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PROGRESS REPORT

MULTIPHOTON IONIZATION OF IONS, NEUTRALS, AND CLUSTERS

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Abstract

Scientific results are summarized from a three year research program on multiphoton ionization in aromatic molecules, clusters, and their ions. As originally proposed, the studies elucidated a new cluster ionization mechanism, characterized properties of long range intermolecular interactions, and investigated electronic transitions of aromatic cations cooled in a supersonic beam. The studies indicate that the new cluster ionization mechanism is highly efficient and dominates conventional 1 + 1 resonant ionization. In the case of the dimer of the large aromatic molecule fluorene, the results suggest that excimer formation competes with a direct ionization process. Highly selective excitonic spectra have been identified for several cluster species.

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PROGRESS REPORT

MULTIPHOTON IONIZATION OF IONS, NEUTRALS, AND CLUSTERS

Introduction

Our activities have concentrated on resonance ionization spectroscopy of aromatic molecule clusters that are characterized by weak van der Waals bonding. The major areas of concentration were on cluster ionization mechanisms, geometry of prototype cluster species, stability of preferred cluster conformations (mixed isotopic studies), excimer formation for homomolecular clusters, and ion absorption spectra of neutrals and clusters.

Cluster geometry represents a timely and important area for investigation because it provides a critical test of long range intermolecular potentials. Currently, it is impractical to derive high quality potential fields by accurate *ab initio* theoretical calculations because molecular wavefunctions are not accurate at long internuclear distances (4-7 A).[1,2] (The variational energy is relatively insensitive to the long range portion of the wavefunction.) Multipolar expansions of the potential have been notably unsuccessful in modeling intermolecular interactions between large molecules at even the qualitative level.[3] Unfortunately, direct measurements by high resolution rotational spectroscopy is not currently practical for application to large molecule cluster species. Therefore, there is a growing need for improved measurement and modeling of the long range intermolecular potentials of importance to chemical and biological processes.

Clusters can provide a wealth of spectroscopic information previously available only from low temperature molecular crystal studies. Clusters represent a simplification relative to crystals because there is no complicating band structure. Therefore, there is great promise in applying results from experimental cluster spectroscopy in order to test and refine theoretical force field models.

The cluster structure calculations of van de Waal[4] and also by Williams[5] inspired our approach to this problem. An empirical 6-12 potential function was applied to benzene

[1]A. D. Buckingham, P. W. Fowler, and J. M. Hutson, Chem. Rev. **88**, 963 (1988).
[2]E. Dykstra, J. Phys. Chem. **94**, 6948 (1990); J. M. Hutson, Ann. Rev. Phys. Chem **41**, 123 (1990).
[3]G. W. Robinson, Ann. Rev. Phys. Chem., **21**, 429 (1970).
[4]B. W. van de Waal, J. Chem. Phys. **79**, 3948 (1983); ibid., Chem. Phys. Lett., **123**, 69 (1986).
[5]D. E. Williams, Acta Cryst. **A36**, 715 (1980).

geometry studies that started from a crystal geometry. In this case, their idea was to overcome the problem associated with an overwhelmingly large configuration space characterized by multiple local potential minima, by starting with a known crystal geometry. Using this approach, they predicted unusual stability for a high symmetry icosahedral (non crystal-like) 13 member benzene cluster. Later, Whetten and coworkers[6] confirmed that the 13 member benzene cluster stands out as highly stable and that it is characterized by unusually sharp and simple spectra. Later on, as described below, Easter, Whetten, and Wessel[7] carried out isotopic substitution experiments that supported van de Waals predicted structure. This provides justification for attempting to use and extend these simplified force fields in order to understand and predict geometries of complex systems. However, one example does not prove a case. There is some experimental evidence[8] suggesting that the simple models may not provide a reliable or unique solution to the intermolecular potential problem.

Currently, we are investigating application of force field models to the small clusters we previously studied experimentally. The results are not entirely consistent with the observed spectra. At the present time it is not known if the problem involves the model or the interpretation of the experimental data. As a side issue, the general characteristics of the potential curves are being used to understand the observed tendency to form specific mixed isotope conformers, to the exclusion of nominally expected conformers. (For example in the naphthalene trimer, the species HDH is formed preferentially, rather than HHD, and for benzene, the protonated molecule in the 13 member h_1d_{12} cluster occupies the central site). If these issues can be resolved satisfactorily, the results are expected to supply the missing thermometry needed for supersonic beam studies of large molecule clusters.

Ionization mechanisms for monomers and clusters also provide an area of considerable interest and relevance to ultrasensitive molecular detection. Our past studies revealed that monomers such as iodine,[9] naphthalene,[10] methylnaphthalene, and aniline[11]

[5]D. E. Williams, Acta Cryst. **A36**, 715 (1980).
[6]D. C. Easter, ,M. S. El-Shall, ,M. Y. Hahn, , R. L. Whettern, Chem. Phys. Lett. **157**, 277 (1989).
[7]D. C. Easter, R. L. Whetten, and J. E. Wessel, J. Chem. Phys. **94**, 3347 (1991).
[8]J. Wessel and J. A. Syage, J. Phys. Chem. **b94**, 737 (1990)
[9]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).
[10]J. Wessel and J. A. Syage, J. Phys. Chem. **94**, 737 (1990).
[11]J. A. Syage and J. E. Wessel, J. Chem. Phys. **85**, 6806 (1986).

can have extremely complex ionization spectra, involving dissociative, ionizing, and autoionizing states., The autoionizing states provide examples of extremely useful discrete spectral structure above the ionization limit, combined with large oscillator strength in some cases. Scientifically, the spectra provide a wealth of data available to theoreticians interested in the coupling between Rydberg electrons and ionic cores of complex molecules. However, our searches for the corresponding structure of cluster species has been negative. This result has been explained by a proposed bimolecular excitonic autoionization mechanism which appears to be active in homomolecular clusters. Earlier, Whetten and coworkers[12] proposed that large aromatic clusters ionize by an exciton fusion mechanism, whereby excitations of different molecules diffuse through the clusters and then undergo annihilation on a site where the combined energy of two excitations exceeds the ionization potential. In the case of small clusters considered in our work, the excitonic spectra indicate the molecular transitions are relatively strongly coupled, such that diffusion and energy hopping do not occur. Instead, the mechanism is more closely analogous to ionization in the 2-electron atom, where one electron can be promoted to a bound, high lying state, without greatly effecting transitions of the remaining valence electron. When this valence electron is excited in even a low energy promotion, the total system energy exceeds the ionization limit, and autoionization occurs. The nature of these processes for molecular clusters are important to detection applications because they enhance the rate of multiphoton ionization and thus increase the detection efficiency for these cluster species, relative to the monomers.

During the past two years considerable attention was given to optimizing the pulsed molecular beam source for our cluster studies. This was motivated by the poor reproducibility of operation and frequent need for mechanical alignment of our previous, typical pulsed valve system. These efforts led to a highly reproducible system that uses a standard commercial pulsed valve. The new system operates with greater throughput and with a higher temperature sample injection chamber, which is important for study of large molecule clusters. In addition, the conditions needed to reproducibly achieve cooling to low temperature in the expanding supersonic beam are now relatively well understood.

Excitonic Interactions in Naphthalene Clusters

Much of this work was carried out in a prior reporting period, however, considerable experimental and analytical work related to the earlier studies continues in up to the

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

present. Therefore, the results are briefly summarized and a reprint of the final publication (which is substantially modified relative to the draft manuscript included in a prior progress report) is appended.

Geometric information can be derived from the naphthalene cluster spectra because the excitonic interactions are strongly dependent on the angles of the transition moments of monomer units of the cluster. In favorable cases, the geometry can be determined if a single transition moment gives rise to a spectral feature of the cluster. Naphthalene is highly favorable for this analysis because there are two separate transition moments in the S_1--S_0 transition system. The weak origin and the totally symmetric a_g mode system are long axis polarized, the stronger vibronically induced b_{3g} system is short axis polarized. Representative spectra for naphthalene dimer, trimer, and tetramers, obtained previously, are presented in Figure 1. The basic vibrational structure resembles the monomer spectrum, with the exceptions that considerable broadening occurs for the dimer, and multiplet structure appears in transitions of the larger clusters. Nonetheless, it is easy to identify each spectral band (multiplet) of a cluster and associate it with the corresponding vibronic transition of the monomer. It is clear from the well-resolved spectra that excitonic interactions dominate the spectra. Analysis indicates that inequivalent sites occur in the tetramer spectra, however they are clearly absent in the trimer.

Ionization Mechanism in the Naphthalene Trimer

Whereas, monomer aromatic species ionize by a stepwise resonant ionization process, we recently concluded[13] that the naphthalene trimer ionizes by a process analogous to 2-photon autoionization of the 2-electron atom which is also closely related to biexcitonic autoionization of semiconductor crystals, as shown in Figure 2. In related work, Whetten and coworkers[12] concluded that large benzene clusters ($n > 20$) ionize by an exciton fusion mechanism, involving sequential excitation of two or more molecules in the cluster. This is followed by diffusion and annihilation, whereby a pair of excited states combine on one molecular site, thus accounting for the anomalously high efficiency observed for cluster photoionization. Previously, biexcitonic annihilation was identified in bulk molecular crystals.[3] Our investigations suggest that a biexcitonic autoionization process occurs for the naphthalene trimer cluster. The spectra indicate that the biexcitonic states of van der Waals clusters are attractive and short lived.

[13]J. Wessel, Phys. Rev. Lett. **64**, 2046 (1990).

The experimental investigations are based on 2-color pump probe spectroscopy of the naphthalene trimer cluster. The recorded difference spectra represent processes requiring a photon from each of the two sources. In Figure 3 the 1-color spectrum of the nontotally symmetric vibration $\overline{8}_0^1$ for the isotopically pure h_8 cluster (a), is compared to the directly recorded 2-color spectrum (b) and to the W1 + W2 difference spectrum, (c). The difference spectrum is centered near the 1-color transition, and it is substantially broadened relative to the 1-color spectrum. Ionization is enhanced whenever both W1 and W2 beams are overlapped and tuned to the vicinity of S_1--S_0 vibronic transitions. This is distinctly different from typical ionization step spectra (IP--S1) observed for the monomer. In this case the signal rises abruptly to a plateau once the total energy exceeds the ionization potential. The new spectral characteristics suggests the ionization mechanism involves two ground state based S_1--S_0 transitions.

The 2-color ionization spectra were modeled by incoherent population rate equations, and the predictions closely simulate the observed 2-color spectra. At low W1 and W2 fluences, sharp spectra are predicted, and broadening occurs as W2 increases. With increased W1 fluence, the amplitude of the sharp transition decreases and rounded shoulders appear on the wings, extending approximately 30 cm^{-1} from line center.

The above considerations support the resonant 2-photon autoionization mechanism for trimer ionization. One-color spectra obtained by this technique are governed by a convolution of spectra for the first and second photon, leading to a characteristic broad, intensity dependent pedestal. We predict that small size homomolecular van der Waals clusters will ionize by the autoionization mechanism and be characterized by similar intensity dependent spectral characteristics, provided the intermediate state is stable on the time scale of the excitation pulse.

Collaborative Cluster Geometry Studies

Whetten and coworkers established that the size distribution of benzene clusters favors special sizes, such as $benzene_{13}$, and these clusters can display highly discrete spectroscopic structure. The observations were consistent with the shell model for geometries developed by van de Waal. His calculations identified an icosahedral structure with 13 benzenes as being highly stable and slightly preferred relative to structure most

similar to the benzene crystal. (The calculations also identified a zigzag trimer structure that was later supported by experimental results from Schlag's group.[14])

Based on these results, we decided to carry out isotopic substitution experiments on the benzene clusters. A small amount of benzene-h_6 was mixed in with larger quantities of benzene-d_6. The resulting ionization mass spectra had distinct mass peaks corresponding to h_1d_{12}. Spectroscopy was carried out on this mass peak and the results were compared to h_{13} and d_{13}. In the case of h_{13}, the spectra consisted of three regions for each molecular vibration, as shown in Figure 4. In the low energy region (-200 cm^{-1} relative to the corresponding monomer transition) the vibronically induced 6_0^1 line had one weak sharp component at lowest energy (-216 cm^{-1}), and a rising weak background to higher energy. Then in the central region (ca. -150 cm^{-1}) there is a sharp group of intense components. At highest energies (-100 to -150 cm^{-1}), there is a near continuum.

The origin system, which is forbidden in the monomer, lacked the lowest energy weak, sharp feature. It does show the broad weak baseline that is present in 6_0^1. The central and high energy systems are also similar to those of 6_0^1. It should be noted that 6_0^1 is allowed by symmetry in the monomer.

The h_1d_{12} mixed isotope cluster provided a striking identification of the lowest energy component of the band systems. A 6_0^1 low energy h_1d_{12} component occurs at the precise energy of the lowest energy h_{13} 6_0^1 peak. The origin system did not have a corresponding peak at the lowest energy position. These results are readily interpreted in terms of the excitonic interaction model with strong site effects. The single protonated molecule preferentially occupies the central cluster site. It has the greatest stabilization energy in the unique central site. The transition is symmetry allowed for 6_0^1. However, it is forbidden in the origin system, and thus does not appear in any of the recorded spectra. This absence, confirms that the protonated molecule preferentially occupies the central site in the h_1d_{12} cluster. The other molecules, at lower symmetry sites, have site induced origin bands at the central and high energy positions in the origin system. There is an origin feature slightly above the excited h_1 origin position that has significant intensity. It may correspond to a vibrationally induced transition (intermolecular vibration) or to a less abundant cluster conformation.

[14]K. O. Bornsen, S. H. Lin, H. L. Selzle, and E. W. Schlag, J. Chem. Phys. **90**, 1299 (1989).

Thus, simple spectroscopic arguments favor the icosahedral cluster structure predicted by van de Waal. Apparently, the relatively crude potential model works relatively well in predicting ground state geometry for benzene. This success leaves two puzzles. The first is that it is generally expected that the heavier molecule will occupy the most tightly constrained cluster position, thus minimizing zero point energy. The central position in benzene$_{13}$ is expected to provide maximum constraint due to the higher coordination at this site, which is supported by the large observed red shift for the site. Secondly, the van de Waal potential model, when applied to naphthalene, predicts a structure different from that deduced from the trimer spectrum. This is described in more detail below.

Cluster Stability Studies

One of the most remarkable aspects of the naphthalene and benzene cluster studies is the appearance of only one cluster conformation for each cluster size. A single conformer predominates in each of the following cases: HHH, DDD, HDH, DDH, HHHH, DDDD -naphthalenes (see Figure 5), and for benzene$_{13}$ and h_1d_{12} benzene. The most straightforward explanation is that the preferred structure has the lowest zeropoint energy, and is thus favored during the cooling process. This is easy to understand on a qualitative basis for HDH. The system can be regarded as an analog of a triatomic species. In this case, the H species are bound by one stretching and two bending force constants, whereas the central D molecule is bound by two stretching and four bending force constants. The zeropoint energies are proportional to $(k_{eff}/m)^{0.5}$, thus the larger mass molecules will have the greatest relative zeropoint stabilization when occupying the position with the maximum effective force constant, k_{eff}, refer to (Figure 6). Based on this argument,(assuming the molecules are rigid and similar force constant arguments apply for librational degrees of freedom) when the force constants are scaled to fit the intermolecular stretching frequency observed for the trimer, we deduce that the linear HDH conformer should be stabilized by 5 to 10 cm^{-1} relative to HHD. If this argument is valid, the observed absence of a second conformer indicates cluster cooling is highly effective. Examination of the vibrational hot bands for the monomer and cluster species indicates vibrational cooling to about 50 K or less. Our experiments do not measure rotational cooling, thus the absence of other conformers is the only indication that the lower energy motions are cooled more effectively. This is consistent with behavior of rotational degrees of freedom reported in cases where rotational band structure is resolved.

Currently, we are beginning to refine this analysis by applying potential modeling calculations to the naphthalene systems. The force fields will provide more accurate zeropoint energies for the intermolecular modes, and thus give an analytical assessment of the zeropoint stabilization model. Figure 7 represents a calculated potential field for motion of the planar naphthalene dimer in the xy plane at the approximate distance of the interplanar potential minimum. This potential field model predicts that the most stable dimer configuration has a displaced coplanar configuration. Unlike the case of benzene, interplanar tilting decreases stabilization. A relatively strong secondary minimum is predicted for the sandwich configuration (at a larger interplanar distance). The predicted dimer results cannot be compared to results derived from the dimer spectra because the dimer appears to undergo excimer formation in the excited state, thus precluding an excitonic analysis. However, the predictions should be relevant to some trimer structures. In fact, in the experimentally suggested trimer configuration (60° staggered interplanar angles with a C_2 axis through the central carbon atoms) the overwhelming interactions should be pairwise. However, the model potential calculations predict a weak subsidiary potential minimum for a configuration analogous to the experimental structure (Figure 8), however the potential model gives a minimum at a 90° interplanar angle, as opposed to the 60° experimental angle. The most stable predicted trimer structure is a staggered coplanar structure, which is much different from the experimental configuration. There are two leading explanations for the apparent disagreement between experiment and prediction. The first is that the force field model is inaccurate. Another possibility is that there are at least two stable conformers of the trimer and that photoionization detects only the noncoplanar one. The coplanar structure(s) may be subject to rapid excimer formation, and thus be less detectable by ionization methods. As for the 90° versus 60° interplanar angles, the potential differences responsible for this are relatively small, and the associated motion would have large amplitude with strong mixing of degrees of freedom. Therefore this prediction would not be expected to be accurate.

If this type of potential field can be reliably extended to describe clusters other than benzene, it will provide the force fields needed to quantitatively evaluate the zeropoint energy stabilization model for cluster conformations. This will represent a significant advance in cluster science and potentially, provide improved force fields for general chemical applications.

Competition Between Excimer Formation and Ionization Processes

The fluorene molecule ($C_{13}H_{10}$) is known to undergo excimer formation in the S_1 excited state in solution, and when formed in cold supersonic jet expansions.[15] The excimer fluorescence is spectrally broad and red shifted substantially from the S_1--S_0 absorption energies. The prior supersonic beam work was performed using excimer fluorescence detection. We are in the process of investigating ionization processes in this system, and in the fluorene trimer. Whereas the dimer system was reported to have a complex, broadened excimer fluorescence excitation spectrum, we have observed extensive sharp structure in the higher energy vibronic spectrum associated with S_1--S_0 resonant 2-photon ionization, as shown in Figure 9.

The dimer species is formed in abundance in our high temperature supersonic beam. The monomer spectrum obtained under identical conditions indicates excellent cooling conditions. The dimer spectrum displays a broad origin system. This is consistent with the prior fluorescence detection results. However, at higher energies, numerous relatively narrow linewidth vibronic bands are resolved. The linewidths vary greatly from line to line, with some features as narrow as 4 cm^{-1}. The vibronic spectrum is extensive, with linewidth generally narrowing at higher energies. The relative efficiency of ionization appears to persist anomalously high into the vibronic spectrum.

This behavior is consistent with a relatively simple model for ionization in the presence of excimer formation. The origin level is apparently strongly coupled to the excimer state. The large 53 cm^{-1} linewidth of this band may be associated with an unresolved vibrational progression in the intermolecular coordinate associated with excimer formation. This band resembles the characteristics of the naphthalene dimer bands, which are all indicative of excimer formation. In fluorene, even some of the low energy modes are relatively well resolved, for example the +870 cm^{-1} mode has a linewidth of 15 $cm,^{-1}$ versus 53 cm^{-1} for the origin system. One of the weakest observable modes, at about 820 cm^{-1}, has a width of about 5 cm^{-1} which is close to the instrumental linewidth. The narrow vibrational lines must represent modes that are poorly coupled to the excimer state. When these modes are excited, formation of the excimer is effectively blocked. The fluorene ionization limit is sufficiently low, relative to twice the S_1 <-- S_0 transition energy,

[15]H. Saigusa and M. Itoh, J. Phys. Chem. **89**, 5486 (1985).

so that both vertical ($v_{ion} = 1 <-- v_{S1} = 1$) and adiabatic ($v_{ion} = 0 <-- v_{S1} = 1$) ionization can occur in these 1-color experiments. It is also possible that the (1 , 1) transition could provide a cross section enhancement for the autoionization process, as occurs in naphthalene and stilbene. The propensity for intramolecular vibrations to block excimer formation will require analysis. At this preliminary stage, we suggest that the effect can be explained by a rule that generally applies to nontotally symmetric vibrations in exciton interactions. Namely, in the Condon approximation, the electronic interaction matrix elements coupling two molecules are modulated by the vanishing vibrational overlap integral, whenever there is a change of a nontotally symmetric vibrational quanta. In this case, the nontotally symmetric vibrations of one molecule in a cluster cannot undergo resonant excitonic interactions with the adjacent molecule. Lim and coworkers[16] deduced that excitonic interactions dominate excimer formation in aromatic clusters. Therefore, to the extent that the directly excited states are free of strong non-Condon effects and the Lim model is valid, excimer formation will be blocked by nontotally symmetric vibrations. (This argument is complicated by the fact that the transition intensity of the nontotally symmetric modes is completely dependent on vibronic coupling, which is a non-Condon interaction.) In addition, although the fluorene monomer spectrum is extremely simple, this is deceptive in that the symmetry is low and many planar modes are potentially Franck-Condon active. Therefore, rigorous assignments for the dimer modes will be exceedingly difficult. The monomer point group C_{2v} can provide vibrations with the required symmetries. Out-of-plane vibrations of species B_1 transform as rotation operators that connect A_1 and B_2 species. A_1 and B_2 transform as in-plane vectors, thus the B_1 vibration will be vibronically active. This suggests that the narrow features are associated with B_2 species, whereas the A_1 species are broadened due to excitonic interaction combined with excimer formation.

No conclusive results can be reported at this time concerning the ionization mechanism in the fluorene clusters. Double resonance spectra were recorded for the dimer and trimer in the regions where direct 1 + 1 ionization is expected. We did not observe the steps in the 1 + 1 ionization spectra that are characteristic of monomers. The overall ionization efficiency is extremely high relative to naphthalene and other aromatics. This is consistent with a biexcitonic autoionization process. In the case of the dimer, it would require that biexcitonic autoionization occurs before excimer formation occurs. This is plausible, based on the high autoionization rate deduced for naphthalene (10^{13}/s). The observed 1-color 2-photon ionization line profiles in both the dimer and trimer spectra are

[16]H. Saigusa and E. C. Lim, J. Phys. Chem. **94**, 2631 (1990).

not inconsistent with the pedestal structure, which was observed to be characteristic of biexcitonic autoionization in naphthalene.

Ion Spectroscopy

Extensive searches have been made for discrete ion absorption spectra in the cations of naphthalene, methylnaphthalene, aniline, and fluorene. In the case of naphthalene, the dimer and trimer cations, and for fluorene, the dimer cation, have also been investigated. Resolved vibronic bands were previously reported for the naphthalene cation monomer[17], occurring in the region 600-800 nm. The measurements were performed by monitoring ion fragmentation induced by absorption of the visible light. The spectra were relatively broad bands, and closely resembled perviously reported spectra for the same ion in solidstate media at low temperature. Based on indirect arguments, we concluded at that time that the broadening was intrinsic, due to rapid relaxation to lower energy states of the ion. In the studies reported here, we monitored cation absorption by measuring fragmentation of the weakly bound clusters involving the ion of interest. This was done for naphthalene dimer and trimer ions. In both cases, measurements performed from 600 to 800 nm were essentially structureless. We believe this represents excitation into broad dissociative states of both the dimer and trimer cluster ions. Attempts were made to prepare naphthalene$_1$--argon van der Waals complexes and thus to measure dissociation from a relatively unperturbed naphthalene cation. This was not productive due to low signal levels, however the weak signals recorded were consistent with the previously observed broad spectra.

More extensive studies were performed on the fluorene$_1$-krypton cation and the fluorene dimer cation. For the dimer ion we observed strong cluster ion dissociation throughout the range 600-950 nm. There was some indication of decreasing fragmentation at long wavelengths, but the changes were gradual and were less than experimental errors in wavelength dependent fragmentation efficiency. In the fluorene-krypton experiments, the signal levels were excellent, therefore the recorded continuum spectra are believed to be correct. Beam characterization experiments were performed repeatedly in order to verify the low temperature of the cluster beam. Fragmentation was performed at intensities low enough to avoid power broadening effects. Based on these experiments, the fluorene monomer appears to have broad transitions throughout the region 600-950 nm. This presumably consists of a set of strong, broad, overlapping electronic transitions. The high efficiency of dissociation implies that absorbed energy relaxes rapidly into vibrational

[17]J. A. Syage and J. E. Wessel, J. Chem. Phys. 87, 3313 (1987).

energy thereby dissociating krypton . In the case of the dimer cation, the transition may be similar to the dissociative continuum transition of the naphthalene clusters. Based on these limited studies, we conclude that the prospects for useful dimer and trimer cation spectroscopy is poor. The noble gas van der Waals complexes of the aromatic monomer cations are not subject to the charge exchange interactions that occur for dimer and trimer cations, therefore they should have well resolved discrete structure in the near infrared. Currently, we are configuring a dissociation laser source based on mixing dye laser output with the Nd:YAG laser 1.06 μm fundamental in order to pursue this expectation.

Conclusion

The spectroscopic investigations described in this report provide structural information on important prototype molecular clusters. In addition, they identified new cluster ionization mechanisms. The systems studied ranged from predominantly weakly interacting clusters (benzene$_{13}$) to an intermediate case of naphthalene$_n$ in which the dimer undergoes excimer formation and larger cluster molecules interact weakly, to fluorene, in which strong excimer and weak cluster interactions occur in the same molecule. In each case, the spectroscopic results are being used to understand the applicability of long range intermolecular interaction potentials and to elucidate the ionization processes of cluster species. Although significant progress has been achieved, the studies point to a number of areas that require significantly improved understanding.

Reprints:

Excitonic Interactions in Naphthalene Clusters

Biexcitonic Autoionization of the Naphthalene Trimer Cluster

Spectroscopic Evidence for High Symmetry in $Benzene_{13}$

Figures

1. Resonance 2-photon ionization spectra of the naphthalene dimer, trimer, tetramer, and pentamer clusters.

2. 2-photon ionization processes include (a) resonant (1 + 1) ionization, (b) exciton fusion where the wiggly arrow represents exciton transport and the curved arrow represents ionization subsequent to exciton annihilation, and (c) resonant 2-photon autoionization, where the multiplet of levels in S_1 represent trimer exciton components and the discrete levels within the ionization continuum represents the doubly excited trimer state undergoing autoionization.

3. Observed cluster ionization spectra for $\bar{8}_0^1$ of the isotopically pure protonated trimer (HHH) recorded (a) with W1 only (1-color) (b) 2-color with overlapping beams, and (c) the difference spectrum, where the nonoverlapping beam spectrum is subtracted from the overlapping beam spectrum. The difference spectrum represents processes that require two separate photon absorption events, such as biexcitonic autoionization.

4. 1-color resonance 2-photon ionization spectra of the pure and isotopically mixed $benzene_{13}$ clusters. The weak, sharp feature at -216 cm-1 in the h_{13} spectrum is present in all the vibronically active 6_0^1 spectra, however it is always absent in the origin bands for both pure isotopic clusters and the mixed cluster, as shown at the bottom. The origin transition is symmetry forbidden for a molecule at the central site of the icosahedral structure, the transition is allowed for this site in the 6_0^1 spectrum, thus supporting the structure predicted by van de Waal.

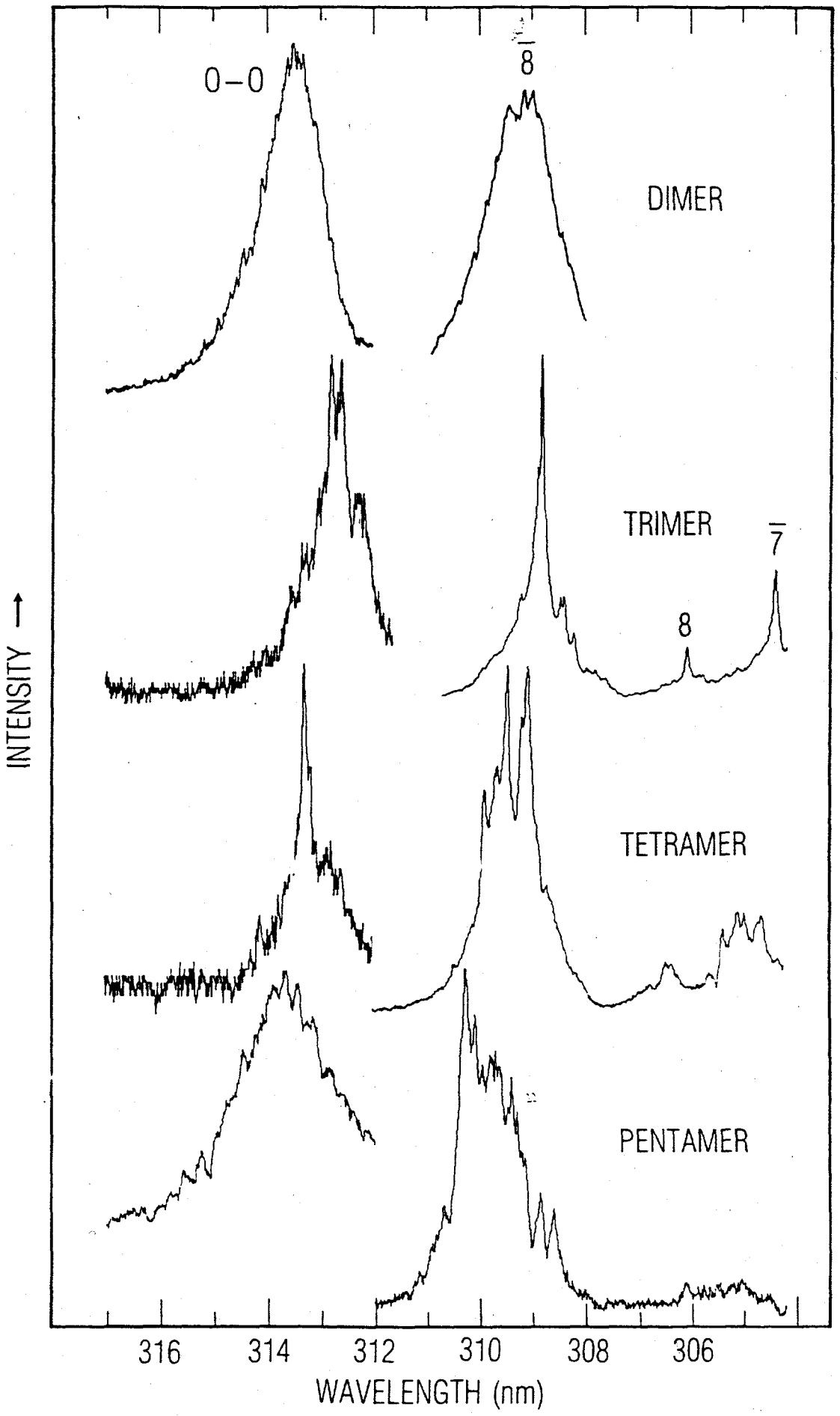
5. Naphthalene trimer spectra for the isotopically pure (a) HHH and (b) mixed isotope HDH clusters exhibiting single conformer structures.

6. Zero point stabilization model. ZPS refers to the zeropoint stabilization for a deuterated molecule substituted at the site. Thus, the stabilization change is greatest when the deuterated molecule is present at site b, rather than a or c.

7. Naphthalene dimer force field for parallel naphthalene molecules separated at the distance of the interplanar potential minimum. The potential increases for tilted molecules.

8. Experimental naphthalene and benzene cluster geometries.

9. 1-color resonance 2-photon ionization spectra of the fluorene (a) dimer and (b) trimer.


0–0
$\bar{8}$
DIMER
TRIMER
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TETRAMER
PENTAMER
INTENSITY →
316
314
312
310
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306
WAVELENGTH (nm)

FIGURE 1

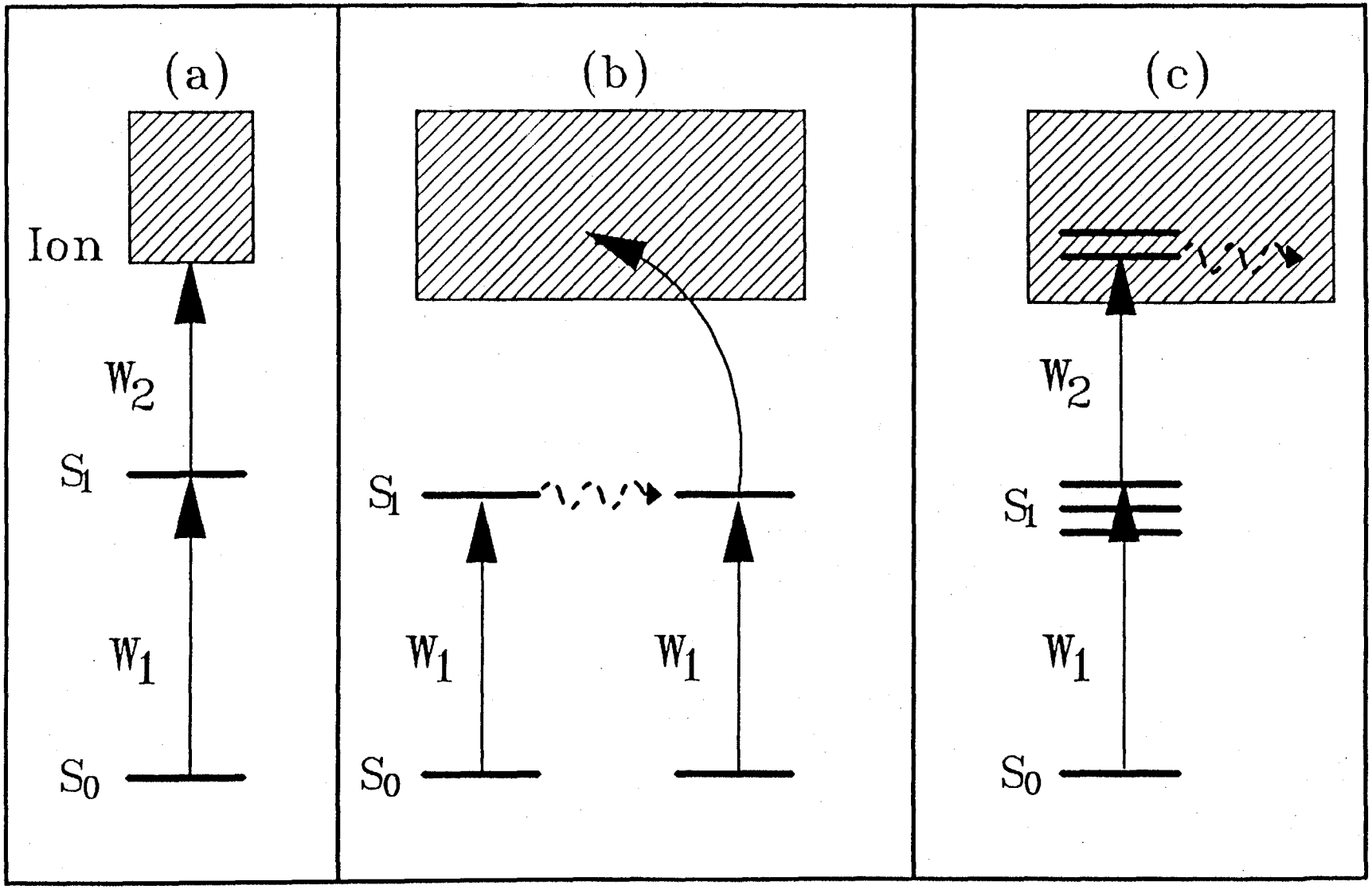
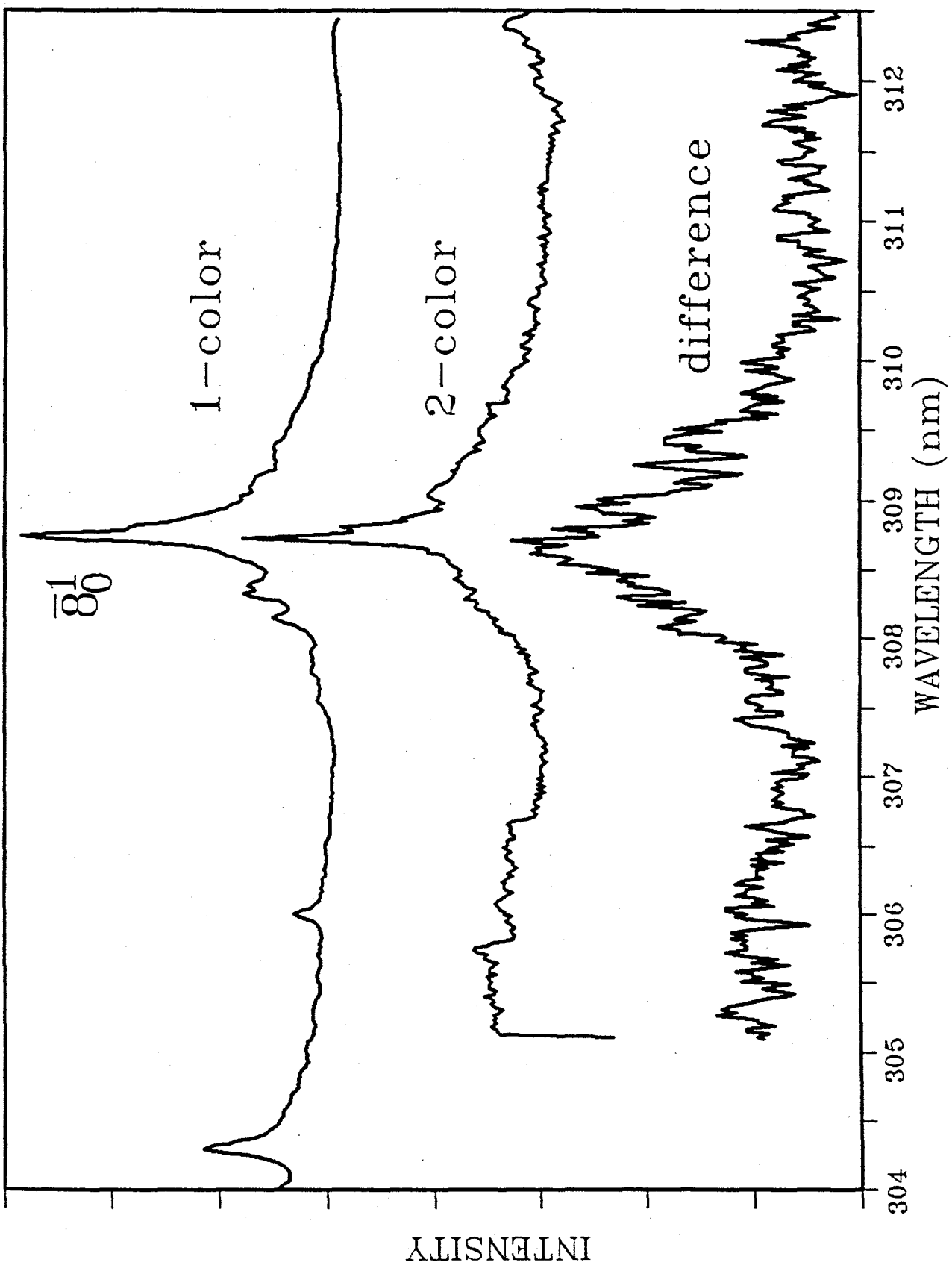


FIGURE 2


$\bar{8}_0^1$
1−color
2−color
difference
INTENSITY
304
305
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WAVELENGTH (nm)

FIGURE 3

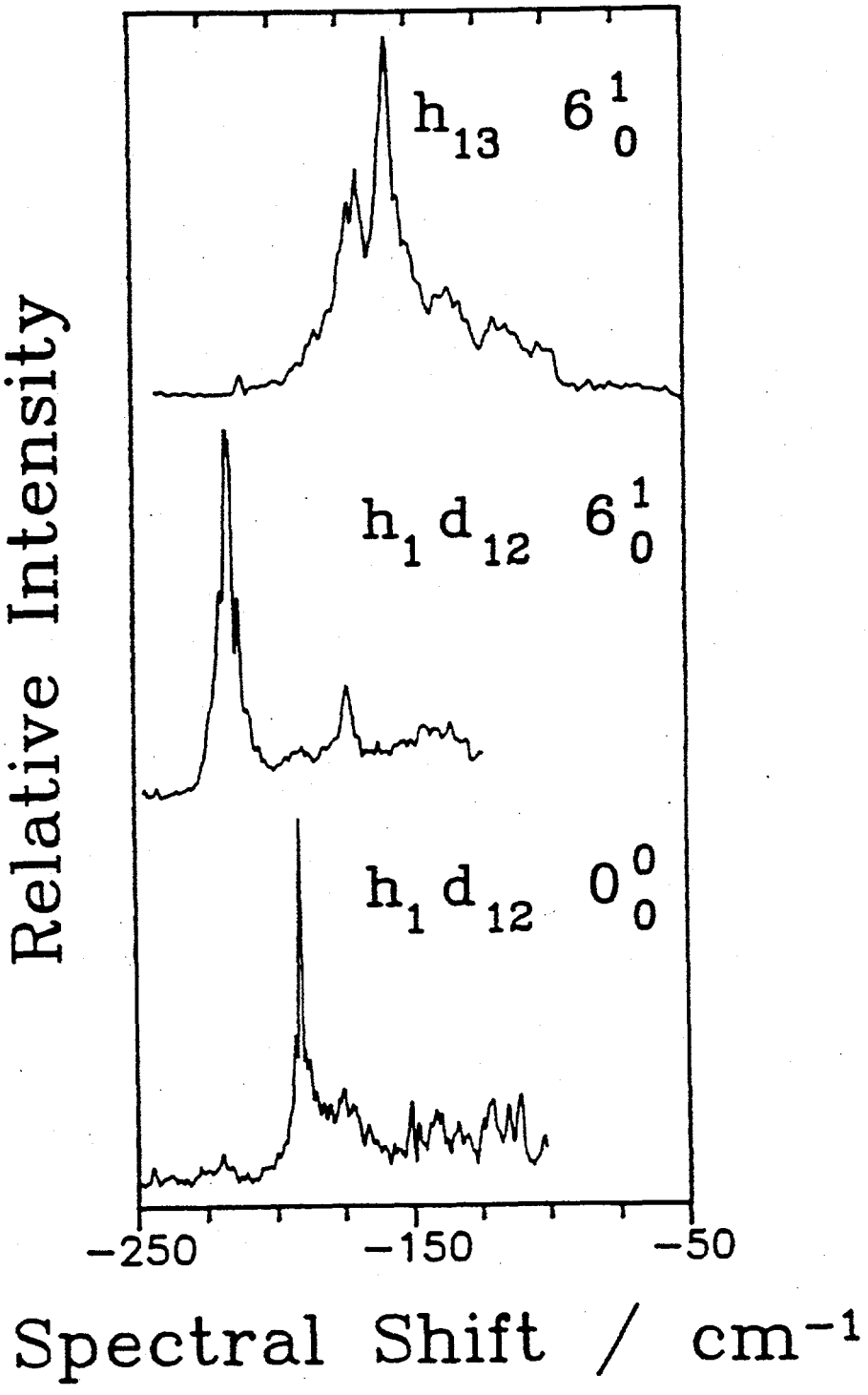


Figure 4

FIGURE 4

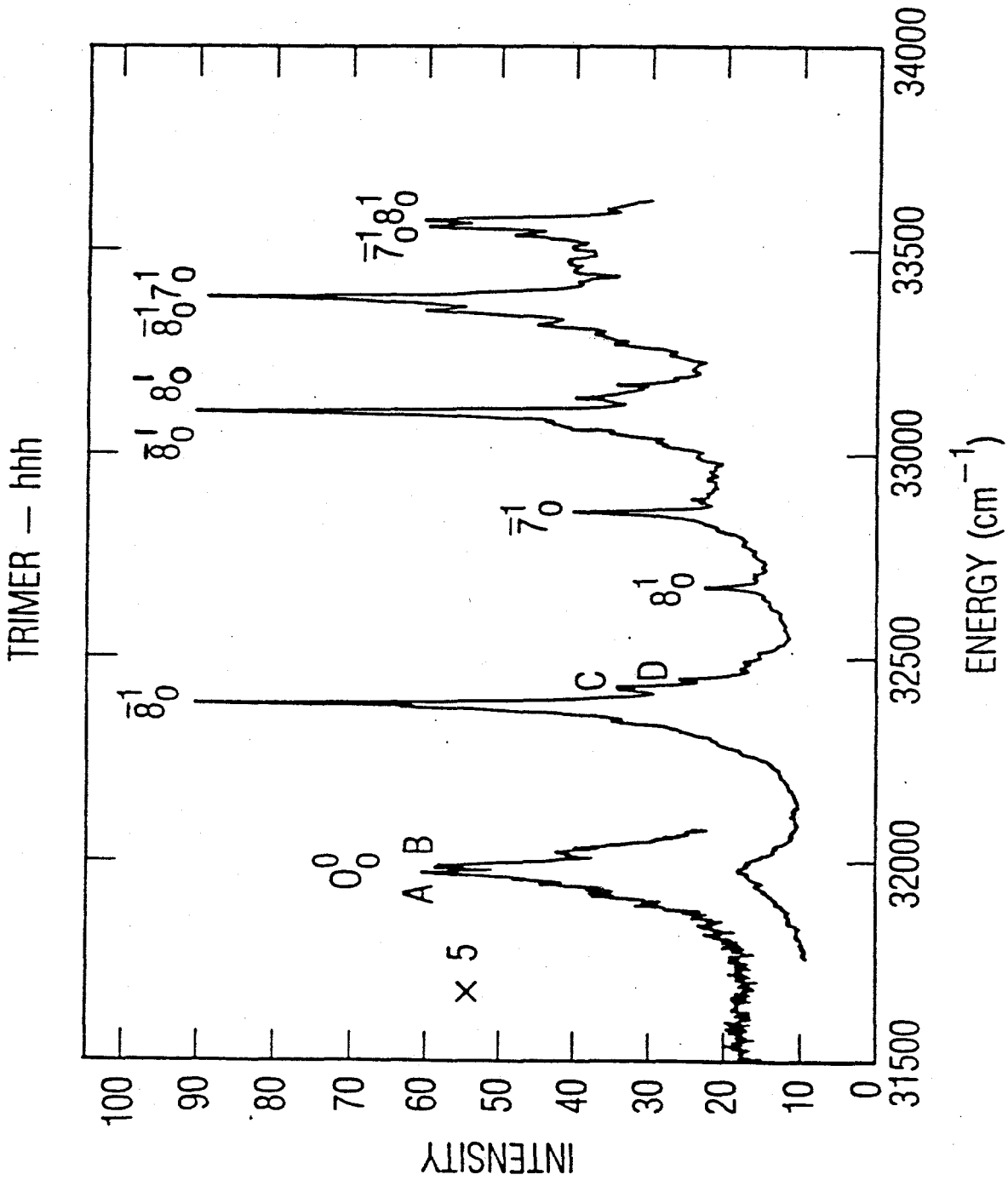

TRIMER — hhh
INTENSITY
ENERGY (cm^{-1})
100
90
80
70
60
50
40
30
20
10
0
31500
32000
32500
33000
33500
34000
$\bar{8}^1_0$
0^0_0
A
B
× 5
C
D
8^1_0
$\bar{7}^1_0$
$\bar{8}'_0\ 8'_0$
$\bar{8}'_0\bar{7}^1_0$
$\bar{7}^1_0 8^1_0$

FIGURE 5A

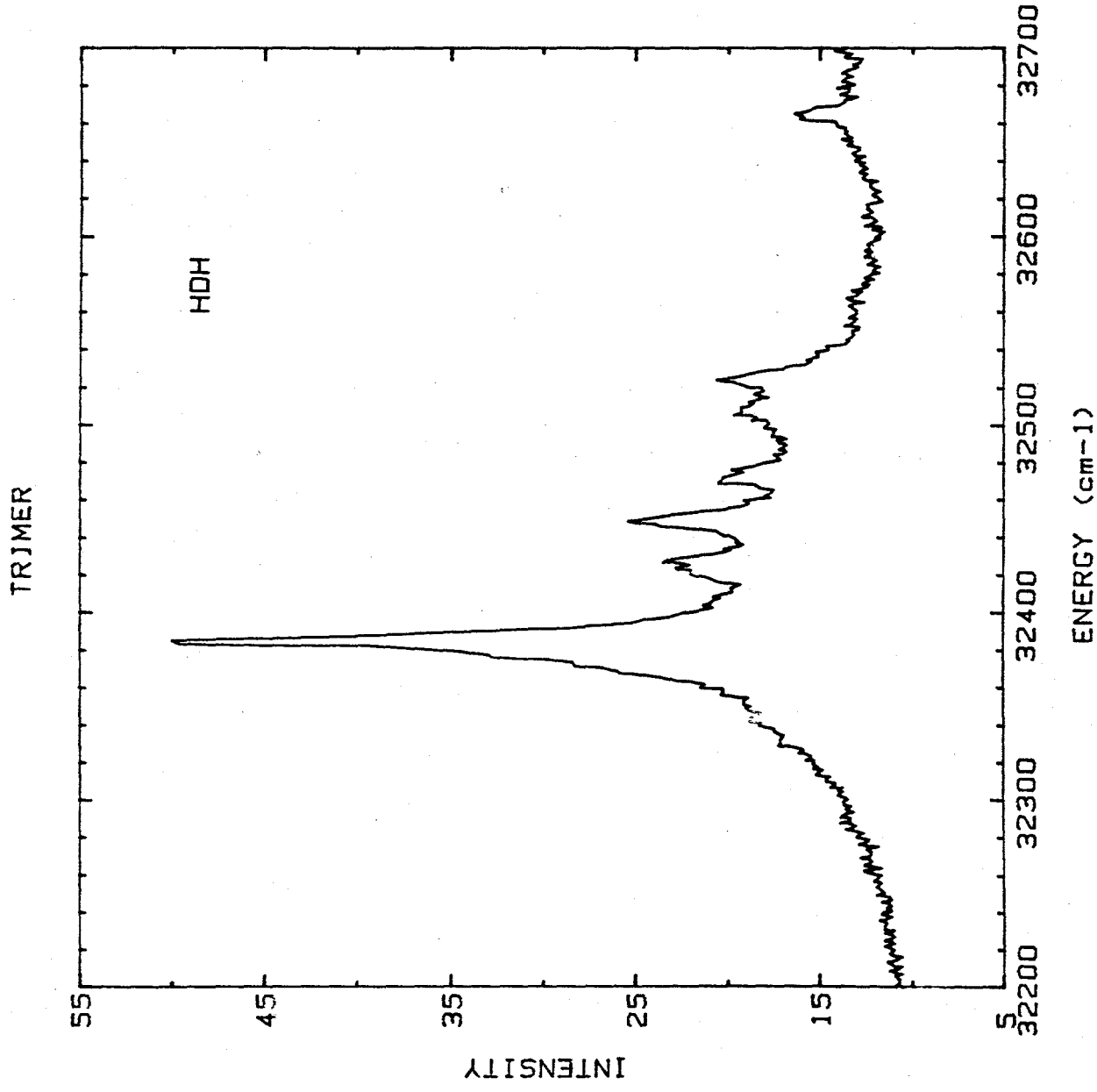

TRIMER
HDH
INTENSITY
55
45
35
25
15
5
32200
32300
32400
32500
32600
32700
ENERGY (cm-1)

FIGURE 5B

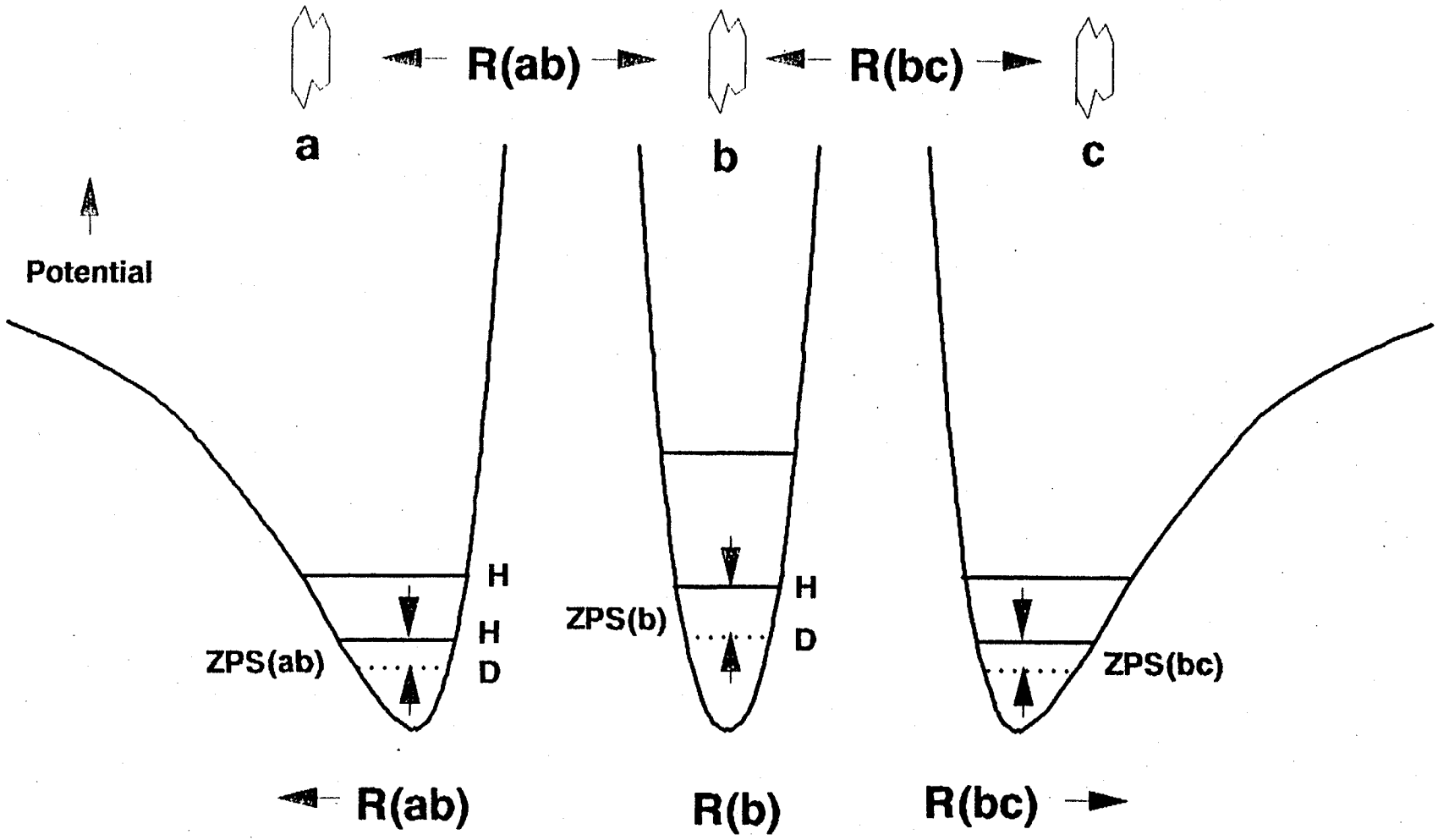
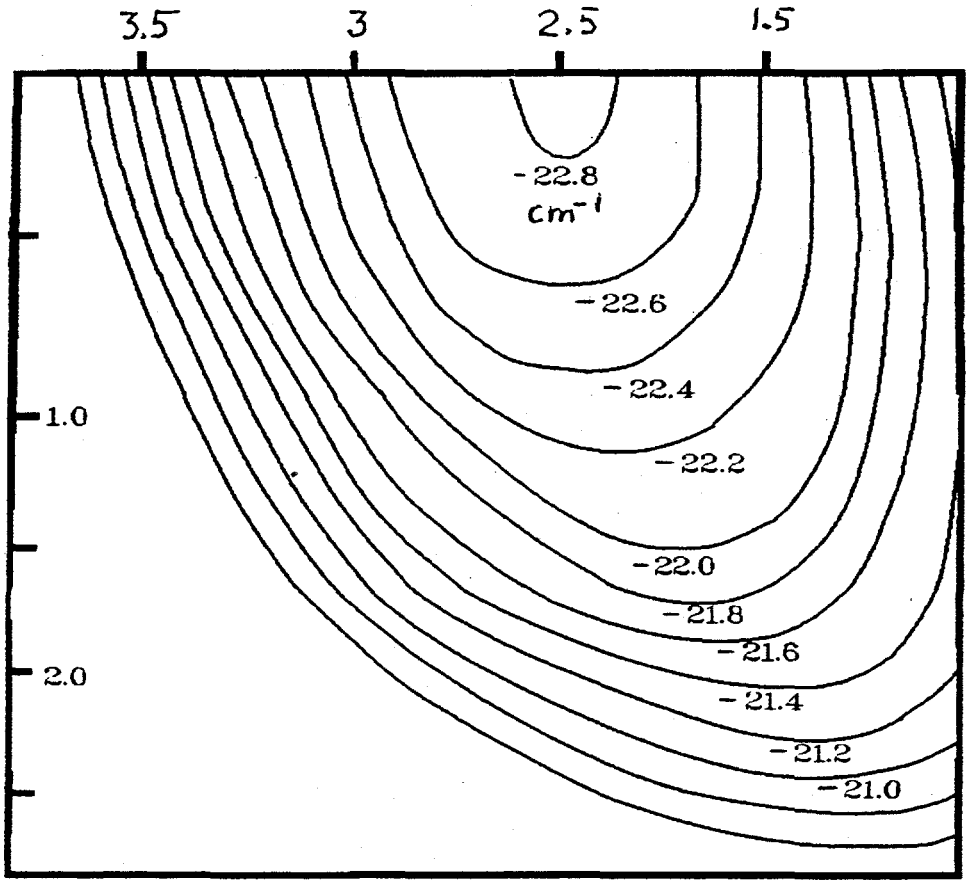


FIGURE 6



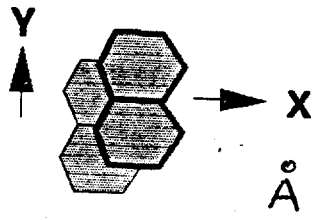


FIGURE 7

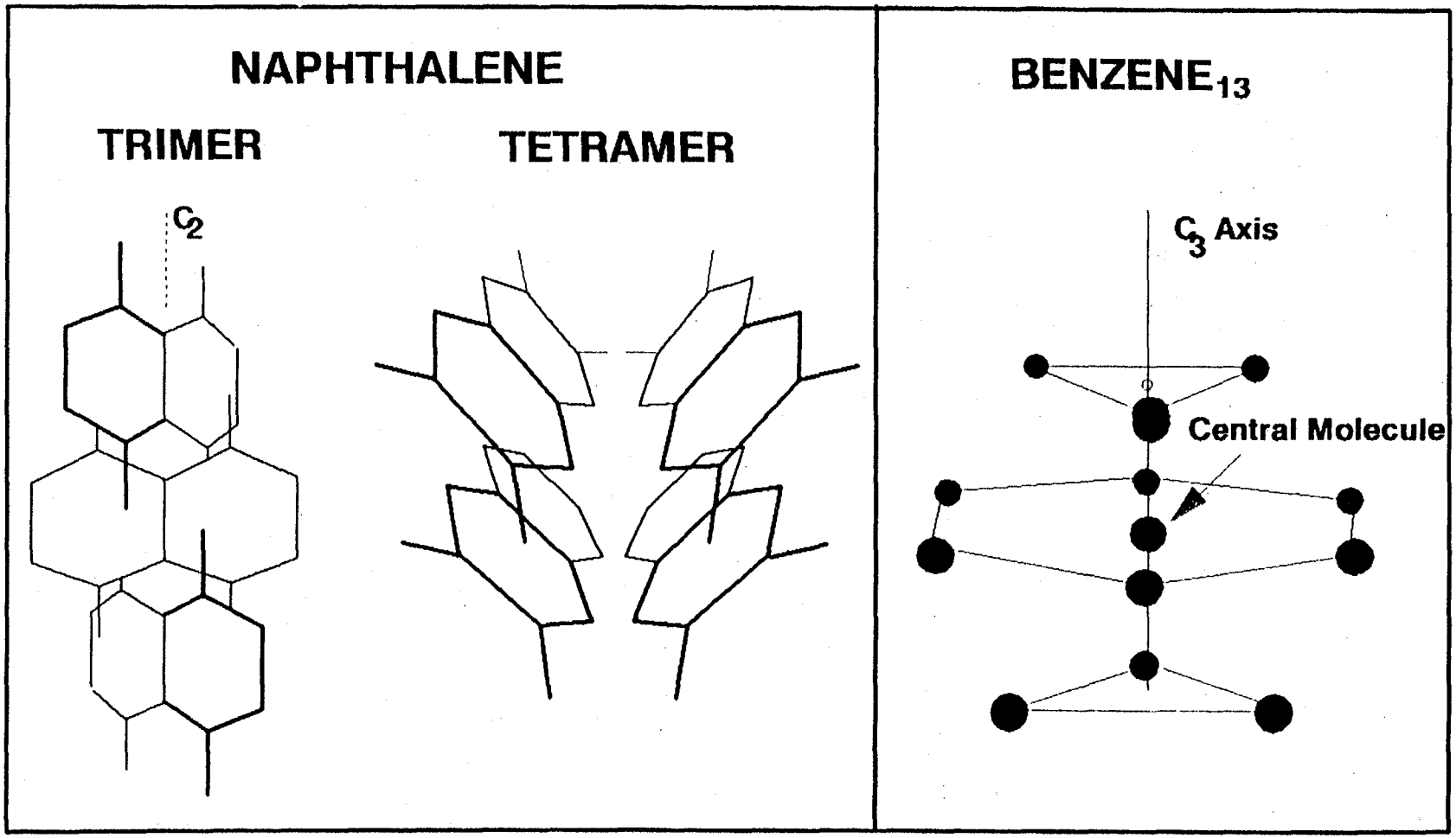

NAPHTHALENE
TRIMER
TETRAMER
C_2
BENZENE$_{13}$
C_3 Axis
Central Molecule

FIGURE 8

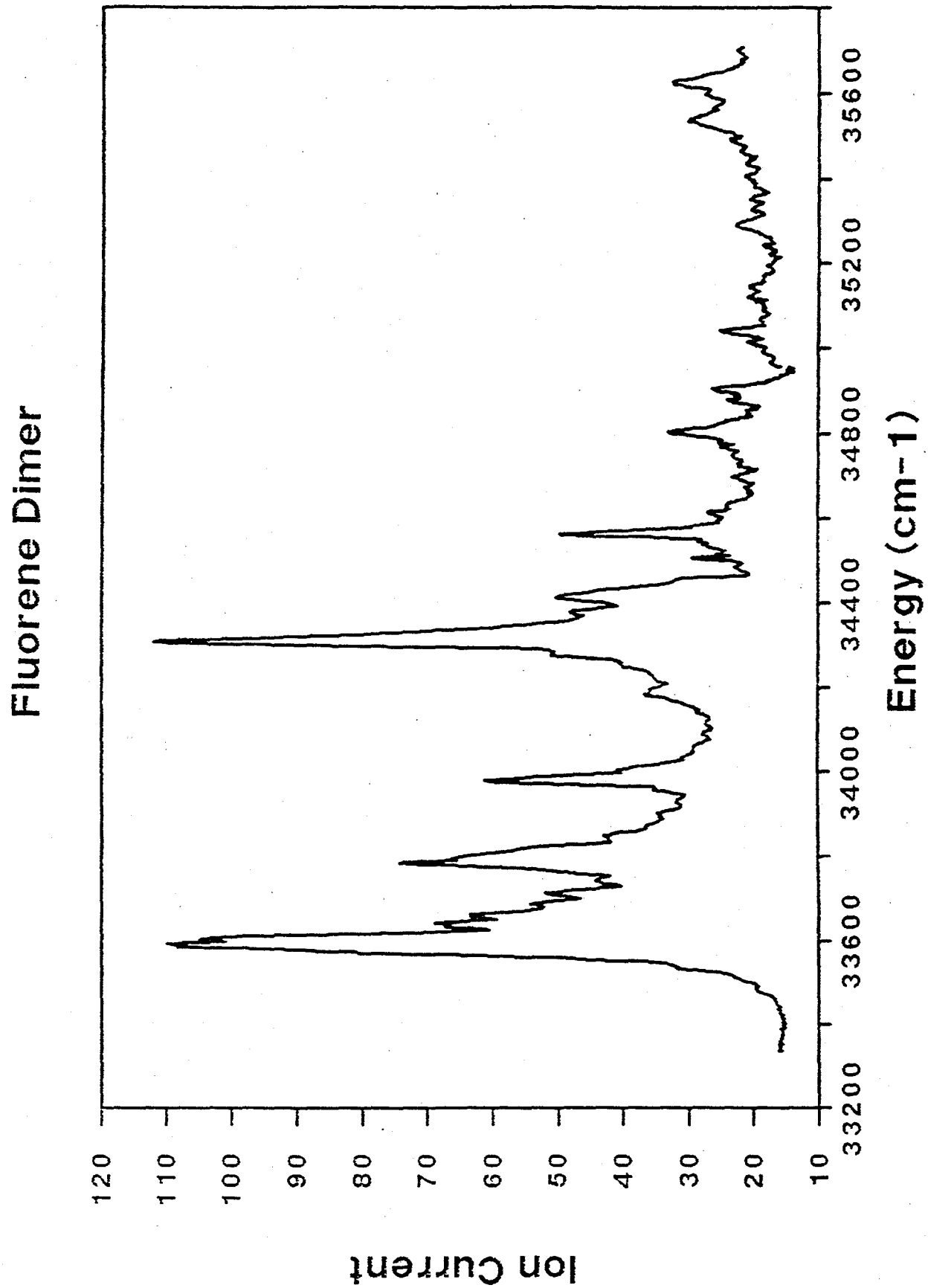

Fluorene Dimer
Ion Current
120
110
100
90
80
70
60
50
40
30
20
10
33200
33600
34000
34400
34800
35200
35600
Energy (cm-1)

FIGURE 9A

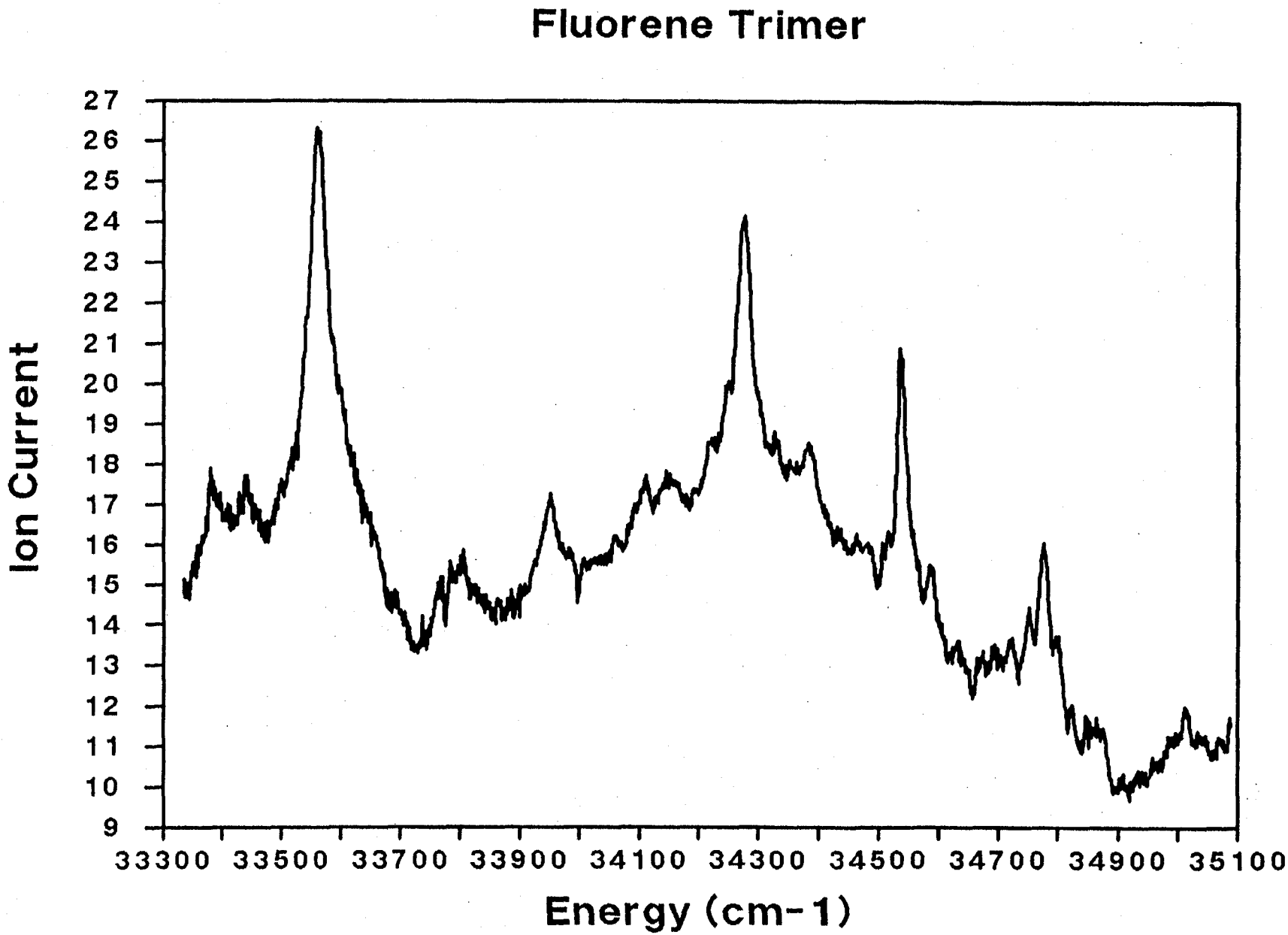

Fluorene Trimer
Ion Current
27
26
25
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
33300
33500
33700
33900
34100
34300
34500
34700
34900
35100
Energy (cm-1)

FIGURE 9B