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PROGRESS REPORT

ION DIP SPECTROSCOPY OF COLD MOLECULES AND IONS

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PROGRESS REPORT

Ion Dip Spectroscopy of Cold Molecules and Ions

John Wessel, The Aerospace Corporation

Introduction

During the past year, the main emphasis in our research program has been on multiphoton ionization spectroscopy of aromatic clusters. This is being pursued in addition to continuing work in areas of ion dip spectroscopy and ion fragmentation spectroscopy. The program has the overall objective of developing improved ultrasensitive molecular detection methods based on multiphoton laser spectroscopy. Photoionization techniques are employed due to their extreme sensitivity combined with mass selectivity. The combination of these two features has led to the current capability to study molecular clusters of specific sizes with high spectral resolution. Clusters are formed in abundance in a supersonic expansion, where they are excited and ionized by an ultraviolet laser beam. The studies reported here are principally based on simple resonant excitation of clusters, followed by one-photon ionization. For the naphthalene clusters, a single laser wavelength suffices for both excitation steps. Additional investigations have been carried out to measure excited state cluster ionization spectra and cluster ion fragmentation spectra. Results from these measurements are not yet sufficiently advanced to report in detail, however the preliminary data support the importance of recently proposed new fundamental ionization mechanisms in clusters. This brief report summarizes results described in more detail in the appended preprint titled: "Resonant two-photon ionization spectroscopy of naphthalene clusters" and the preprint titled: "Resonance interactions in naphthalene clusters". It also briefly describes preliminary undisclosed results of current invesitgations.

Background

Other laboratories have studied a variety of dimer cluster, using a number of spectroscopic techniques, including multiphoton ionization [1-8]. High resolution rotational spectroscopy provided definitive structures for species such as the s-tetrazine dimer and s-tetrazine rare gas clusters [2-5]. These clusters have weak van der Waals bonding, low intermolecular vibrational frequencies, little distortion of monomer vibrational frequencies, small electronic energy shifts for the excited states and ions, and relatively large intermolecular distances. Most of the dimers have multiple conformations. This contributes considerable spectral complexity, and presented a potential problem for spectroscopic applications involving clusters of large molecules.

Many other dimer species are characterized by increased intermolecular interactions in the excited states and ions. Pure dimer clusters often form excimer excited states [9,10], wherein the cluster molecules form new, more tightly bound excited states. For mixed dimers, these states are referred to as exciplexes, denoting an excited state complex. They are well documented in liquid and solid media [9,10], where they are typically associated with broad, red shifted fluorescence emission. In the gas phase, this type of interaction also leads to broadened spectra, caused by dynamic processes or by activation of long Franck-Condon progressions in intermolecular vibrational modes. The result is spectra with appreciable energy shifts, relative to the monomer, combined with broadening that greatly reduces the spectroscopic utility of the transitions. Trimers and larger clusters of large aromatics are relatively unstudied. One experimental problem in the past has been identifying spectral signatures from clusters of a specific size. Time-of-flight mass spectroscopy was applied to cluster studies in order to isolate and identify spectra of selected clusters of different sizes. Hopkins, Powers, and Smalley [7] reported spectra for benzene dimers, trimers and tetramers. The spectra were discrete, however they were complex, and spectral overlap occurred between large and small cluster spectra, because large cluster ions can fragment, yielding cluster ions of smaller mass. Thus, the early studies yielded limited information concerning cluster structure and ionization mechanisms.

Results

Recently, we applied multiphoton ionization spectroscopy to study naphthalene clusters formed in a supersonic beam. The beam was operated under temperature and pressure conditions favoring cluster formation. Roughly 20 per cent of the ion signal derived from dimers, and several per cent of the signal consisted of larger clusters. Spectra recorded for the dimer were red shifted and drastically broadened, relative to the monomer. When measured with high laser intensity, sharp spectral features appeared, which were superimposed on the broad bands observed at low intensity. The relative strength of these features was highly sensitive to laser intensity, and to beam expansion conditions. A study of higher mass clusters indicated that the discrete components can be resolved for the trimer and tetramer clusters. The larger cluster ions dissociate at high intensity, contributing dimer ions at wavelengths where the dimer ion can be multiphoton ionized. We conclude from this work that the dimer spectrum is inherently broad and that intermolecular interactions change appreciably in the S_1 excited state, inducing a Franck-Condon active progression of low energy intermolecular vibrations in the S_1 spectrum. At present, we do not know if the S_1 cluster state is stable, or if it undergoes rapid decay. Attempts were made to locate the adiabatic ionization threshold of the S_1 dimer state, and to observe Rydberg and autoionizing transitions. This was done by exciting the dimer to S_1 using one laser wavelength, and then introducing a second wavelength, which is scanned across the S_1 ionization threshold. No sharp threshold for ionization was resolved, nor were discrete features such as Rydberg and autoionizing transitions observed. These experiments are inconclusive in that they can be explained on the basis of an unstable, rapidly decaying S_1 state, or by the possibility that the dimer ion geometry is greatly distorted, relative to the initial S_1 state.

Extensive attempts were made to measure the dimer ion fragmentation spectrum. An intense red laser beam was highly effective in inducing dimer ion fragmentation, however no spectral structure was observed when this wavelength was scanned in regions of known monomer ion absorption bands. Spectra were carefully recorded as a function of intensity in order to minimize saturation effects, which we previously encountered studies of monomer ion spectroscopy. This did not reveal spectral structure. A primary motivation for studying dimer ion spectroscopy was that ionization saturation problems should be reduced, relative to monomer ion spectroscopy, because one photon should be effective in fragmenting the weakly bound dimer ion, as opposed to the multiphoton process required in the visible and infrared region in order to fragment the strongly bound monomer. The fact that no spectral structure could be observed suggests that the dimer ion spectrum is shifted appreciably to the red of the monomer, and thus, that extreme spectral congestion occurs in the region probed. Studies of absorption bands located farther into the infrared will be required to resolve this question.

The presence in the dimer cluster ionization spectrum of intense, discrete spectral lines associated with larger clusters suggested that studies be extended to larger species. Spectra were recorded for the trimer, tetramer, and pentamer, by setting the mass spectrometer to the corresponding masses. In each case, a unique, discrete spectrum was recorded, that did not vary in character with excitation intensity. The spectra consist of groups of transitions that are separated by the characteristic vibrational frequencies of the naphthalene monomer. There is a dramatic difference between spectral bands associated with totally symmetric vibrations of naphthalenes in the clusters and the nontotally symmetric vibrations in the clusters. For the trimer, the totally symmetric origin, which has a transition moment polarized along the long molecular axis, is a distinct doublet, whereas the vibronically induced transitions, which are short axis polarized in the monomer, appear as single components in the trimer. In contrast, the totally symmetric origin of the tetramer displays a single component, whereas vibronic transitions are split into four distinct components.

Conclusions

These structures suggest that strong resonance interactions occur between monomer units of the clusters. The situation resembles the problem studied extensively for excitons in solid state media in the past [11]. Basically, excitation of a monomer unit is shared by resonant transitions of other molecules in the cluster, resulting in new extended cluster states. By applying this type of detailed analysis, we are able to conclude that the single component observed for each short axis polarized trimer vibronic transition implies that the short axes of all three molecules are aligned parallel in the trimer. The origin splitting provides an important indication of the strength of long range interactions in the trimer and the intensities of the origin components indicate that the long molecular axes are angularly displaced by about 60 degrees. Based on this information, and on a transition dipole coupling model for short axis transitions, we derive the trimer structure shown in the accompanying Figure 1. A detailed analysis supporting this conclusion is presented in the appended manuscript. Perhaps, the trimer has a discrete spectrum because its geometry precludes reorientation to the sandwich configuration needed for strong excimer type interactions. The fact that there are no related, slightly different, potentially stable configurations may account for the absence of other conformers in the spectrum. Another possibility is that other configurations are present, but not detected, and this conformation has high detection probability.

The general conclusions are similar for the tetramer, although the geometry is drastically different, with parallel long molecular axes and staggered short axes. This suggests a herringbone structure, as depicted in Figure 1. The long vibrational progressions observed in the S_1 tetramer spectrum, indicates that the tetramer is extremely stable and that the monomer vibrations are not greatly perturbed by intermolecular coupling. Short axis polarized transitions appear to couple by the dipolar mechanism, whereas the weak long axis origin transition is coupled by another mechanism. Apparently, geometry or delocalization in the tetramer are such that excimer type interactions are not important. In fact, there is no prominent evidence for excitation of intermolecular modes in the tetramer spectra, and no clear evidence of other conformations. The sharp spectral structure also implies that the trimer and tetramers are effectively cooled in the supersonic expansion.

Currently, we are studying the spectra of mixed isotopic clusters and of larger species. Some of the resonance interactions are blocked in the mixed cluster, therefore this is a powerful method to sort out the interactions and understand the clusters in more detail. The results support considerable theoretical interpretation. Hopefully, they will lead to a better understanding of long range intermolecular interactions between aromatic molecules and ions. These are the basic processes responsible for selective interactions in many biological systems, therefore they are of considerable potential importance. Another area that may be impacted by this new capability is studies of order-disorder transitions such as those involved in solid-liquid phase transitions [1]. Currently it is not clear how these transformations occur in small systems such as clusters. It should be possible to study the order-disorder transitions, related to melting in macroscopic systems, for clusters of varying size, using molecular orientation as a diagnostic.

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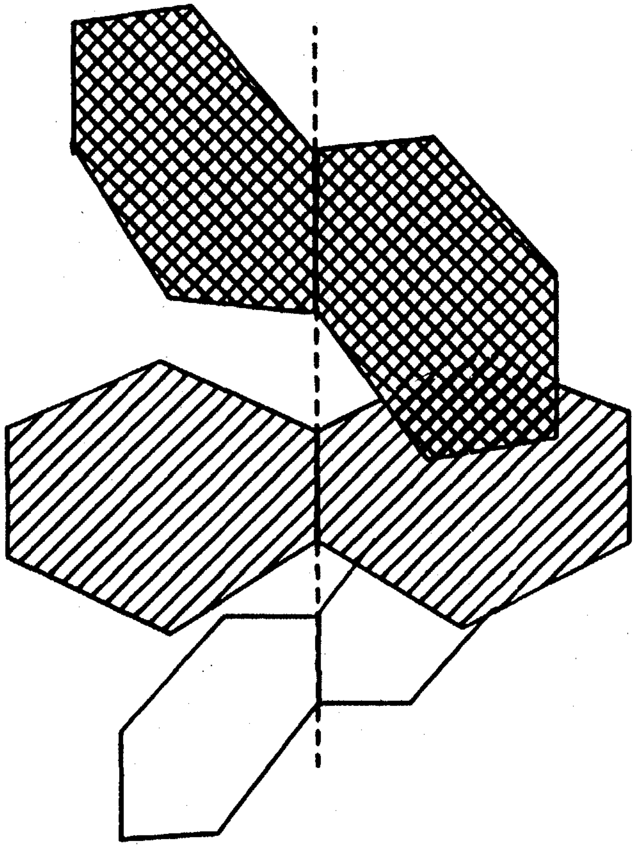
Figure

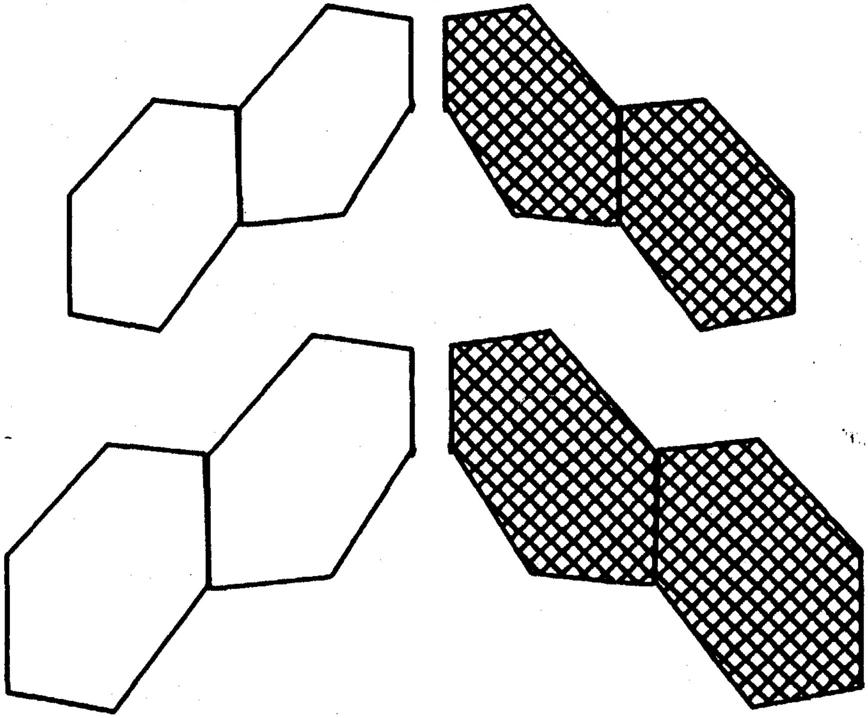
1. Structures for (a) the trimer and (b) the tetramer naphthalene clusters derived using weak interaction theory and the dipole-dipole interaction potential.

Trimer



a

Tetramer



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