

## Continuation Proposal and Annual Technical Progress Report

## Resonance Ionization Spectroscopy of Molecules, Clusters, and Ions

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## Abstract

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Supersonic beam studies of the dimer of the aromatic molecule fluorene reveal both excitonic and excimer properties. The high resolution spectra obtained for the cold clusters suggests that it will be possible to elucidate the coupling between these types of states. The accumulating evidence indicates that both types of states occur generally for aromatic clusters. Their relative contributions to the spectra are not currently understood. This problem is the emphasis of the ongoing investigations. Future work will address the intermolecular potential functions of these species in increasing detail.

## Introduction

Excimer states of large aromatic molecules were discovered more than two decades ago. These stable excited state complexes between two molecules (unstable in the ground state) were studied extensively in solution media. The primary evidence was a major red shift of the fluorescence emission spectrum as the concentration of the molecular species is increased. The most dramatic effects were observed for mixed complexes, which are termed exciplexes, and the correlation was made that the strongest exciplexes (highest stability and largest red shifts of fluorescence emission spectra) are formed between species that have the largest difference in electronegativities. Eventually, a number of homomolecular systems were identified (for which there is no difference in electronegativity), and the corresponding complexes were termed excimers. (Gas phase noble gas excimer spectroscopy was explored in a latter period.) Properties such as the emission lifetimes changed drastically for the aromatic excimers, relative to monomer fluorescence. Over the years, attempts have been made to identify the electronic states responsible for excimer formation. Initially, it was suggested that excitonic type interaction between the monomers leads to the excimer stabilization. However, the observations of exciplexes, combined with theoretical prediction that the excitonic interaction strength is inadequate to cause excimer formation, based on monomer-like states, led to rejection of

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this possibility. Charge transfer states were finally suggested as the most likely precursors for excimer formation, however there is no compelling evidence.

Recently, it has become possible to use a supersonic beam prepare cold, isolated dimer and higher clusters of species that were previously known to form strong excimers or exciplexes in solution. Saigusa and Itoh<sup>1,2,3</sup> first reported observation of exciplexes between the electron donor triethylamine and the acceptor cyanonaphthalene which were formed in a supersonic beam. Following that work Saigusa et al. reported on an interesting series of exciplexes and excimers, involving aromatic hydrocarbons<sup>4,5</sup>. This work confirms that exciplexes and excimers are stable without solvation. (Although the fluorescence results do not rule out a requirement for noble gas solvation.) Overall, the low temperature gas phase results are quite similar to the earlier solution observations. However, the new work suggests the opportunity to apply high resolution gas phase spectroscopic studies to the important unresolved problems concerning the nature of the intermolecular potentials that are responsible for these species.

Saigusa, Itoh, Lim, and coworkers published work on fluorene dimer spectra measured in a cold supersonic beam using fluorescence detection. They observed red shifted fluorescence emission, which was drastically different from the fluorescence excitation spectrum. They attributed their spectrum to the dimer, as opposed to larger clusters, which might otherwise be expected to account for greatly red shifted emission.

We have a long standing interest in dimer clusters of the related molecule, naphthalene. In earlier studies of this species,<sup>6</sup> we concluded that the dimer spectra are inherently broad and that the lowest energy monomer transition ( $S_1 \rightarrow S_0$ ) is drastically red shifted in the dimer. This suggested that excimer formation occurs for the naphthalene dimer, although we were not able to observe excimer fluorescence emission. Excimer formation in the dimer was perplexing, because the higher clusters did not show evidence of excimer formation and the intermolecular interactions deduced from the trimer and tetramer cluster spectra were insufficient to account for excimer formation.

<sup>1</sup>H. Saigusa and M. Itoh, Chem. Phys. Lett. 106, 391 (1984).

<sup>2</sup>H. Saigusa and M. Itoh, J. Chem. Phys. 81, 5682, (1984).

<sup>3</sup>H. Saigusa and M. Itoh, M. Baba, and I. Hanazaki, J. Chem. Phys. 86, 2588 (1987).

<sup>4</sup>H. Saigusa and M. Itoh, J. Phys. Chem 89, 5486 (1985).

<sup>5</sup>H. Saigusa and M. Itoh, J. Phys. Chem 94, 2631 (1990).

<sup>6</sup>J. Wessel and J. Syage, J. Phys. Chem. 94, 737 (1990).

## Results and Discussion

We decided to investigate the fluorene system using photoionization techniques, in order to definitively identify the mass of the fluorene excimer species responsible for emission. The dimer ionization spectrum, measured by monitoring the corresponding ion mass peak, is presented in Figure 1. Whereas, the monomer photoionization spectrum is virtually identical to results reported by Itoh et al., our dimer photoionization spectrum is considerably different from Itoh's fluorescence excitation spectrum. The differences currently occupy our attention. Our spectrum is interesting, in that it consists of a highly broadened origin region, characterized by a shape that suggests an unresolved progression of low energy vibrational modes. Currently, we speculate that this corresponds to a progression in the intermolecular mode that induces excimer formation.

The vibronic additions in the spectrum that correlate with high energy intramolecular vibrational excitations, range from relatively broad for low energy modes, to reasonably narrow for some high energy modes. This is the inverse of normal behavior for aromatic clusters. Normally, the higher energy modes, particularly overtones and combinations, undergo strong coupling with combinations of lower energy modes, resulting in a high density of highly mixed modes, thus leading to broadening. The inverse behavior observed for the fluorene dimer suggests that increased vibrational excitation reduces coupling to the excimer state, which provides the dominant broadening for this system.

This analysis does not explain why the photoionization spectrum should differ from the fluorescence excitation spectrum. We are beginning to probe this question by repeating the experiments of Saigusa et al.<sup>6</sup> At the present time, we are unable to reconfirm their fluorescence excitation spectrum, although we observe similar strong excimer fluorescence. Our excitation spectrum is also different from the photoionization spectrum, at least to the extent that there is highly resolved structure in the origin region of the excimer fluorescence excitation spectrum, whereas the photoionization spectrum is broadened. The structure is highly suggestive of intermolecular modes that are strongly coupled to a lower energy excimer state. The coupling is much stronger than that in the naphthalene trimer and tetramer, but much weaker than for the naphthalene dimer.

Considering the possibility that differing experimental conditions are responsible for the significant differences observed in the different types of spectra, we are investigating the influences of change in expansion conditions (pressure, temperature, skimmer parameters, carrier gas composition, and mechanical sources of shock waves and molecular reflections off of system components) on the spectra. Molecular beam reflections from the detection chamber components appear to be highly important. Elimination of these reflections led to the excellent fluorescence excitation spectrum presented in Figure 2.

Similar improvements will have to be implemented in the ionization detection chamber before we can conclude that the ionization and fluorescence excitation spectra differ. Additional experimental improvement is expected when we begin using a newly acquired high resolution laser system.

#### **Proposed Research for January 1993-January 1994**

At present, it is tempting to speculate that the fluorescence spectra reveal the intermolecular vibrations that couple the directly excited state into the more stable excimer state. Resonance photoionization/mass resolved spectra of mixed isotopic spectra will be acquired in order to definitively resolve this issue. The results should identify the fundamental origin of the excimer state (eg. excitonic or charge transfer in nature).

After the fluorene problem is resolved, we intend to return to spectroscopy of the naphthalene clusters. Saigusa, Sun, and Lim<sup>7</sup> report evidence of excimer species for naphthalene in a supersonic beam, based on fluorescence excitation and emission studies. Using a very sophisticated fluorescence detection system, they resolved structure that we did not observe in the trimer ionization spectrum. With the new cooling capability and a new high resolution laser system, we expect to be able to increase the spectral resolution by an order of magnitude. We believe that it will be possible to resolve a number of important unanswered questions concerning the nature of the intermolecular potential for the large molecule clusters, given the increased spectroscopic resolution. The information obtained from this comparison between fluorene and naphthalene systems will help to resolve the question of why some aromatic clusters form strongly bound excimers and others do not.

We will continue applying traditional isotopic substitution approaches in order to characterize stable cluster conformations and thereby improve the understanding of intermolecular potentials. This work will be coupled to potential modeling studies, whereby we will seek to adjust and extend existing force fields in order to adequately account for the observed stable cluster conformations. In this respect, we expect to develop a successful model explaining the stability of specific mixed isotope conformers in terms of zero point energy stabilization. Results from these analyses will be used to quantitatively measure temperatures in large molecule clusters obtained under varying beam conditions.

Ionization and fragmentation processes involving excimer states of various molecular clusters will be studied by photoionization and fluorescence excitation spectroscopy. This will evaluate the general importance of excimer formation processes for aromatic hydrocarbon clusters.

<sup>7</sup>H. Saigusa, S. Sun, and E. Lim, J. Phys. Chem. 96, 2083 (1992).

**Statement of Work**  
**January 1993 to January 1994**

1. Mass resolved resonance ionization spectra will be obtained for isotopically mixed fluorene molecule clusters. These spectra will identify the nature of coupling between the excited states of the fluorene molecules within the cluster species.
2. Studies will be performed on naphthalene clusters cooled to lower temperatures than have been previously attained and measurements will be performed with higher spectral resolution than has been used previously. The results will be used to establish the intermolecular potential between naphthalene molecules within clusters of various sizes. Photoionization and fluorescence excitation methods will be employed.
3. Empirical potential models will be applied to the spectroscopic results in order to elucidate cluster geometries and vander Waals interactions in ground state clusters.
4. Photoionization processes will be studied in the fluorene molecule clusters. This will be performed by pump-probe spectroscopic techniques, which can distinguish between direct resonance ionization and biexcitonic autoionization processes. This will resolve important problems regarding the ionization mechanism in clusters that undergo excimer formation.