

Spectroscopy Using Sum- and Difference-Frequency Generation in Molecular Solids

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Both sum- and difference-frequency generation in organic materials are demonstrated and explored under conditions where all three waves (ω_1 and ω_2 ingoing and $\omega_1 \pm \omega_2$ outgoing) are resonant with molecular transitions. The experiments are carried out in centrosymmetric media in which a small electric field is used to distinguish the polar sublattices. Unique electric field dependences of the parametric signals were discovered. The spectroscopic line narrowing and dephasing-induced coherent-emission resonances of these $\chi^{(2)}$ processes make them useful new spectroscopic methods.

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We report the first experimental observation of both sum- and difference-frequency optical parametric processes under fully resonant conditions. These are also the first sum- and difference-generation measurements in molecular solids. The fully resonant condition refers to the outgoing wave and both of the ingoing waves being in resonance with specific vibrational-electronic transitions of the molecular system. These results are the realization of some recent predictions.¹

Most organic solids that are composed of dipolar molecules are nevertheless centrosymmetric so that the second-order dipole susceptibility $\chi^{(2)}$ vanishes identically. The sublattices formed by translations of each of the polar molecules in the unit cell have a finite $\chi^{(2)}$. The sublattice $\chi^{(2)}$ can be fully utilized in second-order nonlinear processes which involve electromagnetic radiation chosen to be resonant with vibrational-electronic transitions of only that sublattice. The transitions of the different sublattices are distinguishable in the presence of a dc electric field directed along appropriate crystallographic directions.² The same considerations apply if the

polar molecules are substitutionally dissolved in a host lattice consisting of nonpolar molecules. This is the type of system used for the experiments reported here which consist of sum- and difference-frequency generation in the system azulene (the "resonant" polar molecule) in naphthalene (the host) induced by a dc electric field. The relevant level scheme appropriate to the reported experiments consists of the electronic ground state (S_0) of azulene, and the vibrationless levels of the first and second excited electronic states (S_1 and S_2) of azulene at 14 651 cm^{-1} and 28 048 cm^{-1} , respectively. The sum- and difference-frequency experiments correspond to generating light at frequencies near to the $S_2 - S_0$ and $S_2 - S_1$ separations, respectively.

The formulas for the susceptibilities given in Ref. 1 for three-level systems are readily adapted to the present situation by adding the energy shift $\Delta\vec{\mu} \cdot \vec{E}$ for each transition and summing over the orientations of the two sublattices. The values of $\Delta\vec{\mu} \cdot \vec{E}$ are known from previous studies of the Stark effect in this mixed crystal.³ The susceptibilities for sum- and difference-frequency generation are

$$\chi_{\text{sum}}^{(2)} = \sum_{n=1,2} \frac{(-1)^n \mu_{01} \mu_{12} \mu_{20}}{[\omega_{10} + (-1)^n \Delta\vec{\mu}_{01} \cdot \vec{E} / \hbar - \omega_1 + i\Gamma_{01}][\omega_{20} + (-1)^n \Delta\vec{\mu}_{02} \cdot \vec{E} / \hbar - (\omega_1 + \omega_2) + i\Gamma_{02}]}. \quad (1)$$

$$\chi_{\text{diff}}^{(2)} = \sum_{n=1,2} \frac{(-1)^n \mu_{20} \mu_{01} \mu_{12}}{[\omega_{10} + (-1)^n \Delta\vec{\mu}_{01} \cdot \vec{E} / \hbar - \omega_1 + i\Gamma_{01}][\omega_{20} + (-1)^n \Delta\vec{\mu}_{02} \cdot \vec{E} / \hbar - \omega_2 - i\Gamma_{02}]} \times \left\{ 1 + i \frac{\Gamma_{12} - \Gamma_{02} - \Gamma_{01}}{[\omega_{21} - (-1)^n \Delta\vec{\mu}_{12} \cdot \vec{E} / \hbar - (\omega_2 - \omega_1) - i\Gamma_{12}]} \right\}. \quad (2)$$

The transition dipoles are denoted by μ_{ij} ; the difference in permanent dipole moment is $\Delta\vec{\mu}_{ij} = \vec{\mu}_i - \vec{\mu}_j$; $\omega_{ij} = \omega_i - \omega_j$; and Γ_{ij} corresponds to the homogeneous linewidth of the indicated transition. The generated waves are obtained from the square of the ensemble average of $\chi_{\text{sum}}^{(2)} + \chi_{\text{nr}}^{(2)}$ or $\chi_{\text{diff}}^{(2)} + \chi_{\text{nr}}^{(2)}$ where $\chi_{\text{nr}}^{(2)}$ is the nonresonant contribution.

The experimental arrangement consisted of two dye lasers pumped by the same frequency-doubled Nd-doped yttrium aluminum garnet lasers. Both lasers could be narrowed with etalons and pressure

tuned. Both beams were brought to a common focus on the ab cleavage plane of the naphthalene sample crystal immersed in liquid helium. The static electric field was applied either in the direction of the b axis or, with use of transparent electrodes, perpendicular to the ab face. The latter arrangement gave best results, allowing phase matching by rotation of the crystal around the b axis. Spectra could be obtained with use of other faces and with various polarizations of the laser beams.

With both lasers fixed on resonance, the expression for sum-frequency generation predicts that the signal will first increase quadratically with the applied field just as in conventional electric-field-induced second-harmonic generation.⁴ Figure 1 shows a series of spectra taken with ω_2 fixed and ω_1 pressure tuned over the $S_0 \rightarrow S_1$ resonance for various settings of the applied field. The inset shows the quadratic behavior of the peak sum-frequency signal in the region of low dc field strength. The higher fields separate the two sublattices completely and the peak intensity becomes independent of the dc field strength, while the signal at the center drops to zero (Fig. 1). With both lasers detuned from resonance a nonresonant background signal could be observed which was more than a factor of 1000 weaker than the resonant signal and displayed quadratic dependence on the applied dc field strength. The linewidths of the resonances in Fig. 1 are 0.5 cm^{-1} corresponding to the inhomogeneous linewidth of the $2 \rightarrow 0$ transition,⁵ the

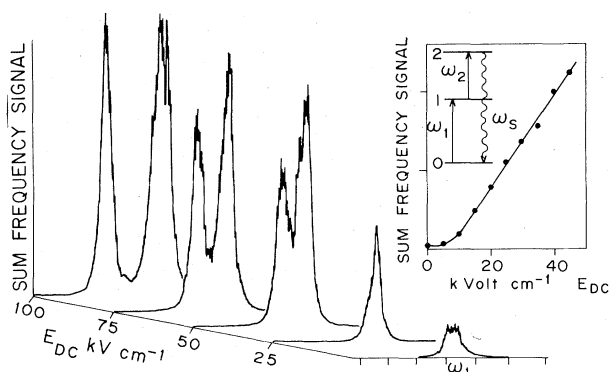


FIG. 1. Resonant sum-frequency generation in dc fields. The ω_1 laser scan is shown for various dc fields with ω_2 fixed on resonance. (Etalon markers spaced by 1.1 cm^{-1} are shown on the frequency axis.) Note that the widths of the resonances correspond to the inhomogeneous width of the $S_0 \rightarrow S_2$ transition and not to the width of the $S_0 \rightarrow S_1$ transition over which ω_1 is being tuned. Inset: The peak intensity of a sum-frequency signal as a function of dc field strength for low fields.

outgoing field resonance.

Spectra similar to those in Fig. 1 were obtained in sum and difference frequency with ω_2 scanned. An example is given in Fig. 2 for difference-frequency generation with the dc field chosen to introduce a Stark splitting that is much less than the linewidth. ω_2 was scanned for various detunings of ω_1 . The plot of the peak intensities versus the detuning (inset) reveals a resonance with 3.5 cm^{-1} width resulting from the twofold convolution of the 2.0-cm^{-1} homogeneous linewidth of the $0 \rightarrow 1$ transition⁵ with the bandwidths of the dye lasers ($\sim 0.7 \text{ cm}^{-1}$ without the etalons). We have also directly observed the $0 \rightarrow 1$ resonance in both sum- and difference-frequency generation using narrow-band lasers. The resonances in Figs. 1 and 2 show the inhomogeneous width of the $0 \rightarrow 2$ transition. This result is expected from theory for the present case, where Γ_{12} is larger than the inhomogeneous width. For systems with inhomogeneous broadening much larger than Γ_{01} , Γ_{02} , and Γ_{12} , the ensemble average predicts line-narrowed resonances depending only on the homogeneous parameters if there is positive correlation between S_1 and S_2 .¹ Another interesting feature predicted for spectra in difference-frequency generation are dephasing-induced coherent-emission (DICE) or extra resonances.⁶ These resonances should appear with increasing temperature when pure dephasing pro-

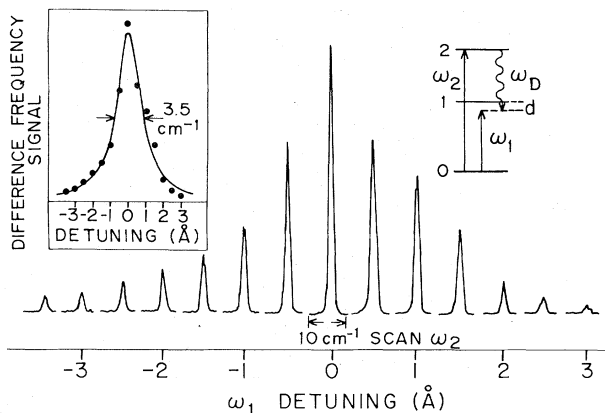


FIG. 2. Resonant difference-frequency generation in dc fields: The ω_2 laser scan is shown for various detunings of ω_1 . The dc field was fixed at 50 kV/cm directed along the c' axis of the naphthalene crystal (ω_1 and ω_2 were polarized along b and $\perp b$, respectively). Inset: The peak intensity of the difference-frequency signal shows a resonance corresponding to the $S_0 \rightarrow S_1$ transition convoluted with the laser widths. The solid line is a fitted Lorentzian.

cesses set in.

Our measurements have revealed that the dipole moment changes $\Delta\mu_{01}$ and $\Delta\mu_{02}$ are in the same direction, since detuning of ω_1 to the lower-energy component of the 0→1 transition in the dc field resonantly enhanced the lower-energy component of the sum-frequency signal and vice versa. The absolute values of $\Delta\mu$ for both transitions are known from Stark experiments to be very similar³ and hence we expect $\Delta\mu$ to be less than 0.1 D.

In conclusion, we report the first observation of high-resolution spectra with use of fully resonant second-order parametric processes. Both sum- and difference-frequency signals have been obtained. The use of centrosymmetric host materials in combination with Stark-effect switching of resonances promises to be very useful and a widely applicable spectroscopic method. The sigmoid shape of the field dependence of the nonlinear signal is unique. Although in this case the levels 0 and 1 were electronic states, the experiment can also be accomplished in the same configuration with vibrational resonances thereby allowing vibrational spectroscopy to be carried out by detecting visible light. The experiments naturally have nanosecond time resolution and

involve the detection of coherent signals distant from the laser wavelengths. Extensions to picosecond time resolution are straightforward.

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¹B. Dick and R. M. Hochstrasser, *J. Chem. Phys.* **78**, 3398 (1983).

²R. M. Hochstrasser, *Acc. Chem. Res.* **6**, 263 (1973).

³R. M. Hochstrasser and L. J. Noe, *J. Chem. Phys.* **50**, 1684 (1969).

⁴R. W. Hellwarth, in *Progress in Quantum Electronics*, edited by H. J. Sanders and S. Stenholen (Pergamon, New York, 1977).

⁵R. M. Hochstrasser and T.-Y. Li, *J. Mol. Spectrosc.* **41**, 297 (1972); R. M. Hochstrasser and C. A. Nyi, *J. Chem. Phys.* **70**, 1112 (1979).

⁶Y. Prior, A. R. Bodgan, M. Dagenais, and N. Bloembergen, *Phys. Rev. Lett.* **46**, 111 (1981); J. R. Andrews and R. M. Hochstrasser, *Chem. Phys. Lett.* **82**, 381 (1981), and **83**, 427 (1981).