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14. ABSTRACT This research focused on three topics that are critical to understanding and exploiting vibrational excitation in photoisomerization dynamics. The first aspect is exploring energy flow within a vibrationally excited molecule and into the surrounding the solvent. The second aspect is intercepting the vibrationally excited molecule at different times to promote it to an electronically excited state with energy in selected vibrational motions, and the third aspect is probing the molecule in its excited state.					
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This research focused on three topics that are critical to understanding and exploiting vibrational excitation in photoisomerization dynamics. The first aspect is exploring energy flow within a vibrationally excited molecule and into the surrounding the solvent. The second aspect is intercepting the vibrationally excited molecule at different times to promote it to an electronically excited state with energy in selected vibrational motions, and the third aspect is probing the molecule in its excited state.

VIBRATIONAL ENERGY FLOW

Direct observation of intramolecular and intermolecular energy flow is an essential preparatory step for all of the studies performed in this research and is the most mature component of our experiments. The energy transfer experiments used ultrafast transient electronic absorption to probe vibrationally excited molecules as they redistributed energy internally and transferred it to the surrounding solvent. Figure 1 schematically illustrates the approach, which relies on changes in the Franck-Condon factor for the electronic transition as vibrational energy flows around the molecule. A 100-fs pulse of infrared light excited a fundamental or overtone vibration, such as the two quanta of C-H stretch of CH_2I_2 shown in the figure,

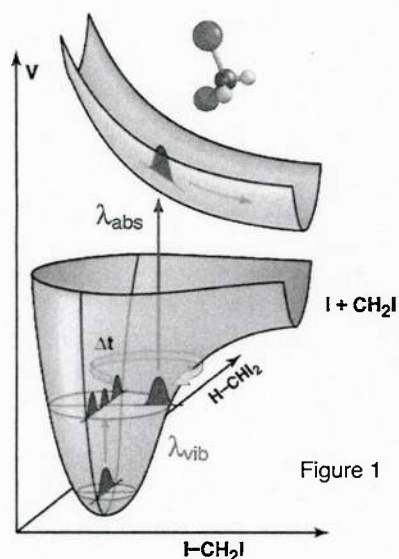


Figure 1

and a second ultraviolet pulse transferred the molecule to an excited state. When the vibrational excitation was in the C-H stretch, there was little absorption because the Franck-Condon factor for reaching the excited state is poor. However, the absorption increased when energy flowed into modes with better Franck-Condon factors, such as the C-I stretch.

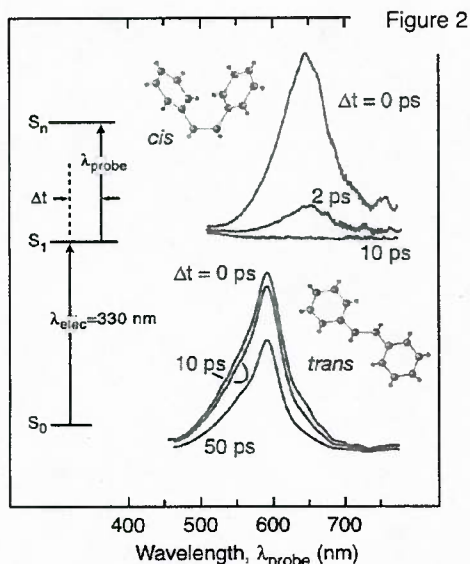
The rise and decay of this absorption mirrored the flow of vibrational energy around the molecule and into the solvent.¹ This approach has monitored energy flow in gas phase molecules^{2,3} and, most important in the present context, in solution phase molecules.³⁻⁸ For example, the measurements showed that intramolecular energy flow takes about 10 ps and intermolecular energy flow (into the solvent) takes about 70 ps in CH_2I_2 molecules containing two quanta of C-H stretching excitation.⁴ One of the most important observations was that some molecules have multiscale intramolecular energy redistribution in which vibrational energy initially flows into a subset of the available states and subsequently

enters the remainder, perhaps on the same timescale as it flows into the solvent.^{3,8} Another important observation was that initial vibrational relaxation in stilbene, one of the target molecules for photoisomerization studies, occurred within a few ps and was different for the *cis* and *trans* isomers.⁸

EXCITED-STATE DYNAMICS

Intercepting the vibrationally excited molecule during its relaxation allowed both the observation of energy flow and the transfer the molecule to unique regions of an electronically excited surface. The approach to studying excited-state dynamics used in this research was broadband, transient electronic absorption. This approach provided the time-resolved excited-state absorption spectrum of the molecule as it evolved in the excited state. Figure 2 shows transient absorption spectra of *cis*- and *trans*-stilbene at different times after one-photon excitation with $\lambda_{elec} = 330$ nm to the excited state (S_1) in hexane solution. The broadband continuum pulse came from focusing a small amount of 800-nm light on a sapphire sub-

strate, and passing that light through the sample and dispersing it, along with a reference beam, onto a pair of photodiode arrays produced the excited-state spectrum ($S_n \leftarrow S_1$) after excitation to S_1 .



These spectra monitored the evolution of the excited-state population. For example, the *cis*-stilbene absorption decayed in about 2 ps as the molecule left the Franck-Condon region and returned to the ground state through a conical intersection. However, the *trans*-stilbene signal survived for almost 100 ps because there is a barrier to its leaving the excitation region and moving toward the conical intersection, behavior that is consistent with extensive previous studies of the one-photon excitation.⁹ We also monitored the rotational diffusion in the excited state using excitation and probe light with both parallel and perpendicular relative polarizations.

Our goal was to explore the effect of vibrations on excited-state dynamics, and a major step toward that goal was a vibrationally mediated isomerization experiment on stilbene. In this measurement, we monitored the evolution

of the population of the electronically excited state following promotion of a vibrationally excited molecule from its ground electronic state. We were barely able to observe such a signal using our original laser system, but its replacement with a modern ultrafast laser made those experiments work well and opened the door to an ambitious new set of measurements.

The experiment was essentially the same as the excited-state absorption measurement described above except that two-step excitation through a vibrationally excited intermediate state replaced the one-photon excitation. Figure 3 shows the excitation scheme and data that for *trans*-stilbene. A pulse of infrared light (λ_{vib}) prepared the molecule with two quanta of C-H stretching excitation, and a second pulse of ultraviolet light (λ_{elec}) that arrived at a variable time Δt_{S_0} after the vibra-

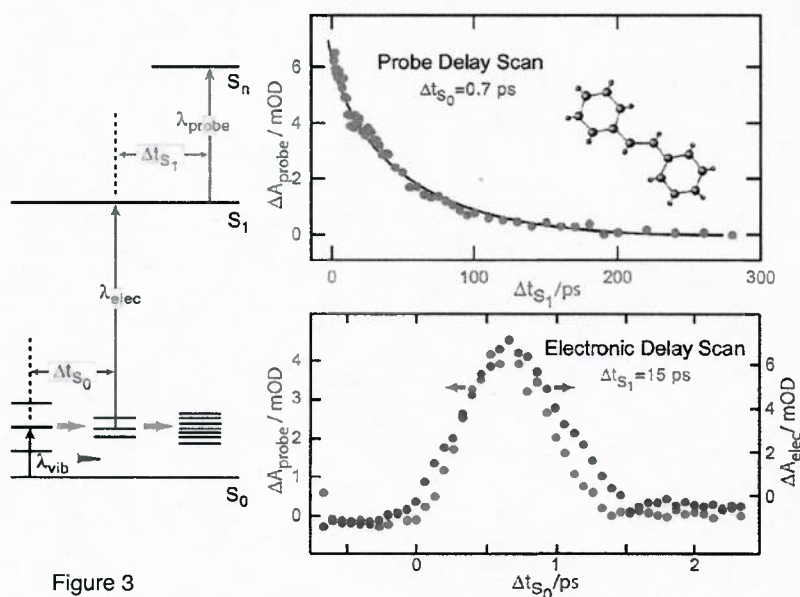


Figure 3

ultraviolet light (λ_{elec}) that arrived at a variable time Δt_{S_0} after the vibrational excitation pulse promoted the molecule to the excited state. The broadband continuum probe pulse (λ_{probe}) arrived at a time Δt_{S_1} after the electronic excitation pulse, and changing the two delays allowed observation of the evolution of the vibrationally excited molecule. Varying the delay Δt_{S_0} tracked the evolution in the ground state, and varying Δt_{S_1} monitored the progress of the molecule in the excited state. (The horizontal arrows in the figure schematically indicate the flow of energy among the vibrational states.)

The upper panel in the figure is an example of the signal obtained by varying Δt_{S_1} with the ground-state delay fixed at $\Delta t_{S_0} = 0.7$ ps. It shows the decay of the excited-state absorption following electronic excitation of a *trans*-stilbene molecule initially prepared with two quanta of C-H stretching excitation in a solution of deuterated chloroform (CDCl_3). The decay time of about 40 ps was shorter than the 60 ps measured for single-photon excitation. Careful measurements, including the dependence on the relative polarization of the three pulses, permitted comparison of the excited-state behavior at the same total energy for different excitation schemes. These comparisons, which allowed probing of the influence that the vibrational excitation has on the dynamics in the excited state, would be impossible without the improved stability and pulse energy of our new laser system. The experiment captured the entire broadband absorption spectrum between 400 nm and 700 nm even though the figure only shows the evolution at the maximum of the excited-state absorption.

The lower panel shows the ground state evolution probed by simultaneously monitoring the electronic absorption (ΔA_{elec}) of the vibrationally excited molecule (blue points-right axis) and the excited-state absorption (ΔA_{probe}) of the electronically excited molecule (red points-left axis) at a time $\Delta t_{S_1} = 15$ ps. The measurement of ΔA_{elec} was the same as our previous vibrational energy transfer experiments in which we monitored the evolution of the transient electronic absorption of the vibrationally excited molecule. However, the measurement of ΔA_{probe} added an additional dimension because it reflects both the probability of a transition to the excited state *and* the probability of absorption from that state to the higher electronic state. In favorable cases, this absorption carries information on the changes that arise from intercepting the vibrationally evolving ground electronic state molecule at different times.

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