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THEORETICAL AND EXPERIMENTAL STUDIES OF MOLECULAR DYNAMICS

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October 24, 1984

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962-7199

Captain Lee Meyers
Department of the Air Force
Air Force Office of Scientific Research
Bolling Air Force Base, D.C. 20332

Dear Lee:

As discussed in our last telephone conversation this letter contains my annual report for Air Force Contract #49620 83C0002.

During the period of support October 1, 1983 to September 30, 1984 the work described in the following papers was completed. Please note that four of these papers were cited as submitted for publication in my last report. They are included here for completeness since they actually appeared, with changes asked for by the referees, during the period in question.

Shot-Noise-Limited detection scheme for two-beam spectroscopies. Laszlo Andor, Andras Lorincz, Jeanne Siemion, Duane D. Smith and S.A. Rice, Rev. Sci. Instrum 55, 64 (1984).

We describe a single-sideband frequency demodulation scheme with large dynamic range which gives linear response and is capable of shot-noise-limited performance when used with time-resolved pump and probe, polarization, and three- and four-wave mixing spectroscopies.

$^1B_{2u} \leftrightarrow ^1A_{1g}$ Spectroscopy of Jet-Cooled Benzene: Single Vibronic Level Fluorescence Studies. Thomas A. Stephenson, Patricia L. Radloff and Stuart A. Rice, J. Chem. Phys. 81, 1060 (1984).

As part of an investigation of intramolecular energy transfer in jet-cooled $^1B_{2u}$ benzene, an extensive study of one photon $^1B_{2u} \leftrightarrow ^1A_{1g}$ spectroscopy

has been carried out. Our data lead to an assignment for ν_8 in the $^1B_{2u}$ state (1516 cm^{-1}), to a number of new assignments involving activity in ν_{18} and ν_4 , and they show that many of the higher vibrational levels in the $^1B_{2u}$ manifold are mixed. The activities of components of combination levels with different vibrational angular momenta have been observed and used to resolve several controversies concerning assignments in the $^1B_{2u} \leftrightarrow ^1A_{1g}$ spectrum of benzene.

Vibrational State Dependence of Radiationless Processes in $^1B_{2u}$ Benzene.

Thomas A Stephenson and Stuart A. Rice, J. Chem. Phys. 81, 1073 (1984).

An extensive examination of the vibrational state dependence of fluorescence lifetimes in supersonic jet-cooled $^1B_{2u}$ benzene, and the inferred vibrational state dependence of the non-radiative rate constants, are reported. The qualitative features of our results agree with those obtained from previous investigations using room temperature vapor phase samples. The spectral simplification achieved in the supersonic jet expansion has, however, allowed measurement of the fluorescence lifetimes of a number of $^1B_{2u}$ vibrational levels not previously studied. These data indicate that excitation of ν_4 , ν_5 , ν_8 , and ν_{10} result in enhanced non-radiative decay, which suggests that these vibrations are promoting modes. A previously unobserved sensitivity of the non-radiative rate constant to the vibrational angular momentum of the initially excited level has been demonstrated. Finally, fluorescence decays which do not have simple exponential form have been observed from vibrational levels in the vicinity of the "channel three" region. We discuss the significance of all of these observations in terms of the existing theory of radiationless processes and with respect to other recent experimental investigations.

Relaxation Dynamics of Photoexcited Benzene-Rare Gas van der Waals Complexes.

Thomas A. Stephenson and Stuart A. Rice, J. Chem. Phys. 81, 1083 (1984).

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The vibrational relaxation/predissociation dynamics of various benzene-rare gas van der Waals complexes have been investigated. These studies indicate that the pathways of vibrational redistribution within the complex are highly selective and involve only a small subset of the energetically accessible levels. While in general energy gap law behavior is observed, i.e. large benzene vibrational energy changes are disfavored, the sensitivity of the relaxation dynamics to this constraint varies with the vibrational level initially excited. This behavior is ascribed to varying degrees of sensitivity to the details of the atom-molecule potential and is related to the scheme of nuclear displacements involved in the benzene normal modes. Some, but not all, of the relaxation dynamics can be understood in terms of a very simple model that expresses the atom-molecule potential as a sum of atom-atom interactions and assumes a rigid geometry for the complex. A kinetic analysis that assumes only first order processes allows crude vibrational relaxation-predissociation rate constants to be extracted. The variation of the rate constants with rare gas and vibrational level is consistent with the energy gap law.

Comment on Vibrational Energy Redistribution in the Isolated Dimethyltetrazine Dimer Duane D. Smith, Andras Lorincz, Jeanne Siemion and Stuart A. Rice, J. Chem. Phys. 81, 2295 (1984).

Vibrational energy redistribution from the $6a'$ intramolecular ring mode to the intermolecular van der Waals modes in the dimethyltetrazine dimer was measured directly using time resolved spectroscopy. The relaxation time is 35 ± 10 ps, in fairly good agreement with the 66 ± 22 ps obtained from line broadening data.

Wave Packet Evolution in Isolated Pyrazine Molecules: Coherence Triumphs over Chaos. Andras Lorincz, Duane D. Smith, Frank Novak, Ronnie Kosloff, David J.

Tannor and Stuart A. Rice, J. Chem. Phys. (in press).

We report new measurements of the rotational state dependence of the initial fluorescent decay of the vibrationless $^1B_{3u}$ state of pyrazine. Through examination of excited state dynamics from several points of view the apparently inconsistent data from several sources is reconciled. The relationship of our analysis to recent ideas dealing with quantum chaos is discussed.

Relaxation of Large Molecules Following Ultrafast Excitation. Andras Lorincz, Frank A. Novak and Stuart A. Rice. Proceedings of Conference on Ultrafast Phenomena (1984).

Intramolecular relaxation of large molecules following ultrafast excitation is determined by the temporal properties of the light pulse if the density of coherently excited zero order states within the vibronic manifold is uniform. Consequently, longitudinal and transverse relaxations within the excited manifold appear to be instantaneous.

Rotational State Dependence of Pyrazine Fluorescence: Initial Decays for the Vibrationless $^1B_{3u}$. Frank Novak, Ronnie Kosloff, David J. Tannor, Andras Lorincz, Duane D. Smith and Stuart A. Rice, J. Chem. Phys. (in press).

Recent measurements of the rotational state dependence of the initial fluorescence decay of the vibrationless $^1B_{3u}$ state of pyrazine are analyzed from several points of view. The relationship of these analyses to recent ideas dealing with quantum chaos is discussed.

Relaxation of Large Molecules following Ultrafast Excitation. Andras Lorincz, Frank A. Novak and Stuart A. Rice, Chem. Phys. Letts. (in press).

We demonstrate that the ultrafast relaxation observed in the excited states of large organic molecules in solution may be understood as the

coherent evolution of the initially prepared non-stationary state. It is shown that under femtosecond excitation conditions the relaxation is determined by the characteristics of the light pulse. The analysis of a simple pump-probe experiment suggests a way of measuring the characteristics of ultrashort pulses. The case of fluorescence excited by ultrafast pulses is also analyzed.

Very truly yours,

A handwritten signature in cursive script, appearing to read "Stuart".

Stuart A. Rice

Frank P. Hixon Distinguished Service

Professor of Chemistry

SAR:va