n' are refractive indices corresponding to the velocities of the free wave and polarization wave, respectively. From

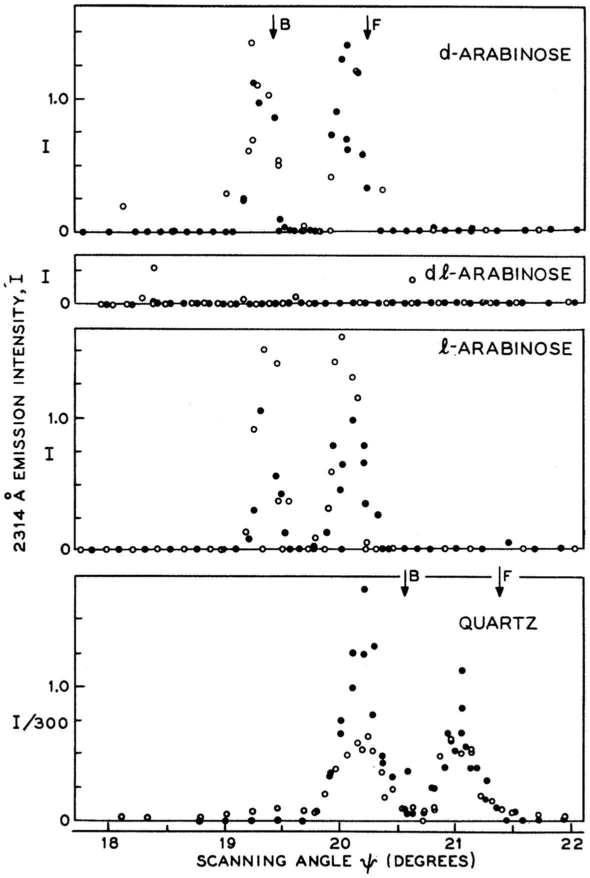

FIG. 2. Angular distribution of 2314-Å sum-frequency radiation from aqueous arabinose solutions and from a quartz reference crystal. The units of *I* are arbitrary but are the same for the four figures. Peak signal for *d*- and *l*-arabinose represents about 5 photoelectrons. The angle is measured from the direction of the 3472-Å incident beam, undeviated by the sample prism. On this scale, the undeviated 6943-Å beam is observed at 49°02′. The arrows show expected positions of radiation from the forced wave (*B*) and the free wave (*F*), which are separated as a result of the prismatic sample geometry (Ref. 8). Data collected on different days, identified by open and closed circles, have been shifted by the same amount (less than 11 min of arc) to locate the observed peak positions at the average peak position, correcting for day-to-day fluctuations in alignment. The discrepancy of the peak positions from the expected values is within the experimental error introduced by the alignment fluctuations.

published refractive index data, $l_c = (2.18 \pm 0.12) \times 10^{-4}$ cm.

The transverse polarization P_T for the arabinose solution is calculated from Eq. (1) to be

$$P_T^2(\omega_1+\omega_2) = 0.160\chi^2 E^2(\omega_1)E^2(\omega_2). \tag{3}$$

The coherence length is $l_c = 2.28 \times 10^{-4}$ cm. From the above data, and the approximation that the peak intensity is proportional to $P_T^2 l_c^2$, it follows that $\chi/d_{111} = 0.17 \pm 0.07$. Taking $d_{111} = 1.15 \times 10^{-9}$ esu,[13,14] one obtains χ (arabinose, $2.46M = 1.8 \times 10$ esu.

Preliminary data show that (1) χ increases with concentration according to M^n, where $n = 1.3 \pm 0.6$, (2) the dependence of sum-frequency intensity on the polarization of $\vec{E}(\omega_1)$ and $\vec{E}(\omega_2)$ is consistent with Ref. 1, (3) χ values for concentrated solutions of glucose and sucrose are comparable with arabinose, and (4) the sum-frequency angular distribution in nicotine, which absorbs strongly at 2310 Å, shows only one peak (B), as expected.

Three estimates of χ were made as follows: (1) From the measured optical rotatory power φ, where both φ[15] and χ[16] are accounted for in terms of a single-electron anisotropic oscillator model with anharmonic potential A_{xyz}, $\chi \sim 6 \times 10^{-11}$, in satisfactory agreement with experiment. (2) From φ, on the basis of a coupled oscillator model for φ,[17] without an explicit cubic anharmonicity,[18] $\chi \sim 3 \times 10^{-12}$. (3) On the basis that a crystal of completely aligned anharmonic arabinose oscillators has $\chi_{123} \sim \chi_{132} \sim \chi_{213} \cdots \sim d_{111}$ (quartz)[12] and that a factor of 10^{-2} estimated from the single-electron theory[16] takes into account random orientation, $\chi \sim 4.59 \times 10^{-12}$.

The large observed value of χ leads us to conclude that the single-oscillator model plays an important role in the optical activity of arabinose. For large conjugated molecules such as hexahelicene, however, in which high optical activity arises from a large distributed magnetic moment, rather than from orbitals localized at specific asymmetric carbon atoms, χ is expected to be proportionately much smaller. It is interesting that for the simplest case of the coupled-oscillator model,[16] consisting of coupled x and y oscillators separated by Δz, χ vanishes[15] since $\mu_z^e = 0$. A more complete account of the theory will be published elsewhere.

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