DOE/ER/60391--T5

OE-FG03-86ER 60391

PROGRESS REPORT

MOLECULAR DETECTION USING RYDBERG,
AUTOIONIZING, AND CLUSTER STATES

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Prepared for the
Office of Health and Environmental Research
Office of Energy Research
Department of Energy

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August 15, 1990

Abstract

We report on investigations of multiphoton ionization spectroscopy in pure clusters of aromatic molecules and mixed clusters of an aromatic molecule with a rare gas atom. Conditions needed for efficient production of ion clusters are discussed. Experimental results that establish geometry of naphthalene and benzene clusters are described.

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Introduction

Cluster spectroscopy is providing an immense amount of new information concerning the energetics, geometries, and dynamics of molecular clusters.¹ Supersonic jet sources can generate diverse types of homomolecular and mixed clusters. Clusters of specific size are readily separated for individual study by time-of-flight mass spectrometry. Recent work relevant to the results presented below has been reviewed in the literature.^{1,2} During the past year we have concentrated on applying multiphoton ionization spectroscopy to the study of weakly bound van der Waals clusters formed by the aromatic molecules naphthalene, benzene, and aniline, and their complexes with rare gas atoms. We remain in the process of data acquisition and analysis for the studies described in this report.

The principal emphasis of our current work is on establishing conditions most favorable for cluster spectroscopy of the van der Waals molecules, and elucidating their spectroscopy, geometries, and dynamics. This will lead to improved methods for selective detection of complex molecular species.

The propensity for cluster formation is of considerable interest to the objectives of the program. It is usually straightforward to select conditions that produce either monomers or very large clusters in a supersonic beam expansion. However, optimization for a desired distribution of size and temperature remains an empirical art. There is a rapidly developing literature related to this subject. Early on, Smalley and Levy³ outlined conditions desired for optimal cooling a decade ago. The following salient points remain relevant to the present experiments.

1. Cooling is related to the quantity PD^2 , where P is the source pressure of the expanding gas, and D is the nozzle diameter.

¹A. W. Castleman, Jr. and R. G. Keese, *Science* **241**, 36 (1988).

²R. L. Whetten and M. Y. Hahn in *Atomic and Molecular Clusters*, edited by E. R. Bernstein (Elsevier, Amsterdam, 1990), pg. 765.

³R. E. Smalley, L. Wharton, and D. H. Levy, *Acc. Chem. Res.* **10**, 139 (1977).

2. Cooling ceases when the gas has reached the terminal Mach number, and this occurs at a distance on the order of 10 D from the nozzle.

3. The terminal temperature, T_m , for expansion of a monoatomic gas is given by

$$T_m = T_0 (1 + 0.5 (g - 1) M_t^2)^{-1}$$

where g is the ratio C_p / C_v and M_t is the terminal mach number, given by

$$M_t = 133 (P_0 D)^{0.4}$$

for argon, and P is in atmospheres, D is in centimeters.

4. Clustering is proportional to the density of the clustering species

It is readily feasible to expand from several atmospheres into a vacuum maintained below 10^{-4} torr. Thus, helium carrier gas is expected to cool below 4 K. The helium-helium van der Waals bond is exceedingly weak, therefore this gas does not cluster appreciably at these temperatures. The translationally cold gas can cool guest molecules translational and rotational degrees of freedom efficiently. Experiments in our laboratory and elsewhere confirm that vibrational cooling is appreciable, although not complete, for the aromatic molecules of interest. Helium is also capable of forming mixed van der Waals clusters with aromatic molecules, however the binding energy, and hence abundance, is substantially less than for heavier carrier gases such as argon.

Expansions of the heavier carrier gases tend to form large clusters of the rare gas atoms. This is a consequence of the more attractive van der Waals interactions between these atoms. Expansions of pure argon, for example, tend to form liquid argon droplets. Therefore, expansions of mixtures of rare gases with a helium carrier are in common usage in order to suppress droplet formation. Helium expansion provides the low translational temperature, and the larger rare gas atom provides more efficient energy transfer from the hot molecules to the cold helium gas. This, combined with the increased van der Waals bonding between argon and aromatic molecules, leads to efficient formation of mixed clusters.⁴

Control of clustering has been used to considerable advantage in studies of mixed aromatic-rare gas atom clusters between an aromatic and one, two, or three rare gas atoms.⁵ It has been possible to use high resolution rotational spectroscopy to deduce

⁴e.g. S. M. Beck, M. G. Liverman, D. L. Monts, and R. E. Smalley, *J. Chem. Phys.* **70**, 232 (1979); A. Amirav, U. Even, and J. Jortner, *Chem. Phys. Lett.* **67**, 9 (1979); **72**, 17 (1981); *J. Chem. Phys.* **86**, 3345 (1982); D. V. Brumbaugh, J. E. Kenny, and D. H. Levy, *J. Chem. Phys.* **78**, 3415 (1983); J. L. Knee and P. M. Johnson, *J. Chem. Phys.* **80**, 13 (1984).

⁵D. H. Levy, *J. Chem. Soc., Faraday Trans. 2*, **82**, 1107 (1986).

geometric structures for several of these species. The results provide unambiguous evidence for formation of multiple stable conformations for species such as tetrazene-argon, toluene-argon, and toluene-benzene. Typically, a rare gas molecule may be centrally located above the aromatic ring, or it may reside on the edge of the molecule. Each of these conformers confers specific energy shifts on the molecular transitions. These shifts are small and uniform among the vibrational levels for mixed clusters, however they are expected to be complex and nonuniform in the case of homomolecular clusters.

Information on cluster ionization energetics and fragmentation dynamics is emerging from a number of research groups. Ground state dissociation energies for the trimer and tetramer are expected to be similar to the measured⁶ benzene dimer D_0 of 800 cm^{-1} . For clusters containing an aromatic molecule with an argon atom, D_0 is expected to be appreciably less. Measurements indicate that in the benzene dimer ion, binding energy increases to 5000 cm^{-1} .⁶ Intermediate binding energies are deduced for S_1 excited states by observing their transition energies and also the break off of cluster emission, due to dissociation, as vibrational energy is increased in the excited state. Mixed complexes with argon have much weaker binding, such that stabilization in S_1 is on the order of 20 cm^{-1} relative to the ground state, and it increases to 172 cm^{-1} in the ion.⁷ There is a relatively strong electrostatic interaction between the charge on the ion with a polarizable rare gas atom or ground state molecule, conferring greater binding energy than for the neutral cluster, by factors ranging from 2 to 10. This is expected to activate long Franck-Condon progressions in the low frequency intermolecular vibrational modes in the ionization spectrum. Whereas these have been observed for some clusters, we did not observe such features for the case of the naphthalene cluster⁸, and were able to conclude, based on this and other information, that the trimer ionizes by a biexcitonic autoionization mechanism. This was consistent with the former result, obtained by Whetten and coworkers,⁹ indicating that large benzene clusters ionize by a bimolecular mechanism, rather than by the direct sequential ionization process characteristic of monomers. Whetten describes the large cluster mechanism as exciton fusion, whereby two molecular excitations diffuse and finally collide, depositing the energy of two individual excited molecules at a single site, thereby exceeding the ionization potential of a single molecule.

Currently, there is considerable interest in cluster geometry because it provides a basis for understanding the evolution from properties of the monomer to those of bulk

⁶J. R. Grover, E. A. Walters, and E. T. Hui, *J. Phys. Chem* 91, 3233 (1987).

⁷L. A. Chewter, K. Muller-Dethlefs, and E. W. Schlag, *Chem. Phys. Lett.* 135, 219 (1987).

⁸J. Wessel, *Phys. Rev. Lett.* 64, 2046 (1990).

⁹K. E. Schriver, M. Y. Hahn, and R. L. Whetten, *Phys. Rev. Lett.* 59, 1906 (1987).

molecular systems. As mentioned above, high resolution rotational spectroscopy provided geometries for relatively simple small molecular clusters. More recently, electron diffraction yielded information on rare gas cluster geometry,¹⁰ and methods based on analysis of isotopic mixed cluster electronic spectra provided indirect structural information about more complex clusters.¹¹ The experimental structure analyses have been complemented by theoretical calculations by several groups. Geometric modeling is based on use of 6-12 potentials. Calculated interaction energy is minimized by varying structural parameters. The only major problem with this procedure is that multiple local minima exist for typical complex clusters. Van de Waal obtained promising results by starting from structures associated with the bulk crystal structure, and then reduced the size of the cluster, molecule by molecule. Changes in binding energy were calculated as a function of displacement from this structure. The results predicted unusually stable configurations for 13 molecule benzene clusters. For the smaller dimer and trimer clusters, sandwich and C_3 symmetry structures were predicted. These are not consistent with with observed geometries.^{12,13}

Ion spectroscopy of monomer and cluster species is receiving increasing attention here and elsewhere. Earlier work in our laboratory relied on monomer ion fragmentation spectra in order to determine the ion absorption spectrum of naphthalene cations¹⁴. Cold ions were formed by gently ionization (leaving little excess vibrational energy in the initially formed ion). The absorption spectra of these ions were recorded by monitoring fragmentation of the ions that was induced by the absorbed energy. The method was highly effective in detecting ion absorption, however, in many situations multiple photon absorption by the ion is required, and this introduces the possibility of adversely broadening the spectra. Nevertheless, the method has been used successfully to obtain the spectra of benzene¹⁵, chlorobenzene¹⁶, and methyl iodide¹⁷ cations. In each case, new electronic states with distinctive vibronic structure have been revealed. Initially, we proposed to improve the method of ion fragmentation spectroscopy for large molecules by forming weakly

¹⁰L. S. Bartell, Chem. Rev. 86, 492 (1986); J. Farges, M. F. DeFeraudy, B. Raoult, and G. Torchet, J. Phys. Chem. 84, 3941 (1984).

¹¹J. E. Wessel and J. A. Syage, J. Phys. Chem. 94, 737 (1990).

¹²K. O. Bornsen, H. L. Selze, and E. W. Schlag, J. Chem. Phys. 85, 1726 (1986).

¹³K. O. Bornsen, S. H. Lin, H. L. Selze, and E. W. Schlag, J. Chem. Phys. 90, 1299 (1989).

¹⁴D. Mordaunt, G. Loper, and J. Wessel, J. Phys. Chem. 88, 5197 (1984); J. A. Syage and J. E. Wessel, J. Chem. Phys. 87, 3313 (1987).

¹⁵K. Walter, R. Weinkauff, U. Boesl, and E. W. Schlag, Chem. Phys. Lett. (1989).

¹⁶X. Ripoché, I. Dimicoli, J. Le Calvé, F. Piuze, R. Botter, Chem. Phys. 124, 305 (1988).

¹⁷A. M. Woodward, S. D. Colson, and W. A. Chupka, J. Phys. Chem. 90, 274 (1966); U. Boesl, R. Weinkauff, and K. Walter, Proc. Intl. Laser Science Conf, ed. Wm. Strwalley, AIP, Ridge, NY, 1989.

bound van der Waals complexes between an aromatic ion and rare gas molecule, and then recording the ion spectrum by monitoring dissociation of the complex. This requires little excess energy, and thus should avoid problems associated with power broadening. As reported below, we readily achieved complex dissociation, although low cluster ion abundances have precluded extensive spectroscopy using our beam apparatus. However, Knight and coworkers recently reported well resolved spectra of chlorobenzene¹⁸, fluorobenzene,¹⁸ and p-difluorobenzene¹⁹ ion clusters, thus demonstrating the practicality of the method.

Experimental

The experimental apparatus was previously described in the published literature.²⁰ Additional aspects relevant to ongoing studies are discussed here. A cross sectional view of a modified pulsed valve modeled on our present in-house constructed solenoid activated pulsed valve is shown in Figure 1. A Kel-F pin is normally held in place by a spring in order to seal the drilled passage way to the valve aperture. In the current device, the valve aperture is a pinhole drilled in a thin plate with a diameter 100, 200 or 500 μm . The input carrier gases are mixed in a manifold and then pass into to thermostated valve body where they are mixed with the equilibrium vapor pressure from the sample material. The mixture expands directly into a vacuum chamber that is pumped by a 6" diffusion pump. The pressure in this region was monitored with a fast ion gage using 10 psig helium on the inlet side of the valve. Expansion chamber pressure varies from approximately 10^{-6} torr for a closed valve to 5×10^{-5} torr when open (200 μm pinhole), with a risetime on the order 500 μs and fall time on the order of 5 ms. A portion of the beam passes through a 0.1 cm aperture in a 2 cm diameter skimmer into an inner mass spectrometer chamber which is pumped to 10^{-6} torr. Ionization and time-of-flight mass spectrometry are performed as previously described. Conditions influencing effective temperature in the expansion include inlet pressure, nozzle diameter, valve drive voltage and valve spring tension, valve opening duration timing of the ionizing laser pulse relative to valve opening, and positioning of the laser beam relative to the expansion axis. Generally the best cooling was obtained with timing adjusted for excitation slightly after full beam intensity is achieved.

¹⁸E. J. Bieske, M. W. Rainbird, and A. E. W. Knight, *J. Phys. Chem.* **94**, 3962 (1990); E. J. Bieske, R. I. McKay, F. R. Bennett, and A. E. W. Knight, *J. Chem. Phys.* **92**, 4620 (1990).

¹⁹E. J. Bieske, R. I. McKay, F. R. Bennett, and A. E. W. Knight, *J. Chem. Phys.* **92**, 4620 (1990).

²⁰J. A. Syage and J. E. Wessel, *J. Chem. Phys.* **87**, 3313 (1987).

Results and Discussion

Naphthalene

Whereas monomer production and cooling is relatively insensitive to experimental conditions, formation of clusters in our system is highly sensitive to mechanical valve adjustment and to electrical pulsing conditions. In experiments requiring formation of homoclusters, linewidth and vibrational hot band population was found to be relatively insensitive to inlet pressure, expansion gas composition, and nozzle diameter. In the case of naphthalene, the ratios of dimer to trimer to tetramer were equal within experimental error ($\pm 30\%$) for inlet pressures ranging from 100 torr to 40 psig, for nozzle diameters from 100 to 500 μm , and for carrier composition ranging from 0 to 20% argon in helium. The ratios were highly sensitive to naphthalene vapor pressure, with the expected result that maximum clustering occurred at high vapor pressure. The unexpected result was that apparent cluster temperature and abundance were highly sensitive to the mechanical adjustment of the valve system and apparently, to the wear condition of the valve pin. Thus, with the current technology, it is difficult to reproduce cooling conditions and cluster distributions. Performance could be improved substantially by modifying the pulsed valve system to increase reproducibility of plunger motion, as shown in Figure 1. In addition, provision for an expansion nozzle cone is being added to increase clustering by confinement during expansion.

Homocluster dissociation dynamics were studied for the naphthalene trimer and tetramer clusters. Using 1-color excitation, the onset of trimer ionization by 2-photon absorption occurs for the $\bar{8}_0^1$ vibrational excitation (32368 cm^{-1} , the trimer origin is $31,965\text{ cm}^{-1}$) in the S_0 - S_1 spectrum. The ionization potential is unknown for the trimer and tetramer, however the monomer ionization potential ($65,666\text{ cm}^{-1}$) is such that the corresponding monomer transition is below the lowest 2-photon ionization limit. Therefore, this excitation is incapable of imparting substantial excess energy to the trimer ion. Nonetheless, there could be sufficient energy to dissociate a weakly bound cluster, provided the Franck-Condon factor for direct excitation of intermolecular motion were sufficiently large or given efficient IVR (intramolecular vibrational redistribution). In this case, the Franck-Condon factors for excitation of intramolecular modes are weak, in that $\bar{8}_0^1$ and observed higher energy modes of the trimer have less than 10% participation by low frequency intermolecular modes. The higher excitations exceed the ionization threshold by over one thousand cm^{-1} . Therefore there is no evidence for direct dissociation. However, we observe that direct 2-photon ionization results in a mixture of ion sizes. For example, when excitation is resonant exclusively with the trimer transition, a typical ratio of signals

from monomer ion, dimer ion, and trimer ion is 1 : 0.1 : 0.05. This ratio does not vary significantly as excitation is scanned across trimer excitation bands, and is essentially unchanged for isotopic mixed trimers. This phenomenon has been studied as a function of intensity, cluster formation conditions (T), and static electric field strength, and no substantial dependence was observed. Currently, the most satisfactory explanation is that the excitonic autoionization process excites dissociative intermolecular modes of the ion. Similar studies were carried out for the tetramer, with essentially the same result.

Fluorescence studies were attempted in order to further elucidate dissociation dynamics, with the hope of increasing the understanding of cluster ionization processes. It was readily possible to record fluorescence excitation spectra for the summed emission of monomer, dimer, trimer, and tetramer clusters by using a photomultiplier detector supplied with ultraviolet cut-off filters designed to reject the directly scattered laser radiation, but to accept emission from the molecular species. However, when a spectrometer was added (with sufficient resolution to isolate emission from each cluster size), only monomer emission could be detected. This was consistent with crude measurements of dimer and trimer S_1 lifetimes made by an ionization technique in which the ionizing laser beam was delayed relative to the $S_0 - S_1$ excitation pulse. From these measurements, we conclude that the cluster lifetimes are less than 5 ns. Based on the likely radiative rates for the cluster transitions, this is consistent with failure to observe dispersed fluorescence emission.

One of the most unusual observations in prior work was the existence of single conformations for the mixed isotopic clusters HDH and DHD, Figure 2. At the time of the initial studies it appeared that effective temperatures were on the order of 50 K and if this were the equilibrium temperature prevalent during cluster formation, then a mixture of conformer species would be expected. During the past year we have extensively remeasured spectra for these species as a function of formation conditions. No clear evidence has been obtained for other isotopic or geometric conformations. The more recent work has established, with reasonable certainty, that the absorption pedestals in the trimer and tetramer spectra are associated with the autoionization mechanism, rather than an inhomogeneous distribution of cluster conformations, or inhomogeneous temperature distributions, as was initially suspected. Therefore, we now conclude that there is a single preferred conformation for each isotopic mixture. During the past three years other research groups have accumulated evidence for preferred isotopic conformers for smaller hydrogen bonded clusters.²¹ As explained in the discussion on benzene, the preferred

²¹W. A. Lafferty, R. D. Suenram, and F. J. Lovas, *J. Mol. Spec.* 123, 434 (1987); "Structure and Dynamics of Weakly Bound Complexes," ed. A. Weber NATO-ASI, Washington D.C., 1988.

structures are stabilized on the basis of zero point energies lower than for alternative conformations. The lack of alternate conformers in our trimer and tetramer spectra confirm that good equilibration occurs between the expansion gas and the intermolecular modes of the clusters and that the effective temperature is well below 50 K. Theoretical calculations of cluster geometry are becoming increasingly important in understanding larger molecular clusters. It is relatively straightforward to apply these calculations to naphthalene clusters with geometries previously deduced by spectroscopy. This was tested for the trimer and tetramer structures. The calculations did not yield a local minimum at the trimer geometry deduced from the dipolar interaction model. In this case the disagreement is attributed to the substantial repulsive interaction predicted between the closest hydrogen atoms on adjacent molecules. It is possible that these interactions are overestimated by the standard empirical potential field. The calculations do predict a potential minimum for a geometry similar to that empirically deduced from the dipolar model for the tetramer.

Finally, formation of mixed clusters of naphthalene with rare gas atoms was performed using mixed carrier gases with manifold pressures on the order of 30 psig. For the case of $\bar{7}_0^1$ ionization, which is the lowest energy allowed 2-photon ionization transition for this cluster, the naphthalene-argon₁ abundance was approximately 2%. This transition is expected to lead to approximately 200 cm⁻¹ excess energy upon ionization, therefore the ion should not be substantially hotter than the naphthalene trimer cluster ion formed by 8_0^1 ionization. However, the possibility existed that the mixed cluster has very weak binding and readily dissociates. Therefore 2-color excitation was performed, whereby a second beam of lower energy was introduced in order to ionize S₁ with minimal excess energy. This did not noticeably increase the abundance of the naphthalene-argon clusters. As a consequence of these negative results, we concluded that naphthalene mixed cluster spectroscopy calls for an improved cluster beam source with an expansion cone in order to increase cluster formation.

Aniline

Subsequent studies were directed to the aniline molecule, which is known to form mixed clusters with appreciable efficiency. Initially, we performed 1-color 2-photon ionization experiments on aniline, aniline-argon, and aniline-argon₂. Zero-point excitation of S₁ aniline leads to direct 2-photon ionization, with 5785 cm⁻¹ excess energy. In this case the aniline-argon₁ and aniline-argon₂ signals represented about 10% and 5% respectively of the ionization signals, as shown in Figure 3. The ratios increased up to a manifold pressure of about 10 psig, and then became relatively constant. Changing beam diameter,

pulse length, and helium-argon mixing fractions did not have a substantial influence on the ratios.

Two-color excitation was studied with the goal of decreasing the excess energy deposited in the ion and thus suppressing cluster dissociation. This was marginally effective. Instead, two color ion dissociation experiments were performed, using visible light from the second laser to induce dissociation of the cluster ions, and thus to record the aniline ion absorption spectrum. A signal is readily obtained in this experiment, however, within the prevailing signal-to-noise constraints, it is wavelength independent in the region from 550-750 nm. An absorption system corresponding to the recently discovered benzene ion B - X system¹⁴ was anticipated in this region, however it may lie in the green region. In order to locate the corresponding transition in the aniline ion. In the future, the modified beam source will be used for these studies in order to improve the ability to recover spectra in currently studied regions. The fact that we observe distinct cluster dissociation in the low energy region studied up to now can be explained by the fact that there may be an underlying weak A - X transition (involving the n-electron). These possibilities will be resolved in the future work.

Benzene

In a collaboration with the UCLA cluster spectroscopy group of Professor Robert Whetten and Aerospace,²² spectroscopy has been performed on the mixed isotopic benzene₁₃ clusters with the aim of providing structural information about large clusters. Large benzene clusters are formed in abundance in the UCLA beam, which employs an expansion cone in order to assist in cluster formation. The isotopically pure clusters have 1-color 2-photon ionization spectra consisting of bands of sharp transitions at wavelengths corresponding to related monomer benzene transitions. The bands generally consist of three distinct regions as shown in Figure 4: (1) a low energy region with either continuous absorption, or a weak sharp low energy transition (about -50 cm⁻¹ from band center), (2) intense sharp complex transition in the middle of the band, and (3) weaker complex structure at high energy (about +50 cm⁻¹). The sharp features are separated by 2 to 10 cm⁻¹, which is typical for resonant interaction energies of degenerate sites of benzene. Thus, the early results suggested the existence of two or three different sites in the cluster, which is consistent with earlier theoretical structure predictions.

Subsequently, it proved feasible to study the h₁d₁₂ mixed isotope cluster. In the vibronic band 6₀¹ which is symmetry allowed, a sharp transition appeared at the bottom of the band, at the exact energy of the lowest energy 6₀¹ component in the h₁₃ cluster. The

²²D. C. Easter, R. L. Whetten, and J. E. Wessel, (submitted to J. Chem. Phys.).

corresponding component was missing in the symmetry forbidden origin system. This result is in startling agreement with predictions based on van de Waals theoretical calculation, which suggests that there is a special central molecule site of high symmetry in the benzene₁₃ cluster, as shown in Figure 5. The protonated molecule in the mixed cluster substitutes in this site because it confers the lowest zero-point energy to the cluster when substituted in this position. The site has C₃ symmetry in van de Waal's proposed icosahedral structure, and thus should be forbidden in the origin band, as observed. Furthermore, molecules in all other sites have lower site symmetry, and thus the band structure corresponding to these sites should appear similar in both the forbidden origin and allowed 6₀¹ transitions, as observed. The spectra are inconsistent with alternative structures, such as the one that is directly related to the crystallographic structure. Thus, it appears that optical spectroscopy combined with mixed isotope experiments provides a structural determination for the large benzene₁₃ cluster, in addition to the previous determinations for benzene₂, benzene₃, naphthalene₃, and naphthalene₄. The benzene₁₃ work has been submitted for publication in the Journal of Chemical Physics.

Conclusion

The on going studies demonstrate that pure cluster ions can be formed in abundance and that spectroscopy of isotopically substituted clusters can be used to deduce the structures of highly symmetric conformations for both the large benzene₁₃ cluster and for benzene₂, benzene₃, naphthalene₃, and naphthalene₄. In cases of benzene₁₃, naphthalene₃, and naphthalene₄, single high symmetry conformations confer stability based on minimum zero-point energy.

The current studies support the feasibility of performing high resolution spectroscopy on neutral and ionic aromatic clusters of pure and mixed composition. Improved cluster sources would be of considerable value in extending spectroscopic capability. Currently the sources capable of high temperature operation favor monomer and small cluster formation. Results on benzene pure clusters obtained with a low temperature pulsed source suggest promising modifications that could be implemented in a high temperature mixed cluster source.

Figures

1. Schematic diagram for pulsed valve modified for improved cluster formation.
2. 2-photon ionization spectra of the naphthalene isotopic mixed clusters DHD and HDH recorded for the $\bar{8}_0^1$ vibronic bands.
3. Time-of-flight Mass Spectrum of naphthalene argon clusters recorded for 0_0^0 excitation.
4. The benzene₁₃ cluster 6_0^1 spectrum for isotopically pure (h_{13}) and mixed (h_1d_{12}) benzene.
5. Proposed structures for the naphthalene trimer, tetramer, and benzene₁₃ clusters.

Reprints

(see attached publications)

PULSED VALVE

Figure 1

Figure 2

Time (μ s) $\rightarrow$

- (A) Aniline
- (B) Aniline-Argon₁
- (C) Aniline-Argon₂

Figure 3

Shift (cm⁻¹)

(with respect to benzene monomer)

Taken from Easter, Whetten, and Wessel
submitted to J. Chem. Phys.

Figure 4

CLUSTER GEOMETRIES

Figure 5