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COMMUNICATION

Observation of Intermode Coupling in the 3 μm IR Multiple Photon Excitation of Propylene

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The mechanism of IR multiple photon excitation through the dense manifold of vibrational states, usually called the quasicontinuum, of a vibrationally excited molecule is one of the unresolved issues in the field of laser chemistry. The effects of deuterium substitution on propylene IR multiple photon excitation are used to identify the vibrational modes leading to efficient excitation. Optoacoustic energy deposition data show that for propylene, 3 μm multiple photon excitation occurs most efficiently at the methyl group, and furthermore that efficient methyl group excitation requires the CH group on the adjacent carbon. Thus 3 μm multiple photon excitation of propylene, while involving energy deposition directly into several spatially discrete intramolecular groups, is found to be enhanced by specific intramolecular couplings. Implications of this result for mechanisms of IR multiple photon excitation are discussed.

A fundamental question remaining to be answered for infrared laser induced multiple photon processes is the mechanism of excitation through the dense quasicontinuum of states of a vibrationally excited molecule.^{1,2} Recent results from experiments using two temporally coincident IR lasers,³ and from comparisons of dissociation data with overtone absorption data⁴ suggest that the quasicontinuum is not structureless, but rather that particular states of the excited molecule enhance the multiple photon process. Un-

derstanding the excited molecular states and how they differ from the lowest energy molecular states provides new insight into the IR multiple photon excitation mechanism. In this article we report energy deposition measurements of 3 μm infrared multiple photon excitation of propylene and deuterated propylenes. Comparison of energy deposition spectra taken under focused laser conditions to spectra taken with an unfocused beam locates the spectral features which most readily undergo multiple photon excitation, while deuterium substitution identifies those molecular groups which are necessary for the excitation process but may not be initially in resonance with the laser.

A Nd:YAG pumped LiNbO₃ optical parametric oscillator operating in the 3 μm region is used in these studies.⁵ The laser has a bandwidth of 1.5 cm^{-1} , pulsewidth of 8 ns, pulse energies of 4–6 mJ and operates at 6 Hz. Pulse energies decrease approximately 25% as the laser is tuned from 3100 cm^{-1} to 2900 cm^{-1} . Laser frequency tuning is accomplished by changing the angle of the LiNbO₃ crystal under computer control. Energy deposition as a function of laser wavelength is measured via the pulsed optoacoustic technique.⁶ Focused (unfocused) output from the laser passes through a 5 cm long stainless steel cell which is equipped with a 0.5 in. diameter B and K microphone, and contains the gas of interest. Focusing is accomplished with a 5 cm focal length CaF₂ lens. The microphone signal is averaged in one channel of a PAR 162/165/164 boxcar integrator while simultaneously, the signal from a pyroelectric detector monitoring the incident laser energy is averaged in the second channel of the integrator. The absorption cross section is proportional to the ratio of optoacoustic signal to incident laser energy.⁶ Measurement of energy deposition under high intensity conditions requires that the microphone view only the focused region of the laser beam. Using a 5 cm focal length lens, the length of the focused portion of the beam is measured to be ~ 1 cm, comparable to the microphone diameter. Further discrimination against acoustic signals due to absorption in lower intensity regions is obtained by time-resolved measurement of the initial acoustic signal.⁶ No differences in focused spectra are seen when using either the 0.5 in. microphone or a smaller 0.25 in. microphone.

Optoacoustic spectra taken with both focused and unfocused beams are shown in Figure 1a–c for propylene, 1,1-propylene-*d*₂ and 2-propylene-*d*₁. Since the volumes defined by the focused and unfocused beams are quite different (and not accurately known) the focused spectra are normalized to match the unfocused spectra in regions where the

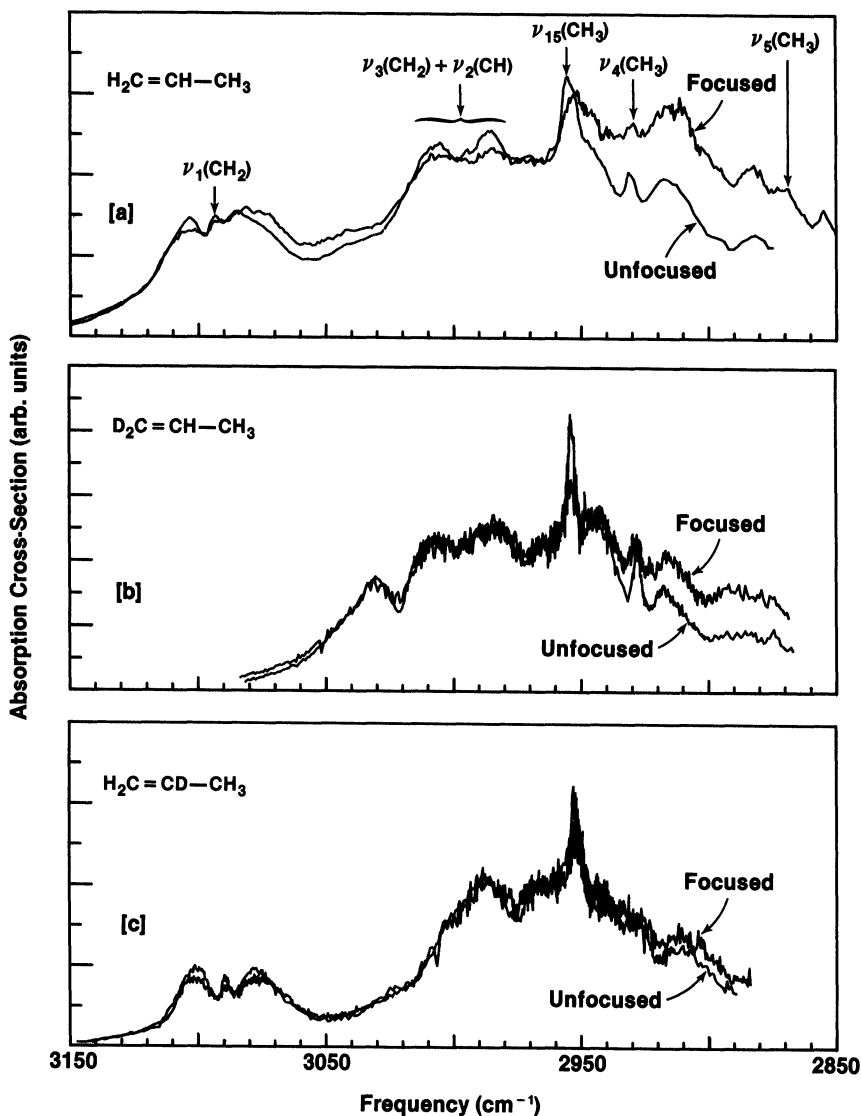


FIGURE 1 Absorption cross sections for deuterated propylenes as determined by optoacoustic energy deposition measurements under focused and unfocused laser conditions. Because of differences in irradiation volume between focused and unfocused beams, the focused data in each case are normalized to the unfocused spectra in regions of similar shape. Pulse energies (4–6 mJ/pulse at 3100 cm⁻¹) decrease slightly as the laser is tuned to lower frequencies. In all experiments a 5 cm focal length CaF₂ lens is used to focus the beam, resulting in fluences of 2–3 Jcm⁻².

shapes of the curves are nearly the same. The unfocused optoacoustic spectra show no significant differences compared to conventional IR spectra, indicating that the unfocused conditions are representative of the intensity regime corresponding to single photon absorption.

Propylene has a characteristic spectrum, indicated in Figure 1a, in which the ν_1 CH₂ group absorption is at 3090 cm⁻¹, mixed ν_3 CH₂ and ν_2 CH group absorptions are near 3000 cm⁻¹ and CH₃ (ν_{15} , ν_4 , ν_5) group absorptions are at 2954, 2932 and 2871 cm⁻¹.⁷ It is readily apparent from Figure 1a that enhanced absorption occurs principally at the CH₃ group relative to absorption at the higher frequency features. Figure 1b shows that the enhanced CH₃ group absorption of Figure 1a is not greatly affected by removal of the CH₂ modes (ν_1 and ν_2) upon deuterium substitution. However, Figure 1c strikingly demonstrates that deuterium substitution at the center carbon, adjacent to the CH₃ group, nearly eliminates the enhanced CH₃ group absorption. The enhancement observed in Figure 1a may be even more pronounced at higher fluences if multiple photon excitation of propylene displays an intensity dependence similar to cyclopropane⁸ (dissociation yields approximately proportional to I^3 , where I is laser intensity).

The usual explanation for red shifted multiple photon dissociation spectra is that rotational state energy compensation is more effective at lower frequencies.⁹ This effect cannot be a major factor in the 3 μ m excitation of propylene as deuterium substitution does not dramatically affect the overall rotational structure, and therefore cannot explain the results in Figure 1. Alternatively, if excitation efficiency were determined primarily by the vibrational state density in the quasicontinuum, every deuterated propylene would show greater absorption cross section enhancements than propylene-*h*₆. This is clearly not the case (Figure 1). Furthermore, preliminary calibrated energy deposition measurements for the deuterated propylenes indicate that every deuterated propylene shows only comparable net energy deposition compared to propylene-*h*₆. Specific states of the excited molecule apparently promote more efficient multiple photon excitation. These observations are qualitatively similar to the 3 μ m excitation mechanism proposed for ethyl chloride,⁴ but show more clearly the extent to which different CH groups within a molecule can participate in the multiple photon excitation process.

One possible explanation for the observed CH group participation is that after the molecule is energized by absorbing one or two photons in methyl group vibrational modes, an excited state transition (e.g., $\nu = 1-2$) within

the higher frequency CH_2 or CH vibrational manifolds (populated by either intramolecular energy relaxation or a mixing of states) comes into resonance with the laser because of vibrational anharmonicity. While such excited state transitions in the frequency range where enhanced absorption occurs ($2850\text{--}2950\text{ cm}^{-1}$) are possible within the CH_2 manifold, the lack of a large spectral change upon deuterium substitution at the CH_2 group (Figure 1b) suggests that this is not a dominant contribution to the multiple photon absorption process. Similar excited state transitions within the CH mode are out of resonance with this frequency range even at $\nu = 1$ due to large anharmonic shifts.¹⁰ Alternatively, an excited state of the CH_2 or CH modes may be at an energy such that it can be the final state for a transition out of an energy level of a CH_3 mode. Excitation from a CH_3 mode into one of the higher frequency modes via such a resonance would then provide a "doorway" to further excitation. Direct optical transitions between vibrational modes are usually forbidden. Sufficient mixing of states may partially allow the process. For a multiple photon excitation ladder initially resonant with the CH_3 group, possible doorway states can be identified using known spectral data for propylene.^{7,10,11} This data indicates that $\nu = 2$ or 3 of the CH vibration and $\nu = 3$ or 4 of CH_2 vibrations are possible doorway states. In addition to the effects of deuterium substitution on the high frequency modes, similar effects on the lower frequency modes ($<2500\text{ cm}^{-1}$) must also be considered. Several combination states derived from low frequency modes are in the correct range for absorption from $2900\text{--}2950\text{ cm}^{-1}$.⁷ The modes primarily involve the CH_3 group and are not strongly altered by deuterium substitution at the center carbon, thus it is unlikely that such overtone excitation is significant. It is not readily apparent whether or not an excited state of a low frequency mode can act as a doorway state as described above. The question of participation of low frequency modes in these experiments will have to await a detailed accounting of all those states which have energies such that they can contribute to multiple photon excitation.

These data have important implications for current discussions of intramolecular vibrational energy relaxation in IR multiple photon excitation.¹²⁻¹⁴ If energy is deposited directly into spatially separate molecular states within the molecule, then some degree of internal energy randomization is guaranteed. A critical question which must be addressed is the spatial extent of intermode coupling during IR multiple photon excitation. The data in Figure 1 indicate that the CH_2 group farthest from the CH_3 group participates less than the CH group on the carbon next to the CH_3

group even though the ν_3 CH₂ fundamental is at nearly the same frequency as the adjacent ν_2 CH fundamental. The effects of intermode coupling during 3 μm multiple photon excitation apparently decrease substantially when the CH groups are separated by more than one atom in the molecular chain, indicating that "region specific" intramolecular excitation may be possible. Furthermore, it may prove possible to design molecules with appropriate molecular structure selected to create efficient chromophores for multiple photon excitation, markedly enhancing energy deposition rates. Excitation rates capable of effectively competing with rapid intramolecular and collisional energy relaxation processes are thus conceivable.

The present work is being extended to cover a range of fluences, to larger molecules in order to explore the spatial extent of intermode coupling, and to molecules with a variety of CH groups in order to determine which modes couple most efficiently. An important question arising from these results is whether or not the relative enhancement shown in Figure 1a carries through to very high (dissociative) vibrational levels. Preliminary experiments indicate that this may be so, as normalized propylene- h_6 dissociation yields are substantially higher at 2954 cm^{-1} than at 3100 cm^{-1} .⁸ Dissociation experiments with deuterated propylenes are planned to explore these effects at very high vibrational levels.

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