

Observation of Molecular Vibrations in Real Time

In a recent Letter Rosker, Wise, and Tang¹ have reported ultrafast optical measurements on two large dye molecules, malachite green and nile blue 690. Using the transmission-correlation technique with 40-fs light pulses, they measured photoinduced changes in optical transmission and found a response consisting of damped oscillations superimposed on two exponential decays. They tentatively interpreted the oscillations as quantum beats between two eigenstates of the isolated molecule. In this Comment we report Raman and infrared measurements on the same molecules and discuss the implications these measurements have for the interpretation of the data of Rosker, Wise, and Tang.

Quantum beats are observable when a molecule has two (or more) excited states of energies E_1 and E_2 which can both be excited with appreciable probability from the ground state of energy E_0 . A short light pulse which contains a spectrum broad enough to include the frequencies $(E_1 - E_0)/h$ and $(E_2 - E_0)/h$ will generate significant amplitudes in both the excited states. These amplitudes will be coherent. As a result the absorption of a probe pulse delayed by time t relative to the first pulse will have a term varying as $\cos(2\pi\nu_{21}t)$, where $\nu_{21} = (E_2 - E_1)/h$. To have quantum beats occurring at a frequency in the terahertz frequency range, one possibility is for the two excited states to be the same electronic level but with different vibrational quantum numbers. Thus, at least within the harmonic approximation the frequency ν_{21} is then just the frequency of one of the normal modes of the molecule which is coupled to the electronic state as a phonon sideband. In this case there is a good chance that the mode will be observable in the Raman scattering and/or the infrared absorption spectrum.

To test this idea we have taken the data of Rosker, Wise, and Tang, which are in the time domain, subtracted out the exponentially decaying terms, and then taken the Fourier transform. For malachite green there is a large peak in the Fourier transform at 6.7 THz with width at half-maximum of 2 THz. We made Raman measurements in a Spex model 1403 Raman spectrometer with an exciting wavelength of 632.8 nm and an incident power of 0.8 mW. The spectrum was obtained from a solution-cast thin film spun at high speed. There is indeed a peak at 7.0 THz very close to the peak in the Fourier transform. We have also observed an ir absorption band at essentially the same frequency. The only other feature evident in the Raman spectrum is a weaker

peak at 13.2 THz.

The electronic and vibrational states of malachite green can be described approximately by consideration of the central carbon and the three carbons bound to it appropriately weighted to reflect the C_{2v} molecular symmetry. The two- π -electron system of this unit has the ground state 1A_1 , and transitions to A_1 and B_2 states which are dipole allowed as singlet $\pi-\pi^*$ electronic excitations. Six vibrations with the representation $3A_1 + B_1 + 2B_2$ are expected. The stretching modes ($2A_1 + B_2$) are infrared and Raman active and correspond to skeletal deformations of malachite green. We assign the 7.0-THz band to the A_1 central-carbon breathing mode.

In nile blue, a Fourier transform of the data of Rosker, Wise, and Tang gives frequencies² of 4.5, 5.6, 9.1, and 11.1 THz. We have found all of these frequencies, except 4.5 THz, in the Raman and infrared spectra.

These Raman and infrared measurements clearly confirm that the photoinduced changes in optical transmission are due to quantum beats between two states with different vibrational quantum numbers. Thus, the measured oscillations in transmission can be considered to be an observation of molecular vibrations in real time. In the experiments performed so far with malachite green and nile blue, only the low-frequency (skeletal) modes of vibration have been observed. With the advent of even shorter laser pulses³ (in the 10-fs range), it may be possible to study in real time the complete spectrum of vibrations for a typical molecule.

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¹M. J. Rosker, F. W. Wise, and C. L. Tang, Phys. Rev. Lett. **57**, 321 (1986).

²Several lower frequencies are also present. However, these are below the range we can usefully study by Raman scattering.

³S. L. Palfrey and D. Grischkowsky, Opt. Lett. **10**, 562 (1985).