

recognized as a general phenomenon, but its relationship to the initial molecular properties of the parent molecule is not well understood. The capabilities of ILD have made it possible to examine this relationship in great detail for a wide range of radical species. Specifically, one can use ILD to obtain information on (1) the energetic onsets in the photolysis of the parent into radicals, (2) the time-dependent internal energy content of radicals after their photolytic production, (3) the pathways and efficiencies for vibrational and rotational energy transfer within the energy levels of the radical and (4) the rates of reaction between radicals in specific excited-state energy levels with stable species (*e.g.* HCO + H₂CO). When combined with state-selective excitation, ILD can correlate data of the type 1 - 3 with the initially populated states of the dissociating parent molecule.

Results for a variety of dissociative reactions yielding radical products will be presented. The dissociation of CH₃CHO into HCO provides an excellent example. The time for the appearance of HCO following excitation exhibits a strong dependence on the accompanying collision partners. Data in Fig. 1 illustrate this behavior for N₂. The maximum HCO concentration for pure CH₃CHO occurs at 250 μs while the addition of N₂ reduces this time to about 100 μs [5].

The ILD instrumentation used in this work (utilizing a CW dye laser and optical multichannel detection) will also be described.

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TIME-RESOLVED RESONANCE RAMAN SPECTROSCOPY

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Time-resolved resonance Raman (TR³) spectroscopy offers the opportunity to obtain simultaneously structural and kinetic information on reaction intermediates. Thus, not only can TR³ spectroscopy be used to identify the presence of conformationally distinct intermediates, but it can measure their time-dependent lifetime during each stage of a reaction.

TR³ spectra have been obtained with multiwavelength detectors such as intensified vidicons and pulsed tunable laser excitation. The reactions under study are initiated photolytically by a second pulsed laser. The overall measurement has a typical time resolution of 10 ns. The frequency used to generate TR³ scattering is chosen so as to yield maximum resonant intensity enhancements for specific chromophores.

TR³ experiments have examined the ligation reactions of hemoglobin (Hb) with O₂ and CO. The reaction is initiated by the photolytic dissociation of HbO₂ or HbCO. The ligation reaction is then followed by monitoring band intensities of HbO₂, HbCO and Hb in the appropriate TR³ spectrum. At least two distinct rates of reaction are observed (with rate constants of $2.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $1.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$).

Previous workers using flash photolysis and transient absorption techniques have also measured two rates of ligation, the faster rate constant being about $2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. This correlates well with the slower rate measured in this work. Thus, the faster rate observed in our work derives from a stage of the reaction not previously observed. It may correspond with a fast conformational rearrangement of Hb or one step in the sequential binding of the four O₂ molecules bound to Hb.

Resonance Raman bands have also been observed in the TR^3 spectra of hemoglobin ligation reactions which cannot be directly identified with either ligated forms of Hb or Hb itself. The bands may signal the presence of conformationally distinct forms of Hb present only as reaction intermediates.

FLUORESCENCE SPECTROSCOPY OF SUBPICOSECOND STATES IN LIQUIDS

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Experiments with synchronized laser pulses have allowed the observation of fluorescence from weakly emitting states, populated by a consecutive two-photon process. By utilizing different experimental degrees of freedom we are able to obtain fundamental new information about the relaxation properties of electronically excited states of aromatic species. A scan of the emission spectra from upper states and their dependence on excitation wavelengths has furnished evidence of spectral hole-burning. Measurements of the absolute intensities of these spectra give rise to decay time estimates which agree very well with those based on the linewidths of fine structure observed in these low-quantum-yield spectra.

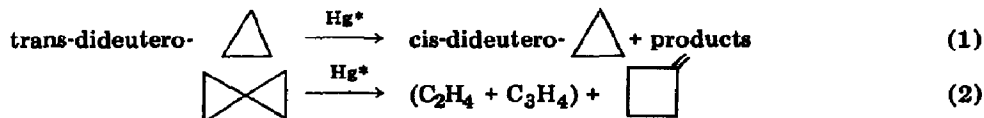
Monitoring the upper state fluorescence intensity as a function of relative excitation pulse arrival time allows an extension of these principles to the direct study of singlet lifetimes longer than about 10^{12} s. We report the first direct measurements of several important photochemically active aromatic species, including acridine, quinoxaline and 9-fluorenone.

THE MERCURY PHOTSENSITIZED REACTIONS OF CYCLOALKANES

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The interactions of $Hg\ 6(^3P_1)$ (Hg^*) with the cycloalkanes have been the subject of many investigations [1]. A controversy over the major primary mode of reaction of Hg^* with cyclopropane concerned the occurrence of C—C (excited molecule) or C—H bond cleavage. This controversy has been settled only recently [2 - 4]. Thus, for the three-membered ring compounds, the major primary interaction leads to the cleavage of a C—C bond, followed by molecular rearrangement or ring closure to the original form:



The sum of the quantum yields of ethylene (or allene) and methylenecyclobutane was 0.5, independent of substrate pressure.

For the larger ring cycloalkanes, the interaction with Hg^* leads primarily to C—H cleavage [1]. Gunning and his coworkers [5] have studied the mercury photosensitized reactions of cyclopentane in detail. They proposed the following mechanism