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Final Technical Report

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Time Resolved Energy Transfer and Photodissociation of Vibrationally Excited Molecules

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ABSTRACT

These experiments use ultrafast laser spectroscopy to study reaction and photodissociation dynamics in solution, probing both photodissociation and intramolecular energy transfer. They have observed the photodissociation dynamics of methylhypochlorite (CH_3OCl) in different solvents by monitoring the disappearance of the Cl atom and have compared the flow of energy in vibrationally excited methyl iodide (CH_3I) in solution and in the gas phase. This second experiment is one of the few direct comparisons of intramolecular vibrational energy flow in a solvated molecule with that in the same molecule isolated in a gas. Because of the importance of vibrational relaxation of molecules after photoisomerization, the other goal has been to probe the vibrational energy flow in both *cis*- and *trans*-stilbene, a prototypical molecule for *cis-trans* isomerization.

INTRODUCTION

Vibrational and electronic motion are central to molecular processes such as energy transfer, bimolecular and unimolecular reactions, and photochemistry, all of which have an array of fundamental and practical consequences. The role of vibrational excitation in photodissociation is one example. The initial vibrational state from which the photoexcitation occurs determines the portion of the excited state potential that the molecule reaches, and the shape of the potential energy surface in that region in turn controls the motion of the dissociating molecule. Isomerization is a more complicated process because it often rearranges several chemical bonds. Both excited state dissociation and isomerization can involve the crossing of two potential energy surfaces in a conical intersection,¹⁻³ and the topology of such an intersection determines the efficiency with which the system evolves along different paths. The subsequent relaxation of the energy released in the dissociation or isomerization, which often appears as vibrational excitation, is an essential step in stabilizing the products. The influence of the initial vibrational state from which electronic excitation occurs can even provide a means of controlling the excited state dynamics, and we have previously studied such processes in isolated molecules.⁴⁻⁶

RECENT RESULTS

The results from our past period of AFOSR support illustrate the variety of processes amenable to study with ultrafast vibrational and electronic spectroscopy and focus on dissociation dynamics and energy transfer in solution. We have observed the photodissociation dynamics of methylhypochlorite (CH_3OCl) in different solvents by monitoring the disappearance of the Cl atom.¹⁰ We have compared the flow of energy in vibrationally excited methyl iodide (CH_3I) in solution and in the gas phase, performing one of the few direct comparisons of intramolecular vibrational energy flow in a solvated molecule with that in the same molecule isolated in a gas.¹¹ Because of the importance of vibrational relaxation of molecules after photoisomerization, we have also taken the first steps toward studying photoswitches by probing the

vibrational energy flow in both *cis*- and *trans*-stilbene,¹² where the time evolution reflects vibrational dynamics akin to those we observe in CH₃I.

Photodissociation of Methylhypochlorite (CH₃OCl)

Excitation of CH₃OCl to either of its first two excited states leads to direct dissociation into a methoxy radical and a Cl atom, as illustrated on the left side of Figure 1. We use 100-fs pulses of 267-nm light, obtained by frequency tripling 800-nm light from a regeneratively amplified Ti:sapphire laser, to photo-

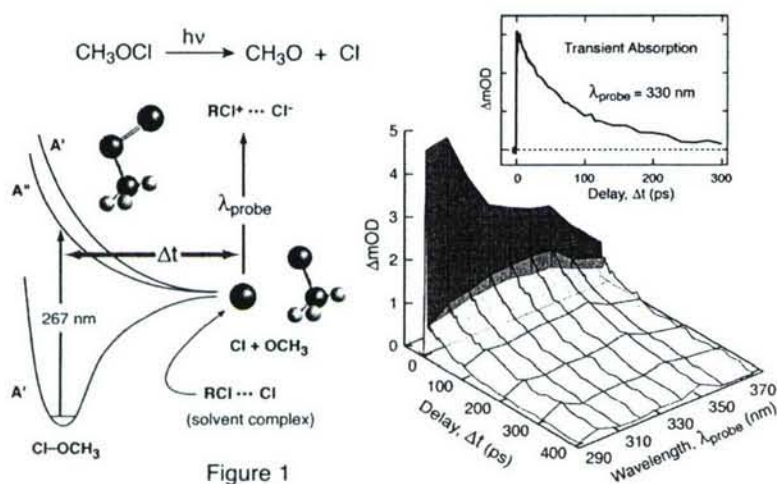


Figure 1

dissociate methylhypochlorite, and we probe the resulting Cl atom with 100-fs pulses at wavelengths between 290 nm and 370 nm obtained from an optical parametric amplifier (OPA).¹⁰ Transient absorption of the Cl atom (in a weakly bound complex with the chlorinated solvent) allows us to moni-

tor the products as shown in the summary plot. The inset shows the transient absorption at one probe wavelength. The short-time evolution of the absorption reflects the diffusive geminate recombination of Cl atoms with methoxy radicals, in which the initially separated methoxy and chlorine radicals diffuse back together and recombine. Measurements in carbon tetrachloride, dichloromethane, *1,4*-dichlorobutane, and chlorocyclohexane show that the diffusive geminate recombination consumes between 30% and 60% of the Cl, depending on the solvent, and the surviving Cl atoms either abstract a hydrogen from the solvent or react with undissociated CH₃OCl. We are able to model the initial separation and recombination quantitatively to obtain initial yields and recombination fractions that reflect the viscosity of the solvent and the initial range of recoil of the atom. In other experiments, we have exploited the transient absorption of photolytically produced Cl atoms to measure the rates of bimolecular reactions in solution.^{13,14}

Vibrational Energy Flow in CH₃I in Isolation and in Solution

We have followed vibrational energy flow by monitoring the change in an electronic transition as vibrational energy initially deposited in a C–H stretch migrates into other vibrations, generally ones with larger Franck-Condon factors, and then into the surrounding solvent.¹¹ In these experiments, a 100-fs infrared or near-infrared pulse from an optical parametric oscillator initially excites the C–H stretch, and ultraviolet light from another OPA probes the vibrationally excited molecule. We have applied this technique to several molecules,^{12,15-18} and during this last period of AFSOR support we have used it to monitor the energy

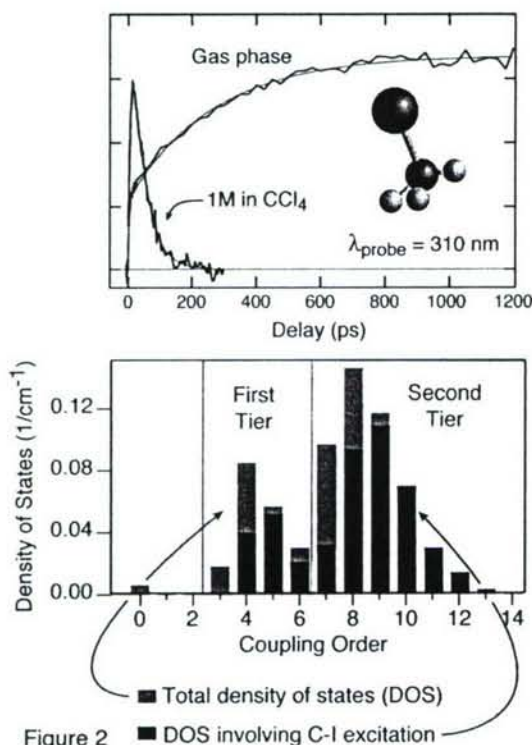


Figure 2

flow of CH₃I both in solution and in the gas phase.¹¹ The upper panel in Figure 2 summarizes the results. In CCl₄ solution, the absorption grows with a time constant of 7 ps as energy flows into Franck-Condon active modes from the initially excited C–H stretching overtone and subsequently decays with a 50-ps time constant as energy flows into the solvent. The situation is dramatically different in a gas-phase measurement using exactly the same technique. The signal rises rapidly, in slightly less than 7 ps, but then continues to grow more slowly over a period of about 400 ps. Analysis of the tier structure of the molecule, shown in the lower panel as a plot of the density of vibrational states for

each coupling order, suggests that the slower rise comes from energy flowing out of the first tier of strongly coupled states into another tier of more weakly coupled states. In solution, vibrational energy does not reach these weakly coupled states before it flows into the solvent. There are other recent examples of such behavior,^{19,20} and we have described this and other informative comparisons between gas-phase and condensed-phase reaction dynamics in a recent review.²¹

Vibrational Energy Flow in *cis*- and *trans*-Stilbene

Most recently, we have studied vibrational energy flow in stilbene in order to make a unique comparison between energy flow rates in two geometric isomers¹² and to prepare the way for the excited state isomerization studies. The two isomers of stilbene shown in Figure 3 differ in the orientation of the phenyl

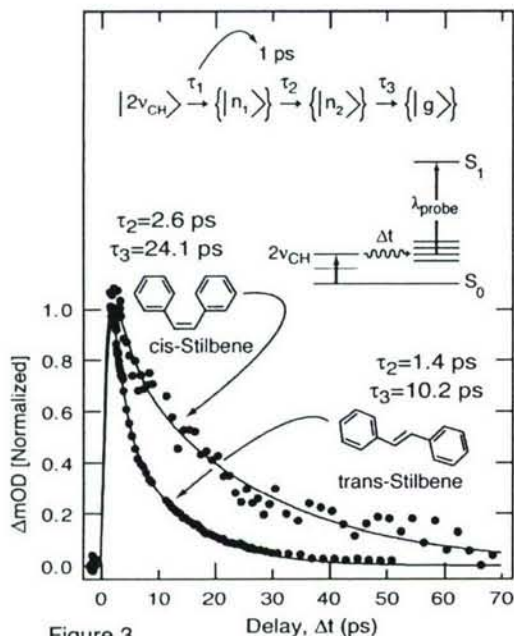


Figure 3

rings about the double bond, and, consequently, some of the vibrational frequencies differ between the two isomers. We have applied the same ultrafast vibrational excitation and electronic probing scheme, illustrated schematically in the figure, that we have used in other studies to *cis* and *trans* isomers of stilbene. As the data clearly show, the signal rapidly rises as the initial vibrational excitation leaves the C-H stretch and enters modes with better Franck-Condon factors. The signal then decays with the two time constants shown in the figure as energy flows through other modes in the molecule. The decay times do not depend on the identity of the solvent, suggesting

that we are observing *intramolecular* vibrational energy flow, but they differ substantially between the two isomers. The flow of vibrational energy in each stage is about twice as fast for the *trans* isomer as it is for the *cis* isomer, as shown by the two decay constants τ_2 and τ_3 obtained from the fits to the data. The scheme at the top of the figure illustrates the sequential coupling through subsets (tiers) of modes in stilbene that accounts for the energy flow times in the two isomers. The difference is another manifestation of sets of energy transfer pathways within a molecule that depend on the exact energies and couplings of the modes, as one expects from a tier model of vibrational energy flow.²¹⁻²³

AFOSR SUPPORTED PUBLICATIONS

Vibrational Relaxation of CH₃I in the Gas Phase and in Solution. Christopher G. Elles, M. Jocelyn Cox, and F. Fleming Crim, J. Chem. Phys. **120**, 6973 (2004).

Recombination and Reaction Dynamics Following Photodissociation of CH₃OCl in Solution. Christopher G. Elles, M. Jocelyn Cox, George L. Barnes, and F. Fleming Crim, J. Phys. Chem. A **108**, 10973 (2004).

Vibrational Energy Flow Rates for cis- and trans-Stilbene Isomers in Solution. M. Jocelyn Cox and F. Fleming Crim, J. Phys. Chem. A **109**, 11673 (2005).

Connecting Chemical Dynamics in Gases and Liquids. Christopher G. Elles and F. Fleming Crim, Annu. Rev. Phys. Chem. **57**, 273 (2006).

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