AD-A192 754 EXCITED-STATE ENERGETICS AND DYNAMICS OF LARGE MOLECULES COMPLEXES AND CLUSTERS(U) TEL-AVIV UNIV (ISRAEL) DEPT OF CHEMISTRY J JORTNER ET AL. OCT 85 1/1

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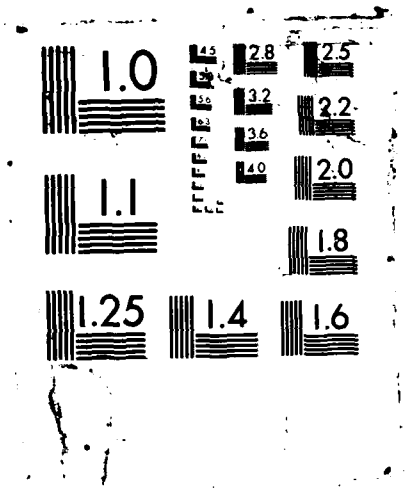
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SECOND INTERIM REPORT

Contract No. DAJA45-85-C-0008

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PROGRESS REPORT FOR THE PERIOD MAY - OCTOBER, 1985

2nd Periodic Report

1. Title: EXCITED-STATE ENERGETICS AND DYNAMICS OF LARGE MOLECULES, COMPLEXES AND CLUSTERS

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6. PROGRESS IN TECHNICAL APPROACH

New techniques for spectroscopy in supersonic expansions and in the development of specific supersonic sources were developed.

6.A *Vacuum Ultraviolet Absorption Spectroscopy in Supersonic Expansions.* We have combined the techniques of vacuum ultraviolet (VUV) spectroscopy together with planar supersonic jets, which allows for the interrogation of absorption spectra of large molecules cooled in supersonic expansions in the near VUV region. The experimental setup consists of a high pressure ~~Xe~~ XENON lamp, ~~CaF$_2$~~ CALCIUM FLUORIDE optics, a vacuum ultraviolet spectrograph and a nozzle slit (0.27x90 mm, repetition rate 9 Hz and gas pulse duration 300 μsec). The characteristics of this spectroscopic setup are: (i) Energy range 6-10 eV. (ii) Spectral resolution 0.1 ~~Å~~ ANGSTROMS. (iii) Routine measurements of high-energy absorption spectra. (iv) Interrogation of fluorescence excitation spectra of the parent molecule or its photoproducts with limiting quantum yields of $Y \geq 10^{-4}$.

6.B *Development of Conical Nozzles for Supersonic Jets.* Conical nozzles (nozzle opening angle $\theta = 30°$, and nozzle diameter $D = 0.3$ mm) were constructed and used in conjunction with a magnetic pulsed valve. The use of conical nozzles considerably enhances clustering in supersonic expansions, facilitating studies of large van der Waals complexes and clusters.

7. ACCOMPLISHMENTS OF OBJECTIVES

7.A *Energetics of Rydberg States of Jet Cooled Molecules.* VUV absorption spectra of benzene, benzene-D_6 and naphthalene cooled in planar supersonic expansions were measured over the range 2000-1600 Å, providing evidence on energetics, line broadening and interference effects.

7.B Intramolecular Relaxation of Rydberg States. Information on intramolecular dynamics of extravalence excitations of benzene was obtained from lineshape analysis. The lineshape of the $^3P_{xy}(0)$ Rydberg is Lorentzian, whose homogeneous width result in the lifetime $\tau = 0.19 \pm 0.02$ psec for C_6H_6 and $\tau \approx 0.22 \pm 0.02$ psec for C_6D_6, implying that (i) the relaxation of the Rydberg is characterized by moderate energy gap(s), and (ii) the electronic relaxation rate of the Rydberg is considerably less efficient than that of the intravalence excitation in the same energy domain.

7.C Interference Effects between Extravalence and Intravalence Molecular Excitations. Pronounced Rydberg-valence interference effects were observed in the absorption spectra of jet-cooled naphthalene in the spectral region 1600-1650 Å, providing information on the homogeneous contribution to high-energy molecular coupling phenomena.

7.D Rotational State Dependence of Intramolecular Dynamics. Rotational effects on interstate coupling are of considerable current interest. Absolute fluorescence quantum yields from photoselected rotational states were measured for the electronic origins of the S_1 state of pyrazine. Strong rotational state dependence was observed providing novel information on interstate coupling for the intermediate level structure. This unique information cannot be extracted from time-resolved decay lifetimes.

7.E Photoisomerization Dynamics of Large Isolated Molecules. Time-resolved fluorescence lifetimes from photoselected states of trans-stilbene and its derivatives were recorded by the techniques of picosecond spectroscopy in jets using a mode-locked dye laser and a fast photon counting system. Decay lifetimes as short as 100±30 psec were recorded. Extensive information on the energy dependence of the isomerization rates of alkyl stilbenes was obtained, providing information on the role of intramolecular vibrational distribution on the photochemistry in an isolated large molecule.

7.F Energy-Resolved Photoisomerization Rates. The dynamics of the S_1 and S_2 electronically excited singlet states of diphenylbutadiene was interrogated by fluorescence quantum yield measurements over the very broad energy domain of 0-7500 cm^{-1} above the (false) S_1 origin. The issues of the lack of mode selectivity and the applicability of statistical theories for the description of isolated-molecule photochemistry were explored.

7.G van der Waals Complexes of Porphyrins. Excited-state energetics and dynamics of large complexes consisting of porphyrins bound to rare-gas atoms were explored. Detailed spectroscopic information on the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions of the free-base porphine·Ar complex was obtained, providing insight into the structure of this complex as well as resulting in a novel mechanism for microscopic solvent shifts induced by configurational distortions, which are due to complexing.

7.H Coupling between Intramolecular and Intermolecular Nuclear Motion in Complexes. Intermolecular vibrations of large van der Waals complexes, which involve the motion of the ligand relative to the large molecule, provide an analogue for surface vibrational motion in a finite system and constitute the precursors of phonon modes in condensed phases. Information on the coupling between intermolecular and intramolecular vibrational motion was obtained for the trans-stilbene·Ar complex.

7.I Electron Localization in Clusters. Small clusters exhibit unique physical and chemical phenomena, which are both of fundamental and technological significance, and provide ways and means to explore the "transition" from molecular to condensed-matter systems. We have provided a theoretical study of the structure, energetics and dynamics of an excess electron interacting with an alkali-halide cluster, which was explored by the quantum path integral molecular dynamics method. These studies establish various compositional, structural and size dependence of bulk and surface localization mechanisms of the dynamic process induced by electron attachment.

8. PUBLICATIONS

The following manuscripts, supported by this research grant, were prepared and submitted for publication:

(1) A. Amirav and J. Jortner
Vacuum Ultraviolet Absorption Spectroscopy in Supersonic Expansions
J. Chem. Phys. (Communication) 82, 4378 (1985)

(2) A. Amirav and J. Jortner
Rotational and Vibrational State Dependence on Intramolecular Coupling and Dynamics in the S_1 State of Pyrazine
J. Chem. Phys. (in press)

(3) J. Troe, A. Amirav and J. Jortner
Energy-Resolved and Thermalized Photoisomerization Rates of Diphenyl-Butadiene
Chem. Phys. Letters 115, 245 (1985)

(4) A. Amirav, M. Sonnenschein and J. Jortner
Interstate Coupling and Dynamics of Excited Singlet States of Isolated Diphenylbutadiene
Chem. Phys. (in press)

(5) U. Even, Z. Berkovitch-Yellin and J. Jortner
Electronic Excitations of the Free-Base Porphine·Ar van der Waals Complex
Canad. J. Chem. (C. Sandorfy-Special Issue) (in press)

(6) D. Bahatt, U. Even and J. Jortner
Coupling between Intramolecular and Intermolecular Nuclear Motion in a Large van der Waals Complex
Chem. Phys. Letters 117, 527 (1985)

(7) U. Landman, D. Scharf and J. Jortner
Electron Localization in Alkali-Halide Clusters
Phys. Rev. Letters 54, 1860 (1985)

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