

Femtosecond Time-Resolved Observation of Coherent Molecular Vibrational Motion

A recent Letter¹ by Rosker, Wise, and Tang (I) discussed femtosecond time-resolved equal-pulse correlation experiments (essentially "pump-probe" experiments) on two dye molecules, malachite green and nile blue, in solution. Resonant $S_0 \rightarrow S_1$ absorption of a femtosecond laser pulse resulted in time-dependent changes in the transmission of a second, variably delayed pulse centered at the same (resonant) frequency. Interestingly, the femtosecond time-resolved data revealed *terahertz-frequency oscillations* superimposed upon monotonic decays. It was speculated that these oscillations arose from quantum beating between unspecified excited-state levels. Malachite green solutions (and, more recently, many other dye solutions²) showed well-defined, periodic oscillations which have also been observed by others.³

The purpose of this Comment is to suggest a simple physical explanation for the observed oscillations. We believe that they are indeed due to quantum beating involving *low-frequency intramolecular vibrations of the dye molecules*. Malachite green, for example, has a skeletal vibrational mode (characteristic of triphenylmethane dyes⁴) of 226 cm^{-1} , as shown in the Raman spectrum in Fig. 1. This corresponds to a vibrational period of 147 fs, which almost exactly matches the 150-fs period reported in I. (The complex, nonsinusoidal temporal modulation observed in nile blue¹ and some other solutions² probably arises from phase-coherent oscillations in *several* low-frequency vibrational modes.) Unlike earlier quantum-beat experiments involving molecular vibrations,⁵ in which the beat frequencies were *difference frequencies between different vibrational modes*, in this case the beat frequency is the *fundamental* frequency of a *single* vibrational mode. Classically, absorption of a photon takes a molecule from near the *bottom* of the S_0 potential and leaves it at a point on the *side* of the S_1 potential, which is displaced along the vibrational coordinate.⁴ The molecule then undergoes damped oscillations about the new potential minimum in S_1 . *If the laser pulse duration is short compared to the vibrational oscillation period, then all the excited molecules will oscillate in phase.* The situation is similar to recent "impulsive" stimulated scattering experiments which permitted time-resolved observation of ground-state vibrational oscillations.⁶

Given this simple interpretation, the results in I take on additional interest. First, they permit characterization of excited-state molecular vibrations which cannot be examined by absorption spectroscopy. For malachite green, the S_1 and S_0 vibrational frequencies are almost identical, but the vibrational *dephasing times* are very different (190 fs reported in I versus 420 fs obtained

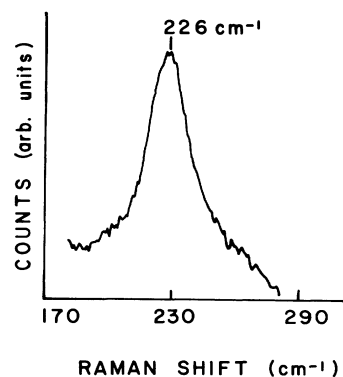


FIG. 1. Partial Raman spectrum of $5 \times 10^{-3} M$ malachite green in methanol solution, taken with 488-nm excitation light.

from the 25-cm^{-1} Raman linewidth in Fig. 1). Second, the results indicate that the $S_0 \rightarrow S_1$ absorption bands of these dye molecules in room-temperature liquid solutions are *inhomogeneously broadened* to a considerable extent. It is inhomogeneous broadening which masks these vibrational features in the absorption spectrum. Recent femtosecond time-resolved hole-burning experiments on rhodamine 6G solutions also indicate inhomogeneous broadening.⁷ Third, time- and frequency-resolved spectroscopy of the coherently vibrating excited-state molecules could yield detailed information about excited-state potentials and Stokes-shift dynamics.⁷

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³J. G. Fujimoto and W. Z. Lin, personal communication.

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