DE-FG03-86ER60391

# Final Report
# Multiphoton Ionization of Ions, Neutrals, and Clusters

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28 December, 1995

DOE/ER/60391--T1

## Abstract

A multiyear research program investigating molecular detection methods based on multiphoton spectroscopy has been completed under DoE sponsorship. A number of new laser-based spectroscopic methods were developed and applied to a variety of aromatic hydrocarbons, including monomer and cluster species. The objectives of sensitivities approaching single molecule detection combined with high selectivity were achieved.

## Introduction

Multiphoton ionization (MPI) spectroscopy is one of the most sensitive detection methods for atomic and molecular detection. It is used extensively in fundamental research and is currently being explored for a variety of applications that demand extreme sensitivity. This program made a significant contributions in developing and exploring new multiphoton detection methods applicable to large aromatic species. The work progressed from demonstrating detection limits approaching a single molecule, to development of highly selective methods, based on combinations of measurements including multiple optical resonances, mass spectrometry, photofragmentation properties, and supersonic cooling. It established that the combination detection methods improve detection capabilities applicable to complex molecules and clusters. In the latter phases of the program, studies were directed to properties of prototypical molecular clusters. These studies yielded detailed information about intermolecular interaction in complex systems.

This report references the status of the field at the beginning of this work and summarizes the significant progress during the period from 1987 onward. Detailed scientific findings from our studies are presented in the published literature referenced throughout this report.

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## Multiphoton Detection Methods

From the onset of studies, it was clear that resonance enhanced 2-photon ionization, (R1P1, where R1 designates that an intermediate state is excited by a photon and P1 designates that the intermediate state is ionnized by a second photon) depicted in Figure 1b, has the potential to detect single molecules of many polyatomic species. As research progressed, it became clear that improved selectivity was a key requirement for applying this capability to large molecular species encountered in typical practical applications. Fortunately, a variety of processes were identified that can provide the enhanced selectivity. This report gives a roughly chronological outline of the development. The status of the field at the start of this effort was reviewed by Letokhov.[1]

Early in the development of MPI methods, researchers discovered that extensive molecular fragmentation occurs in association with multiphoton ionization. This provides the basis for combination MPI/MS detection methods of high molecular selectivity and extreme sensitivity. The initial studies[2] suggested that selective laser induced fragmentation is nonrandom and a high degree of control can be exerted over fragmentation process. As an example, the MPI/MS spectra of benzene is compared to the conventional electron impact ionized mass spectrum in Figure 2, taken from Parker and Bernstein.[3] Note that the MPI/MS spectrum is highly dependent on intensity, whereas there is little control of fragment distributions for conventional ionization methods. Subsequent research demonstrated that most laser induced fragmentation processes are dominated by random statistical processes.[4]

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[1] V. S. Antonov and V. S. Letokhov, Appl. Phys. *24*, 89 (1981).

[2] D. M. Lubman, R. Naaman, and R. N. Zare, Ibid. *72*, 3034 (1980); D. Proch, D. M. Rider, and R. N. Zare, Chem. Phys. Lett. *81*, 430 (1981).

[3] D. A. Lichtin, L. Zandee, and R. B. Bernstein, in Laser in Chemical Analysis (G. Hieftje, J. Travis, and F. Lytle, eds.), Humana Press, Clifton, New Jersey, 1981, Chap. 6; L. Zandee, R. B. Bernstein, and D. A. Lichtin, J. Chem. Phys. *69*, 3427 (1978); L. Zandee and R. B. Bernstein, Ibid. *70*, 2574 (1979); L. Zandee and R. B. Bernstein, Ibid., 71, 1359 (1979; D. H. Parker, and R. B. Bernstein, J. Phys. Chem. *86*, 60, (1982).

[4] J. Silberstein and R. D. Levine, J. Chem. Phys., *75*, 5735 (1981); J. Silberstein and R. D. Levine, Chem. Phys. Lett. *74*, 6 (1980).

In the course of our work, it became apparent that the spectroscopy and dynamics of molecular ions are strongly involved in the MPI/MS processes, therefore the aspects of molecular ion spectroscopy related to MPI/MS were investigated in detail in our laboratory.[5]

Johnson[6] and Dalby[7] and coworkers were the first to exploit MPI for molecular spectroscopy. The molecular work had a major impact on spectroscopic research because the method was easily implemented with common laboratory lasers, was applicable to a broad variety of polyatomic molecules, and provided a rich new source of information about highly excited molecular states. The work was stimulated by previous investigations of multiphoton processes in atoms and diatomics carried out in physics laboratories. A host of new molecular electronic states were accessed, and it became evident that the method provided extreme sensitivity. This latter capability was dramatically exploited in the single atom detection work of Hurst and coworkers[8] at Oak Ridge National Laboratories. They were able to detect alkali atoms down to 10 atoms per $cm^{+3}$ in the presence of $10^{+19}$ molecules/$cm^{+3}$ of buffer gas.

In Figure 1 we compare the ionization scheme used for the early molecular detection work with that used for single atom detection. In both cases, ionization was measured by the simple, but extremely sensitive proportional counter, depicted in Figure 3. In typical experimental use, this type of device readily detects individual ionization events. It evolved from much earlier applications in nuclear chemistry and physics. It exploits a buffer gas, which amplifies the primary ionizing event by inducing a cascade of secondary ionization. This produces a large current pulse that is easily measured.

Unfortunately, the presence of the buffer gas obscures detailed information about

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[5] D. Mordaunt, G. Loper, and J. Wessel, J. Phys. Chem. *88*, 5197 (1984). D. E. Cooper, R. P. Frueholz, C. M. Klimcak, and J. E. Wessel, J. Phys. Chem. *86*, 4892 (1982). J. A. Syage and J. E. Wessel, J. Chem. Phys. *85*, 6806 (1986).

[6] P. M. Johnson, M. R. Berman, and D. Zakheim, J. Chem. Phys. *62*, 2500 (1975); P. M. Johnson, Ibid. *62*, 4562 (1975); P. M. Johnson, Ibid. *64*, 4638 (1976); P. M. Johnson, Ibid. *64*, 4143 (1976); D. Zakheim and P. M. Johnson, Ibid. *68*, 3644 (1978).

[7] G. Petty, C. Tai, and F. W. Dalby, Phys. Rev. Lett. *34*, 1207 (1975); F. W. Dalby, G. Petty-Sil, M. H. Pryce, and C. Tai, Can. J. Phys. *55*, 1033 (1977). C. Tai and F. W. Dalby, Ibid. *56*, 183 (1978).

[8] S. Hurst, M. H. Nayfeh, and J. P. Young, Appl. Phys. Rev. *30*, 229 (1977); G. S. Hurst, M. H. Nayfeh, and J. P. Young, Phys. Rev. *A15*, 2283 (1977).

the molecular ion created in the process. Thus, the technique is primarily applicable in situations were mass spectra and information about the ions created by the MPI process are not required. Nonetheless, we explotied this detection method in conjunction with other analytical approaches, such as gas chromatography, in order to enhance overall selectivity. The principal outcome of the investigations was demonstration[9] that R2PI provides detection limits for large aromatic hydrocarbons, down to about $10^4$ molecules/$cm^3$ in an atmospheric pressure buffer gas environment. Sensitivity was ample to extend detection to single molecule limits, however background signals from contaminants prevented this.

A variety of multiphoton ionization processes are potentially applicable to molecular species. Two-photon resonant, 3-photon ionization (R2P1), as described in Figure 1, was pioneered by Johnson and coworkers* for molecular applications. In subsequent research, other processes such as R2P2 were explored. In this case the intermediate state is ionized by nonresonant 2-photon absorption. Previously, both 1-photon (R1) and 2-photon absorption spectroscopy (R2) were well explored. Since these are crucial components of the overall resonant MPI processes, we review them in below. These techniques, by themselves, have important detection applications. Both approaches provide limited detection selectivity and the 2-photon absorption method is of limited sensitivity. The low sensitivity is a result of difficulty in measuring weak absorption. Direct measurement of beam attenuation is severely limited by shot noise. Indirect detection of absorption by measurement of fluorescence excited by the absorption or by photoacoustic, photodeflection, or transient grating thermal detection methods provides increased sensitivity. However, in each instance, detection limits are generally far from the single molecule limit. (However, recent work[10] involving highly efficient fluorescers has overcome this limitation. In addition, methods based on modulation spectroscopy provide single molecule detection limits for some condensed phase systems at low temperature[11].)

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[9] C. Klimcak and J. Wessel, Appl. Phys. Lett. *37*, 138 (1980).

[10] D.C.Nguyen,; R.A.Keller, J.H. Jett, J.C.Martin, Anal. Chem. *59*, 2158 (1987); C.W. Wilkerson, Jr., P.M. Goodwin, W.P.Ambrose, J.C. Martin, R.A. Keller, Appl. Phys. Lett. *62*, 2030 (1993).

[11] W.P.Ambrose, W.E.Moerner, Nature *349*, 225 (1991); W.P.Ambrose, T. Basche, W.E.Moerner,

Low selectivity for optical detection of large molecules is a problem that is generally associated with thermally induced broadening of molecular vibronic transitions. A multitude of rotational and vibrational modes are populated at room temperature. Each of these gives rise to nearly overlapping transitions, which are additionally broadened by Doppler and homogeneous broadening. Therefore, the 1-photon and 2-photon absorption spectra of large species are generally broad and structureless.

Under conventional ambient temperature conditions, R1P1 spectra closely resemble those observed in conventional 1-photon spectroscopy, and R2P1 spectra resemble 2-photon absorption spectra. This is readily understandable in terms of a simplified rate equation model for the excitation processes. (A density matrix treatment best describes resonant excitation with typical laser excitation sources. Unfortunately, the treatment is too complex for this brief report. Therefore, we employ a simplified rate equation model.

If the excitation rate is denoted by R(I,0), where I is the ion and 0 is the initial ground state, we can write down the approximate expression as

$$R = \langle I|D|k\rangle\langle k|D|0\rangle/(E_k - E_0 - h\omega)$$

where D is the dipole operator, k is a resonant intermediate state of energy $E_k$, and w is the incident laser frequency. Thus, the overall transition rate is proportional to the product of dipole matrix element for 1-photon absorption from the ground state times the matrix element connecting the intermediate state and the ionization continuum. Based on this, the R1P1 spectrum should be approximated by a convolution of the normal 1-photon absorption spectrum with the excited state ionization spectrum. As a first approximation, we anticipate that the 1-photon ionization spectra of intermediate states should resemble step functions. Ionization does not occur at photon energies less than the ionizaition potential and a

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J. Chem. Phys. *95*, 7150 (1991); W.E.Moerner, T. Plakhotnik,; T. Irngartinger, U.P. Wild, D.W.Pohl, B. Hecht, Phys. Rev. Lett. *73*, 2764 (1994).

moderately constant cross section prevails when the ionization potential is exceeded. (This was confirmed by ionization spectra measured from excited intermediate states).

The observed ambient temperature R1P1 spectra, as shown in Figure 4 for naphthalene, is in accord with expectations. The signal is negligible when the 2-photon energy is less than the energy required for ionization (IP($S_1$), where $S_1$ is the first excited singlet state of naphthalene). At higher photon energies, the R1P1 spectrum is essentially equivalent to the 1-photon absorption spectrum, as shown. Thus, there is no appreciable increase in selectivity for the 2-photon process. Similar results were observed for the R2P1 process. Thus, for one-color excitation processes, ionization detection can increase sensitivity dramatically with respect to alternative methods, however the spectra are remarkably similar to those measured directly.

Franck-Condon overlap becomes important when vibrationally excited intermediate states are excited, or if the intermediate state and the ion have substantially different geometries. Little geometry change occurs for Rydberg type intermediate states between the bound state and the ion, therefore vibrational quanta do not change in this case. In cluster species with weak intermolecular bonding, intermolecular motion influences interactions strongly and large changes in quanta occur between the bound intermediate and final ion states. The photoionization spectrum strongly influence the overall ionization spectrum in this case.

Efficiency of the overall ionization process is influenced by relaxation processes in the intermediate state. Established relaxation channels for aromatic hydrocarbon molecules are shown in Figure 5. They include intramolecular vibrational redistribution (IVR), in which the directly excited vibronic mode relaxes into a high density of resonant combination modes, comprised of lower energy vibrational modes in the same intermediate electronic state. The relaxed combination states have poor Franck-Condon factors for transition to the vibrationless ionized state. In the internal conversion processes, relaxation occurs to to a lower energy electronic states, and combination vibrational states accept the remaining energy. If the spin changes during relaxation, it is called intersystem crossing. In both cases, Franck-Condon factors for transition to the vibrationless ion is negligible. Vibrational excitation in the intermediate states normally promote the relaxation processes. The magnitude of the effect can be highly mode specific.

Photodissociation is another important relaxation process. It can form products that are not ionized by the original resonant wavelengths, thereby decreasing the efficiency of ionization detection processes. The dissociation channel can depend on molecular structure. There are a number of common substituents that dissociate readily due to weak bonds to the hydrocarbon, such as halogens. High molecular weight substituents increase spin-orbit coupling, populating triplet states. Weakly bonded substituents dissociate due to the excess vibrational energy in the triplet product-state. If the bond is strong, the triplet may serve as a dark state that is not ionized by the laser source. Generally, the relaxation processes (termed radiationless processes) increase with increased excitation energy. Thus, increased broadening in spectral transitions is common as intermediate state energy approaches the ionization limit. (Some Rydberg states are counter examples. They have unusually weak coupling to dissociative valence states because the Rydberg electron is essentially removed from the bonding and nonbonding electronic structure of the molecule.)

During these studies we realized that it would be possible to introduce an artificial relaxation process by means of a second downward pumping laser source. This second beam would alter ionization efficiency, and thus provide detection sensitivity comparable to the R1P1 process, but offer a second highly selective spectroscopic channel. We termed the method Ion Dip Spectroscopy.[12] A major advantange is that excitation by the first beam prepares a selected subset of specific vibrational and rotation states. The second beam then interacts with these exclusively. We demonstrated the advantages of this method on complex spectra of the iodine molecule, for which we were able to assign and study new, highly excited states that cannot be accessed by conventional spectroscopic probes ("dark states"). Later, we applied it to the aromatic molecule aniline, revealing dark states in the case of a

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[12] D. E. Cooper, C. M. Klimcak, and J. E. Wessel, Phys. Rev. Lett. *46*, 324 (1981). D. E. Cooper and J. E. Wessel, J. Chem. Phys. *76*, 2155 (1982).

complex molecule.[13] This method, and related ionization detected double resonance techniques are now standard procedures for high resolution spectroscopy.

## Combination Detection Methods

Supersonic beam sources largely overcame limitations imposed by thermal broadening of multiphoton spectra. By expanding a gas mixture, consisting of the vapor of interest with about one atmosphere of carrier gas, such as helium or argon, into a vacuum chamber through a orifice of .01 to 0.1 cm diameter, the molecule is effectively cooled to very low temperature. This freezes out vibrational energy, leaving molecules in the zeropoint state. It immensely simplifies the 1-photon and resonant multiphoton spectra of large molecules. Time-of-flight mass spectrometry is readily applied in conjunction with supersonic beam cooling, thus providing a combination of extremely high optical resolution with mass spectra of unit mass resolution or better.

Cooling not only facilitates preparation of cold, isolated intermediate quantum states, it also provides cold ions. This requires some attention to ionization conditions. The intermediate state must not be subject to collisional relaxation or IVR processes, otherwise a hot distribution of states will result in ionization to a distribution of vibrational states in the ion. Even if SVL conditions are maintained in the intermediate state, it is necessary to ionize so as to avoid vibrational excitation in the ion. This can be accomplished by using a low energy ionizing beam, such that only vibrationally unexcited ions are produced. Typically, the first Franck-Condon active vibration of the ion is 500 $\text{cm}^{-1}$ or more above the lowest ionization threshold. Therefore, there is a substantial range of photon energies that avoid vibrational excitation in the ion. In this case excess energy above the lowest ionization limit is imparted to photoelectron kinetic energy. In cases where there is essentially no change in molecular geometry between the intermediate state and the ion, the Franck-Condon factors are diagonal and there is no problem associated with exciting vibrational levels other than that present in the intermediate state. For some molecules a broad range of possibilities exists, therefore excitation conditions must be chosen carefully.

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[13] J. A. Syage and J. E. Wessel, J. Chem. Phys. *87*, 6207 (1987).J. A. Syage and J. E. Wessel, J. Chem. Phys. *85*, 6806 (1986); J. A. Syage and J. E. Wessel, J. Chem. Phys., *87*, 3313 (1987); D. E.

One important prediction of the statistical theory of multiphoton photofragmentation is that structural isomers of a molecule should have identical fragmentation patterns, provided the initial distribution of energy in the excited ion species is identical. Thus, for some combination of wavelengths and intensities, different isomers are predicted to have the same mass spectra. This prediction was carefully tested by several research groups. We examined the methylnaphthalenes, which have similar low resolution R1P1 spectra.[14] The results were decisive. In each case, similar fragmentation patters occur for related isomers. The only significant differences in mass-fragmentation spectra were found for the hydrogen substituent distributions, but the prediction was excellent for overall carbon fragment abundance. Differences in hydrogen species distribution was not understood.

A detailed examination of the intensity dependence curves for the methylnaphthalenes suggested that the fragmentation process occurs by way of a tropylium-like intermetdiate state isomer, in which the methylnaphthalene rings open up and recyclize into an ion with two rings, of 7 and 6 bonds. The intermediate ions are identical for 1- and 2-methylnaphthalene precursors. This explains the similarity in the dissociation spectra of the two isomers.

## Ion Absorption

Based on the above studies, it is clear that the sequential mechanism describes MPI fragmentation processes observed for aromatic hydrocarbons. Application of the model to experimental results requires knowledge of the ion absorption spectra. In the simplest cases, a single photon provides sufficient energy to fragment the parent ion through the lowest energy dissociation channel, such as hydrogen loss. For species such as methylnaphthalenes, this occurs for one UV quantum. Thus, the absorption spectrum should govern efficiency of this simple fragmentation process. We obtained ion absorption spectra for naphthalene and the methylnaphthalenes by using multiphoton ionization to form the unexcited ions. These ions were studied by R1 or R2 excitation using a scanning laser source that induced dissociation. Absorption spectra were deduced from the decrease in the parent

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Cooper and J. E. Wessel, J. Chem. Phys. *76*, 2155 (1982).

[14] D. Mordaunt, G. Loper, and J. Wessel, J. Phys. Chem. *88*, 5197 (1984).

ion mass peak monitored in a time-of-flight mass spectrometer, or by build-up of the fragment ions. Ultraviolet, visible and near-infrared transitions were observed for naphthalene and methyl-naphthalenes, which were similar, although somewhat better resolved, than those previously observed for the corresponding matrix-isolated ions.

The new information derived from these studies concerned the nature of the electronic states of the ions. A broad underlying continuum was observed to the red of the discrete state originating near 660 nm, and extending beyond 800 nm. This diffuse baseline was assigned to the lowest energy excited state of the ion. Its broadening was attributed to an extensive progression of vibronically active combination modes, built on a forbidden origin occurring at much lower energies. The excited state associated with the 660 nm absorption is broadened by resonant interaction with the lower energy state. This energetic scheme is expected to be characteristic for many aromatic ions. Our primary interest shifted to molecular cluster species following the work on molecular ions.

## Molecular Clusters

Large aromatic species have low vapor pressures and tend to aggregate under many environmental conditions. With the advent of mass spectrometry detection and supersonic cooling, it became feasible to study individual cluster species. They are of considerable interest because their properties are intermediate between isolated gas phase molecules and those in the condensed phase. Previously, there was considerable interest in the properties of crystals of these species, however limitations on ability to derive additional information from crystal studies, combined with inherent complexities of the condensed medium environment, diverted many spectroscopists to other areas. Cluster spectroscopy provides a new tool capable of high resolution study of intermolecular interactions between a selected number of otherwise isolated molecules, thereby avoiding the complications associated with condensed media.

Our initial work investigated clusters of weakly interacting naphthalene molecules[15] and of strongly interacting fluorene molecules.[16] The work addressed homomolecular clusters, although most of the research in the field involved mixed cluster species.[17] The homomolecular clusters are particularly interesting because the excited state interactions are stronger than in the ground state species. We found that the spectra are highly dependent on cluster size, as shown in Figure 6. The monomer properties, such as transition moment direction, can be used to deduce geometric information on the clusters, as depicted in Figure 7, from the R1PI1 spectra. The information is not available by other means. This approach was used to study how the interaction between cluster molecules varies among various vibronic states. The data suggested that naphthalene forms a sandwich type dimer the trimer forms a species in which the short in-plane molecular axes are parallel (Figure 7), and the tetramer forms a species with parallel long axes and short axes in a herringbone array. The intermolecular interactions are highly dependent on structure and on vibronic level. The dimer and trimer structures are quite different from the crystal, whereas the tetramer structure is reminiscent of the crystalline array. Other research groups are vigorously pursuing this system. Although the geometries can differ from those observed in crystals, the general nature of the intermolecular interaction forces were found to be similar in both cluster and crystalline environments.

A remarkable example of cluster geometry determination by excitonic spectroscopy was provided by our studies of large benzene clusters. In that work[18] we were able to deduce the likely geometry of $(\text{benzene})_{13}$ by performing extensive isotopic substitution experiments.

Whereas, the excited state interactions were relatively weak in naphthalene and benzene clusters, we proved that they are stronger in the clusters of the fluorene molecule. The origin spectral region of the dimer cluster is extremely complex, fitting no

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[15] J. A. Syage and J. E. Wessel, J. Chem. Phys. *85*, 6806 (1986). J. A. Syage and J. E. Wessel, Appl. Opt. *26*, 3573 (1987). J. A. Syage and J. E. Wessel, J. Chem. Phys. *87*, 6207 (1987). J. A. Syage and J. E. Wessel, J. Chem. Phys. *87*, 3313 (1987).

[16] J. A. Syage and J. E. Wessel, J. Chem. Phys. *101*, 10292 (1994).

[17] E. R. Bernstein, *Atomic and Molecular Clusters*, Elsevier Science Publishers , Amsterdam, 1990.

[18] D. E. Easter, R. L. Whetten, and J. E. Wessel, J. Chem. Phys. *94*, 3347 (1991).

easily recognizable pattern. This species was selected for more intensive study in order to explore systems with stronger interaction. The problem becomes relatively complex because the intermolecular interactions are strongly modulated by the intermolecular motions. The challenges include experimental and analytical complexity. Low temperatures were required to resolve the complex structure and new analytical treatments were needed in order to fit the spectra in terms of a non-Born-Oppenheimer quantum mechanical model. Both problems were overcome, and it was discovered that the spectrum reveals two potential surfaces, corresponding to upper and lower excitonic states. Highly irregular intermolecular vibrational sequences are associated with these two surfaces. An interaction potential with strong quartic interaction is capable of describing these levels. Thus, in the lowest excited state, excitation is shared by two equivalent fluorene molecules, their equilibrium positions are highly displaced from the ground state, and they are severely perturbed near the ground state equilibrium position. On the upper potential surface, intermolecular motion occurs with a higher frequency and the system behaves more like an ordinary dimer. It is fortunate that the complex behavior is described by motion along a single intermolecular coordinate. The species is observed to emit excimer luminescence, indicating that the excited state undergoes rearrangement to a highly distorted geometry in the excited state. The fact that the R1P1 spectrum is fully consistent with intermolecular motion along a single bound, although distorted, potential surface, does not provide insight into the excimer formation mechanism. The mode responsible for the observed spectrum is Franck-Condon allowed. This suggests that excimer formation involves dark modes that induce much stronger interaction, accounting for the red shift of over 2000 cm$^{-1}$ evidenced in the excimer emission.

Following elucidation of the fluorene dimer R1P1 spectrum, we began pursuing the nature of the excimer formation process. These studies remain incomplete. They include investigations of the higher excited states of both naphthalene and fluorene clusters (naphthalene clusters can also form excimers, although not as readily as fluorene), and investigations of larger clusters and mixed clusters. The mixed cluster studies were initiated in order to provide a way to perturb the symmetry between the interacting monomers, and thus reveal the presence of otherwise dark, excimer-forming modes, or alternatively, to sterically interfere with motion along the excimer forming coordinate. At present, the investigations have produced a variety of mixed cluster species with rich vibronic spectra. However, additional spectra of mixed isotope species are needed to support further analyses. Spectral inhomogeneity probably contributes to spectral broadening in the mixed clusters. Therefore, pump-probe experiments are needed in order to isolate contributions from individual conformations. This work was initiated in mid-1994 and discontinued due to experimental complexities during 1995.

## Conclusion

Resonance multiphoton ionization spectroscopy is the most sensitive detection method for a variety of large molecules. This program demonstrated the capability to detect large molecules and various approaches were identified that improve detection selectivity. The later studies involved molecular ions and large-molecule clusters. New molecular states were accessed by the multiple-resonance ionization techniques. Combined methods of detection involving laser excitation, mass selective detection, supersonic beam cooling, and gas chromatography were developed in order to advance methods for selective detection. Studies using these approaches identified the ionization mechanisms involved in the multiphoton processes and subsequent results identified characteristics of some of the molecular, ionic, and cluster states involved in detection applications. The work provides a foundation for future spectroscopic studies of complex species and provide guidelines for development of ultrasensitive detection methods.

## Acknowledgement

Sustained interest from the staff at the Department of Energy, Office of Health and Environment has made this work possible. Encouragment by the DoE peer review community has also been highly beneficial to the efforts. The work depended on the keen interest and efforts of a number of staff associates, including Drs. Charles Klimcak, Donald Cooper, Gary Loper, David Mordaunt, Jack Syage, Steven Beck, Jerry Gelbwachs, Capt. Clark Highstrete, and Mr. John Coffer, and to collaborators at UCLA including Professors David Easter and Robert Whetten. I express deep appreciation for their important contributions to this work.

## Figures

1. Common multiphoton ionization processes of aromatic molecules.

2. The multiphoton ionization mass spectra (MPI/MS) of methyl iodide recorded for various laser intensities compared with the electron impact ionization mass spectrum (EI) by Parker and Bernstein.

3. A. Proportional counter for MPI detection with the laser beam depicted by the light color pencil beam surrounded by the darker color ground electrode. The signal appears as changes in current on the small diameter wire electrode that passes through the cylinder.

4. The ambient temperature R1PI1 specturm of naphthalene recorded in the region of the S1 electronic transition.

5. Relaxation pathways for aromatic molecules. $K_a$ corresponds to the rate of the resonant excitation step R1 in the R1PI1 process. $K_e$ designates the rate of stimulated emission, $K_f$ the rate of spontaneous fluorescence, $K_{ic}$ the rate of internal conversion to the ground state $S_0$, $K_{isc}$ the rate of intersystem crossing to the triplet state $T_1$. Intramolecular vibrational redistribution is shown with rate $K_{ivr}$ to vibrational level $v_2$ in electronic state $S_1$. $v_2$ is a high energy vibrartional mode, which relaxes into combinations of lower energy modes, $v_n$.

6. Naphthalene cluster spectra including dimer, trimer, tetramer, and pentamer. The striking differences are indicative of entirely different geometries.

7. Geometries of the trimer and tetramer deduced from the R1PI1 spectra.

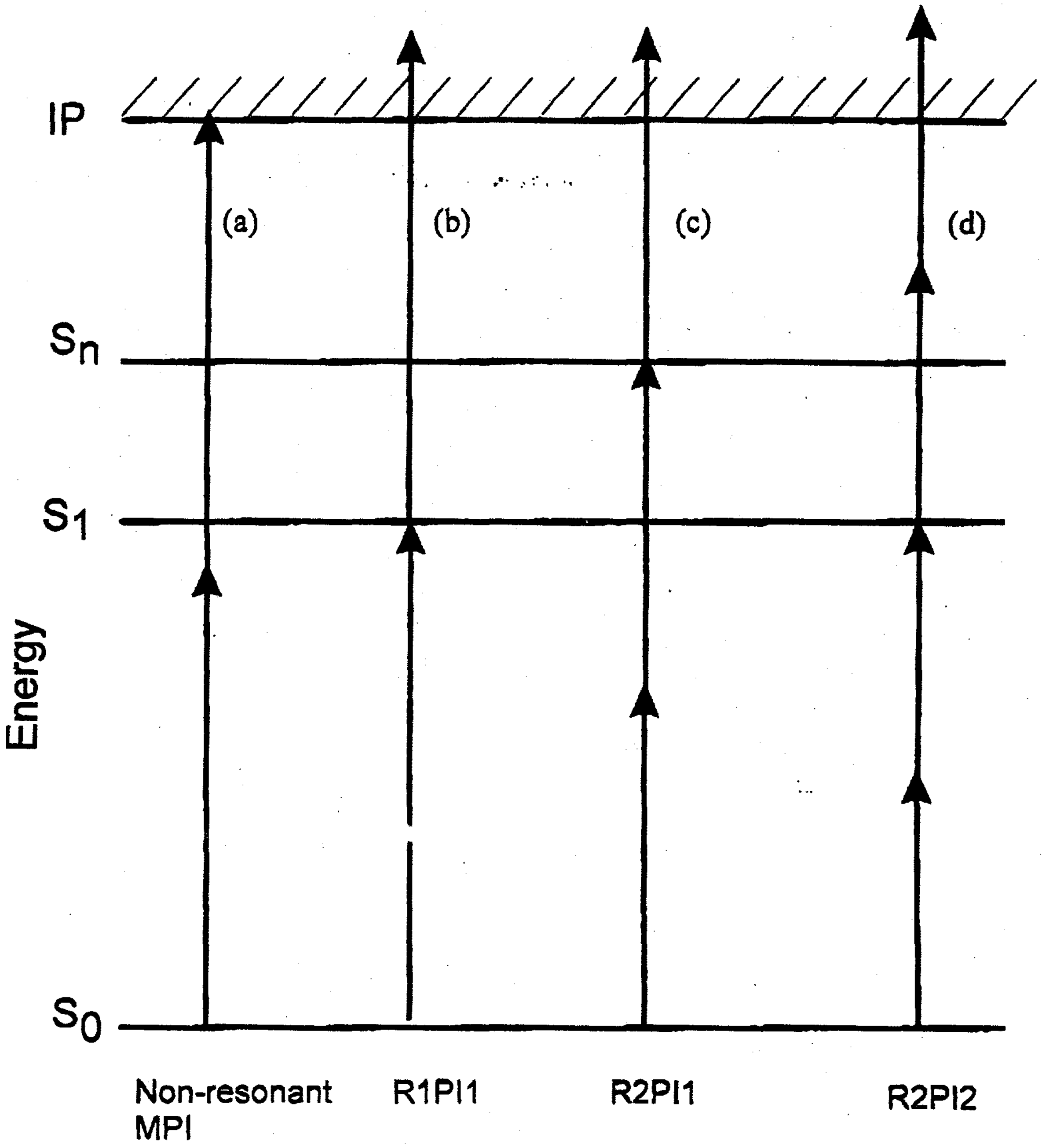


Figure 1

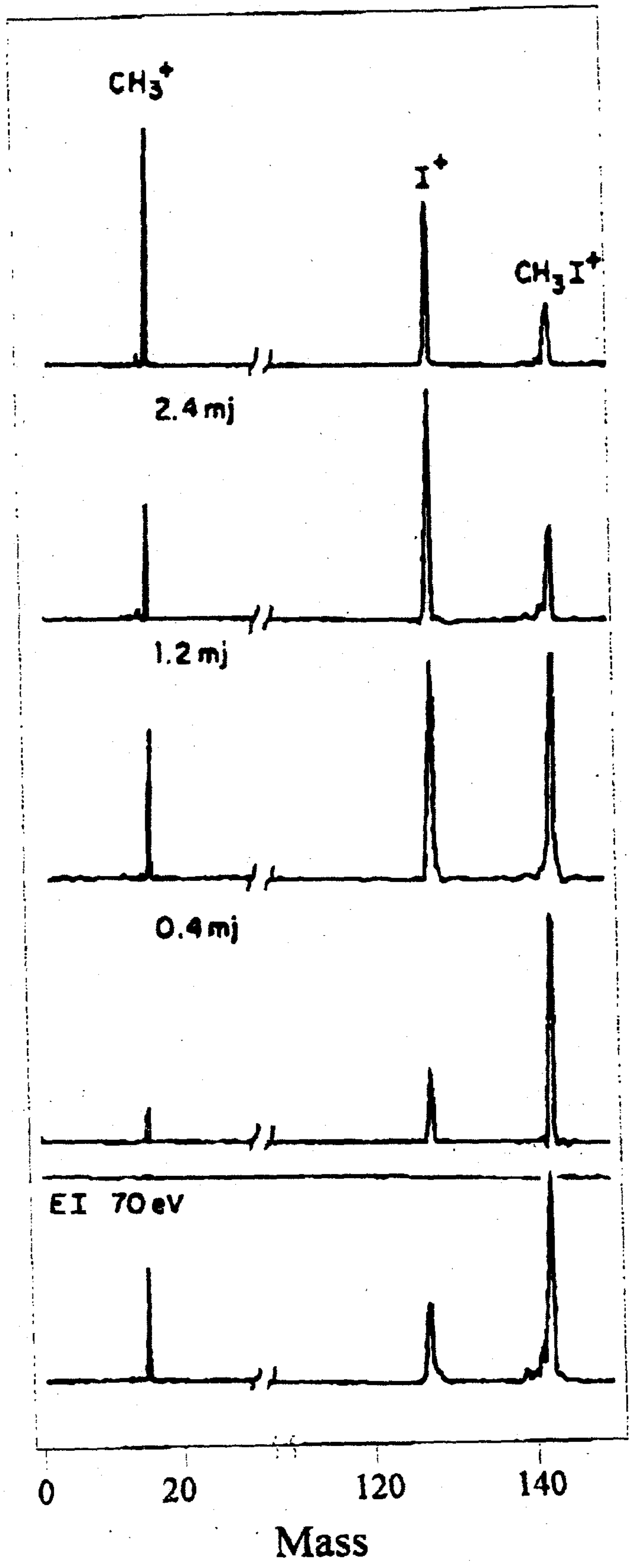


Figure 2

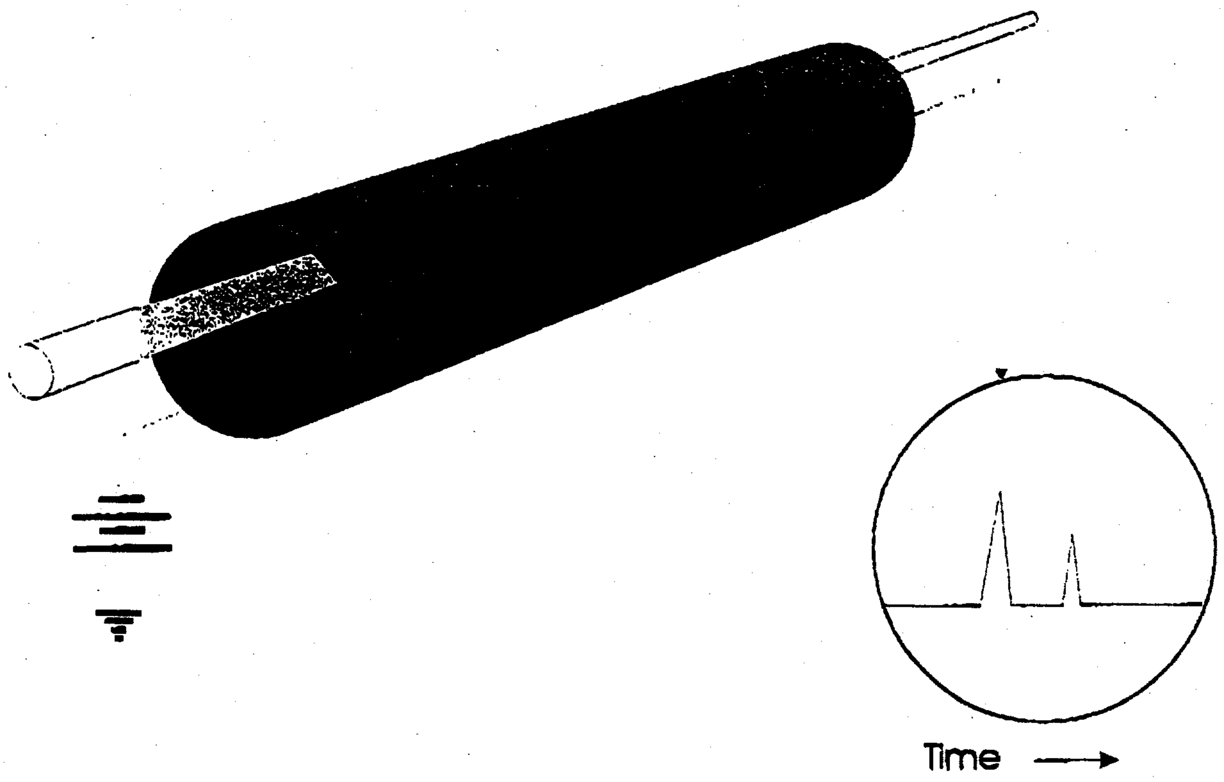
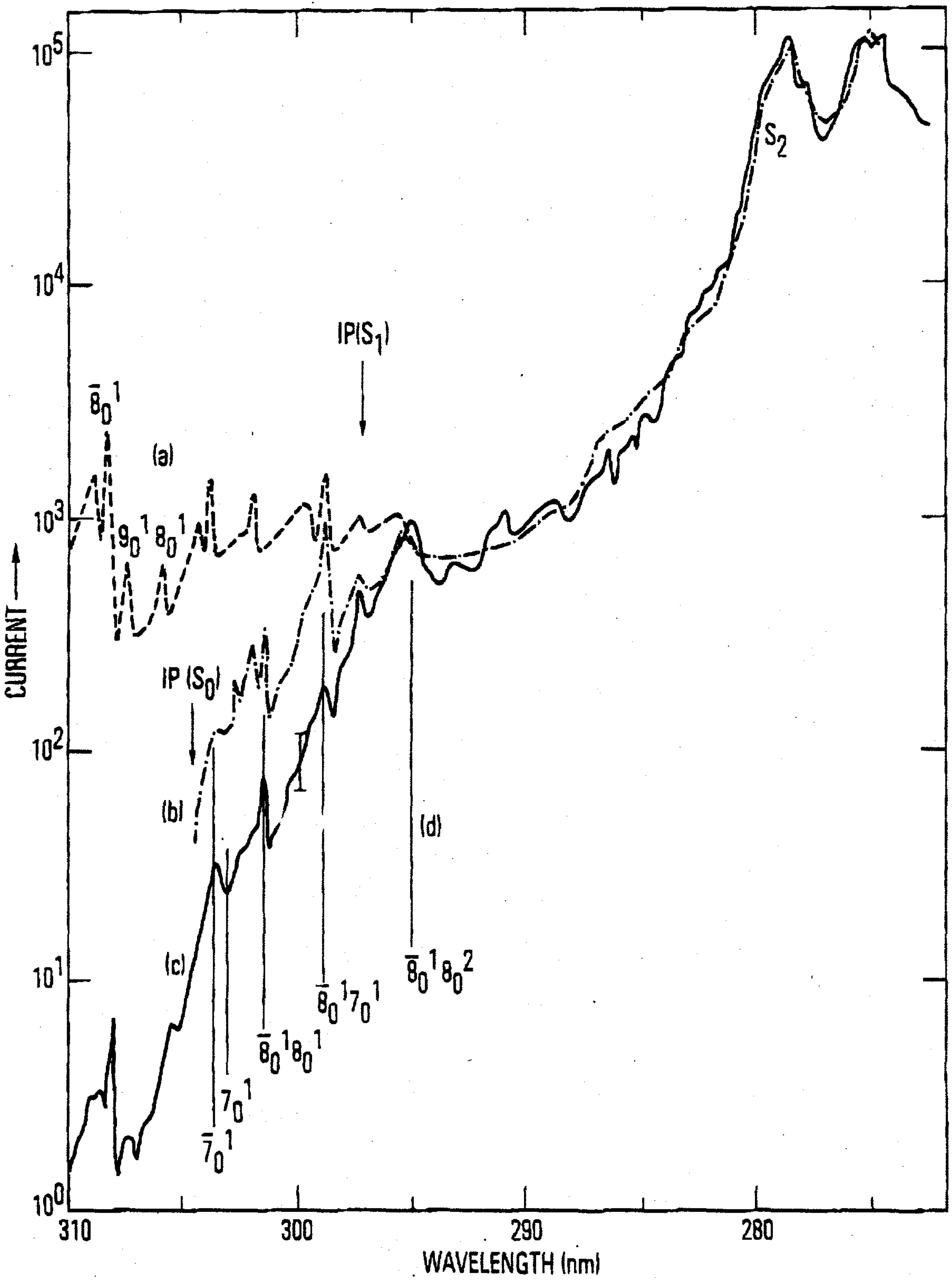


Figure 3



$10^5$
$10^4$
$10^3$
$10^2$
$10^1$
$10^0$
CURRENT
310
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290
280
WAVELENGTH (nm)
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IP ($S_0$)
$S_2$
(a)
(b)
(c)
(d)
$\bar{8}_0{}^1$
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Figure 4

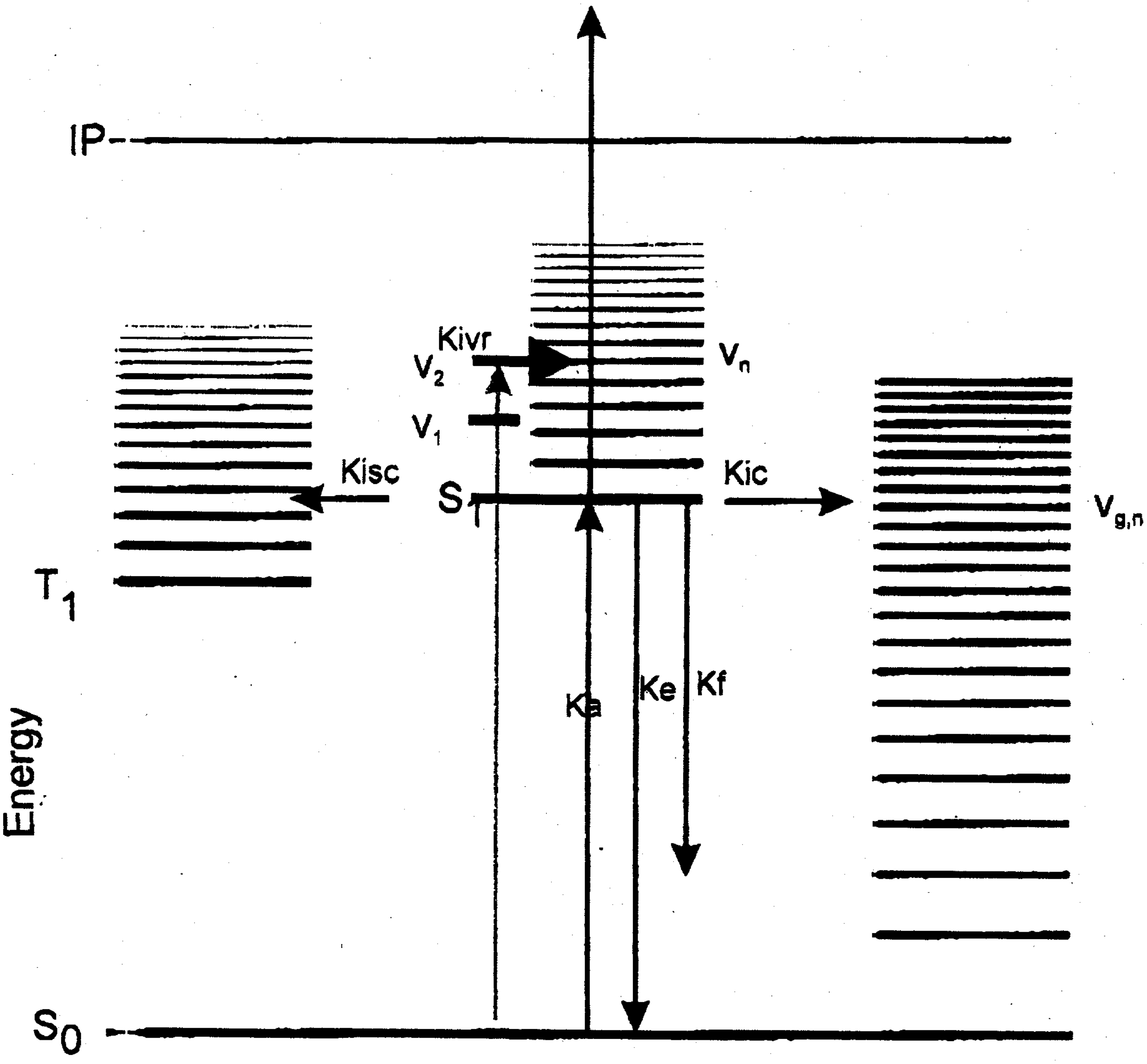
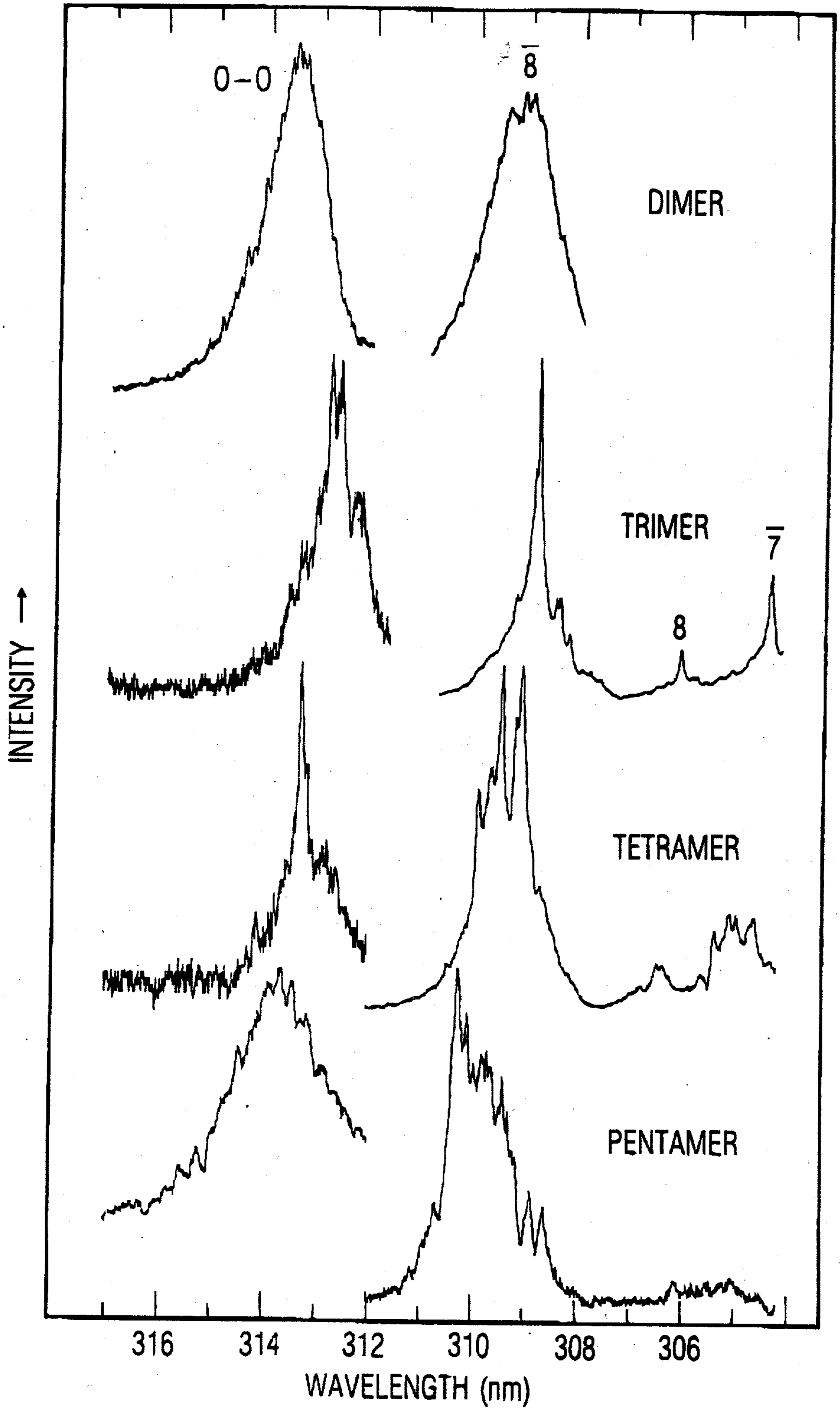


Figure 5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WAVELENGTH (nm)

Figure 6

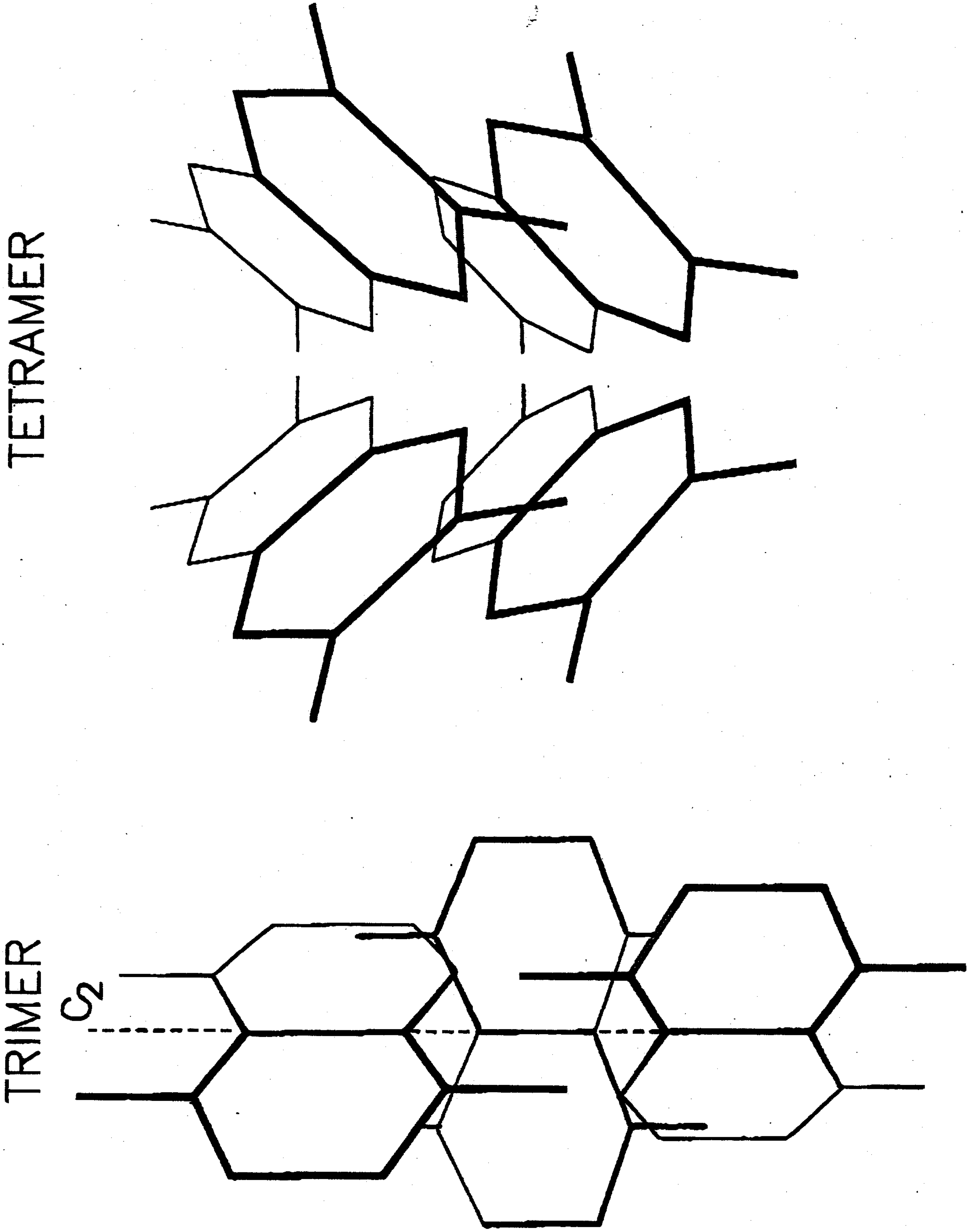

Figure 7