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EXCITED-STATE ENERGIES AND DYNAMICS OF LARGE
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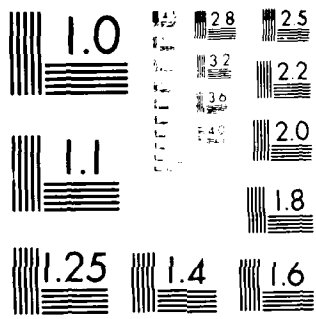
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EXCITED-STATE ENERGETICS AND DYNAMICS
OF LARGE MOLECULES, COMPLEXES AND CLUSTERS

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Seeded supersonic expansions constitute a "new state of matter", where interrogation by laser and other spectroscopic methods open up new horizons in the exploration of energetics, dynamics and photochemistry. We have studied the excited-state energetics and dynamics of some large finite systems with a large number of vibrational degrees of freedom. These involve large collision-free molecules and van der Waals complexes and clusters. We have perpetuated a broad research program of spectroscopy in supersonic jets, with a special emphasis on excited-state energetics in the high-energy domain and ultrashort relaxation phenomena.

Several advanced and unique techniques for spectroscopy in supersonic jets were developed in our laboratory. These involve:

- (a) Conical nozzles for supersonic jets. Conical nozzles (nozzle opening angle $\theta = 30^\circ$ 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.

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(b) Pulsed, planar, supersonic nozzle slits. We have developed a 9-12 Hz, 300 μ sec duration, pulsed supersonic jet sources based on the expansion of seeded gas through a long (35mm-39mm) nozzle. This planar supersonic source is characterized by a long path length and a large concentration of ultracold molecules in the interrogation region.

(c) 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 (6-10 eV) VUV region.

(d) Pulse extraction mass spectrometer. This set-up is characterized by a mass resolution of $\Delta m/m = 10^{-2}$ and allows for the measurements of high ion masses up to $m = 2000$ in supersonic jets. The ions of large molecules and of large clusters, e.g., tetracene \cdot Ar $_{30}^+$, are produced by two-photon two-color ionization.

Spectroscopic studies of jet-cooled large molecules focused on intramolecular dynamics of the first (S_1) electronically excited singlet state and on the relaxation of Rydberg states. Fluorescence quantum yields of anthracene and its derivatives have provided ubiquitous information on intramolecular dynamics pertaining to the rotational effects on intrastate vibrational energy redistribution (IVR), and the coupling between IVR and interstate electronic relaxation. The exploration of the vibrational energy dependence of interstate electronic relaxation from photoselected states of the S_1 manifold of anthracene and seven of its chemical derivatives led to information that mediated intersystem crossing was inferred, which was manifested in resonances in intersystem crossing, dramatic inverse deuterium isotope effects, and modification of the intramolecular dynamics

by microscopic spectral shifts in van der Waals complexes of Ar. Proceeding to the high energy domain, intramolecular relaxation of Rydbergs in benzene and anthracene was studied by (Lorentzian) line broadening and interference effects between several extravalence Rydbergs superimposed on an intravalence $\pi\pi^*$ excitation, which was observed in the (1600-1650 Å) spectrum of naphthalene, providing information on high-energy intramolecular coupling phenomena. Finally, fluorescence quantum yields from Rydberg-excited large aromatics were observed originating in the $S_1 \rightarrow S_0$ emission. These results may be of interest regarding recent astrophysical implications of high-energy photophysics of large aromatic molecules in outer space.

Intramolecular photochemistry of collision-free large molecules is of considerable interest with respect to the issues of its interrelationship with basic IVR and electronic relaxation phenomena, and the possibility of the exhibition of vibrational mode photoselectivity. Picosecond time-resolved spectroscopy of cis-trans isomerization in jet-cooled alkyl-transtilbenes and 1,4 tetraphenyl butadiene have provided strong evidence for the applicability of the statistical RRKM theories for intramolecular photochemistry.

Large van der Waals complexes, consisting of rare-gas (R) atom(s) bound to a large aromatic molecule (M) were studied by fluorescence excitation and by two-photon, two-color spectroscopy in conjunction with mass-resolved detection. These studies provided information on spectral shifts of the S_1 level and of the ionization potential for tetracene- Ar_n ($n = 1 - 5$) complexes, providing central information on microscopic solvent shifts. These studies

were extended to M-metal atom complexes, such as pyrene·Hg_n (n = 1,2), which constitute a new method for the creation of metallic microclusters supported on a "microspace". The electronic-vibrational spectroscopy of M·R_n complexes provide information on large amplitude intermolecular nuclear motion of rare-gas atoms on microsurfaces, which pertain to the interesting analogy between large van der Waals molecules and microsurfaces.

Large insulating clusters formed by the nucleation of R atoms on M molecules were synthesized using small-aperture conical nozzles. We have investigated various spectroscopic and chemical attributes, i.e., the excited-state energetics, the ionization existence of isomer potentials, and the vibrational frequencies of large M·R_n (n = 1-30) clusters. These studies pertain to the evolution of energetic size effects from an isolated large molecule to the condensed phase. Furthermore, the size dependent line broadening and vibrational energetics pertain to the interesting issues of the documentation of isomerization and "melting" in large finite systems.

Our studies contribute towards bridging the gap between molecular, surface and condensed-matter energetics and dynamics.

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