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COLORADO STATE UNIV FORT COLLINS DEPT OF CHEMISTRY
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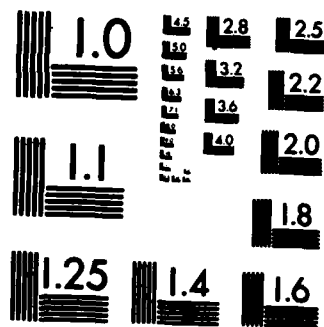
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SUPERSONIC MOLECULAR JET STUDY OF THE LIQUID STATE"

FINAL REPORT

ELLIOT R. BERNSTEIN

OCTOBER 10, 1984

U.S. ARMY RESEARCH OFFICE

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COLORADO STATE UNIVERSITY

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The study of solvation of aromatic molecules (benzene, toluene, aniline) by small hydrocarbons (C_nH_{2n+2}, $n = 1, 2, 3$) in a molecular jet is discussed. The detection of the clusters is through laser induced fluorescence and time of flight mass spectroscopy. The clusters observed (up to 15 solvent molecules) are compared to liquid state systems; simple atom-atom potential calculations are employed to help assign geometry. Dynamical behavior of the clusters is characterized in terms of intramolecular vibrational redistribution, vibrational dissociation, and vibrational energy transfer.			

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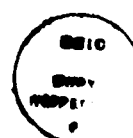
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The material in this report is largely presented in nine publications. These papers are referenced below. The overview here is meant to tie together the body of this work. The unpublished results are largely those data not important enough to appear in papers, or data which need additional work to interpret.

The nine publications incorporated into this report cover the transition from initial experiments with cryogenic liquid solutions, through initial molecular jet experiments with aniline, into the detailed study of the solvation of benzene and toluene, and finally to the study of aromatic dimers. This overview is intended to tie together the major results from these four phases of the work and create an impression of unity and purpose for the study.

Cryogenic Solutions- A large body of the data has been accumulated in this laboratory for small aromatics such as benzene, toluene, aniline, and pyrazine dissolved in small hydrocarbon solvents. Reference 1 reports some of the results for pyrazine, benzene, and OsO_4 . In the pyrazine-propane solution, spectroscopic evidence of aggregation of the solute upon rapid deposition of the gas mixture is presented for the first time. The spectrum of the aggregates is characterized by a large spectral shift similar to that of solid pyrazine. Upon warming the solution, the aggregate spectrum decays to be replaced by the less-shifted monomer solution spectrum (the shift of which is dependent upon solvent). Subsequent cooling of the solution results in precipitation of pyrazine with no recurrence of the aggregate spectrum.



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clusters. Several interesting results were obtained. Upon excitation of An at reasonably high backing pressure ($P_0 \sim 400$ psi) dispersed emission experiments reveal emission from levels lower than the one pumped. Rice and co-workers have studied this relaxation effect very close to the nozzle and determined that the relaxation is due to long range "resonance" interactions with the helium carrier gas. But our observation of similar relaxation in a collisionless region of the beam calls into question these conclusions. We observed that the amount of "relaxation" increases with backing pressure (as does the concentration of An-He vdW clusters). Furthermore, the emission from known vdW peaks consists solely of "relaxed" emission. Apparently excitation of An-vibronic peaks also excites An-He vdW clusters. Excitation of high levels of the clusters fragments them leaving An in a lower vibronic state. An then fluoresces giving rise the "relaxed" emission. This explanation demands that An-He vdW clusters have absorption features coincident with those of An. One color and two-color TOFMS experiments confirm this; the shifts of An-He, and AnHe_2 are 1 cm^{-1} and 2 cm^{-1} respectively. The one-color and two-color TOFMS experiments of An-He and An-CH_4 systems reveal something of the geometry of the clusters. The spectral shifts for these clusters are additive for the addition of one and two solvent molecules. However, both AnHe_3 and $\text{An(CH}_4)_3$ exhibit broad spectra with non-additive spectral shifts. These spectral shift patterns indicate that An has two low energy, equivalent binding sites and that the third solvent molecule adds to an inequivalent and probably less localized binding site.

The two lowest energy sites are presumably above and below the aromatic ring of An. Something of the energetics and excited state dynamics of these clusters can also be learned. The dissociation energy of An-He clusters can be estimated quite clearly by dispersed emission experiments ($145 < D_0 < 155 \text{ cm}^{-1}$). The estimate of D_0 based on fitting the vdW symmetric stretch yields a somewhat smaller value ($D_0 \sim 100 \text{ cm}^{-1}$). Apparently the progression in the symmetric stretch is not well-modeled by a Morse potential; the progression seems to be more anharmonic than expected from a Morse oscillator.

In the An-CH₄ system the dynamics of various excited state processes can be estimated. Intramolecular vibrational redistribution (IVR) is evident in the dispersed emission spectrum as low-lying levels above the 0_0^0 are pumped. This indicated that IVR is faster than the fluorescence lifetime (5ns). However, as levels higher than $6a^1$ are pumped vibrational predissociation (VP) of the An-CH₄ clusters is observed. VP is faster than IVR or fluorescence if the excited state vibrational energy is greater than D_0 for the cluster.

Solvation of Benzene and Toluene- The study of benzene and toluene clustered with methane, ethane and propane has led to detailed information about the structure and energetics of solute- solvent systems. Computer modeling of these clusters has proven essential to the understanding of the spectroscopic data. Through the interplay of the computer modeling of these clusters and the spectroscopic data, it has been possible to assign probable geometries to many of the spectroscopic features. In many cases this allows one to find the spectral shift of a specific geometry of a cluster. The assignment of spectral shifts to the

calculated configurations (with calculated intermolecular energetics) has led to some general conclusions about the interactions responsible for spectral shifts and binding.

The exponential-6 (exp-6) intermolecular potential used for the computer modeling of these clusters is adequate for predicting minimum energy geometries consistent with the spectroscopic results in every case. Furthermore, the binding energies predicted by the computer modeling are within the limits determined spectroscopically. Thus, the dominant binding interaction for these clusters arises through dispersion forces and the exp-6 potential is a good model for this interaction.

Assignment of the computer generated configurations to the spectroscopic features leads to the conclusion that spectral shift is not directly related to binding energy. For these clusters the magnitude of the spectral red shift is directly related to the degree of overlap between the solvent and the aromatic π -cloud of the solute. This generalization, that the spectral shift scales with the amount of overlap of the solvent with the aromatic system of the solute, holds for all benzene-solvent and toluene-solvent clusters reported here.

How do these results pertain to analogous liquid systems? The interaction between solvents and the aromatic system of the solute saturates upon addition of about two solvents. The jet generated clusters do not generally show absorption maxima beyond the shift associated with addition of solvents above and below the ring (although some absorption extends much further to the red). Indeed, for large clusters the absorption maximum appears with spectral shift

much smaller than that expected for solvents bound above and below the ring; this is due to the dominance of anisotropic clusters in the beam (solvent on one side of the ring). In any case, it appears that the interaction of solvent with the aromatic system of the solute cannot explain the large shifts observed in the liquid. Apparently the liquid cage structure produces interactions which are not modeled well by small clusters in the jet. However, it is clear that one important interaction (between solvents and the aromatic π -system of the solute) has been well-modeled in the jet.

The nucleation process in the beam can also be explored. Due to the (estimated) low concentration of solvent monomers in the beam, homogeneous nucleation (addition of one solvent at a time) mostly occurs through the interaction of a solvent dimer (or larger cluster) with the solute. The solute-solvent binding energy is dissipated in part by the dissociation of the solvent dimer; thus, the rate of this nucleation process depends on both the solute-solvent and the solvent-solvent binding energy. A competing process can lead to the addition of more than one solvent per encounter (inhomogeneous nucleation), thus producing a cluster with both solvents on the same side of the ring (anisotropic cluster). The spectra of large clusters indicate that inhomogeneous nucleation dominates for our beam conditions. It is difficult to produce significant amounts of large isotropic clusters which would probably be a more fruitful model of the liquid state.

Aromatic Dimers- Understanding solute-solute interactions

has a bearing not only on the solid phase, but also on liquid solutions. For example, excimers are known to form in liquid solutions containing benzene or toluene. Gas phase spectroscopic data for the dimers should tell us more about these excimers. Also, the observation of solute aggregates in cryogenic solutions shows that ground state solute-solute interactions can be important in dilute liquid solutions. The study of Ben_2 , Tol Ben and Tol_2 has helped us understand these interactions.

Spectroscopic data for Ben_2 clearly demonstrate for the first time that the dominant geometry is not a sandwich parallel-undisplaced or perpendicular configuration. The only reasonable geometry consistent with the spectroscopic data is parallel-displaced. Calculations using the exp-6 form for the intermolecular potential do not predict the correct geometry. Incorporation of a quadrupole-quadrupole interaction term is necessary to predict a parallel-displaced geometry. Since the displacement of the rings arises because of quadrupole-quadrupole interactions, excimer formation can be readily understood. Upon excitation to the $^1\text{B}_{2u}$ electronic state, benzene loses its quadrupole moment. From the exp-6 calculation we predict that the minimum energy configuration for the excited state (barring exchange interactions) would be parallel undisplaced. In the undisplaced excited state configuration exchange interactions could produce the excimer.

The computer modeling of Tol Ben and Tol₂ proved equally useful. Again, multipolar interactions (quadrupole-quadrupole, dipole-quadrupole, dipole-dipole) are necessary for the computation of geometries consistent with the spectra. Excimer formation is predicted (and observed) for excitation of some species; in some cases a barrier to excimer formation is observed (and rationalized). In addition, the very large spectral shift of one geometry of Tol^{*}ben can be understood by qualitatively modeling the excited state of this species. The dipole moment of toluene is thought to increase substantially upon excitation. This would increase the dipole-quadrupole interaction in Tol Ben enough to rationalize the -250 cm⁻¹ spectral shift. All observed shifts of these dimers can be explained in terms of the overlaps of the π -systems, and the increase in the dipole moment of toluene upon excitation.

Computer modeling is an essential component of the study of these vdW clusters. The spectroscopic data are needed to validate the computer modeling techniques, and the calculations help to assign spectra which are otherwise quite puzzling. In this way the interplay between spectroscopy and computer modeling leads to a better understanding of the structure and energetics of both solute-solvent and solute-solute systems.

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