

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

K. J. CHOI, H. B. LIN and M. R. TOPP

Department of Chemistry, University of Pennsylvania, Philadelphia, Pa. 19104 (U.S.A.)

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.

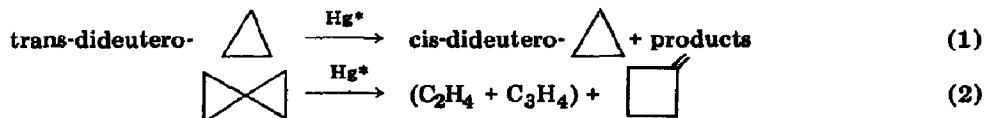
Monitoring the upper state fluorescence intensity as a function of relative excitation pulse arrival time allows an extension of these principles to the direct study of singlet lifetimes longer than about 10^{12} s. We report the first direct measurements of several important photochemically active aromatic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

THE MERCURY PHOTSENSITIZED REACTIONS OF CYCLOALKANES

G. R. DE MARE

Laboratoire de Chimie Physique Moléculaire, Faculté des Sciences CPI 160, Université Libre de Bruxelles, 50 ave. F. D. Roosevelt, B-1050 Brussels (Belgium)

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