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PROGRESS REPORT

MOLECULAR DETECTION USING RYDBERG,
AUTOIONIZING, AND CLUSTER STATES

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Abstract

Continuing investigations of multiphoton ionization processes in naphthalene have established the geometry and spectroscopy of trimer and tetramer cluster states. A new, highly efficient ionization mechanism has been identified in the trimer. It is closely related to autoionization of 2-electron atoms by resonant 2-photon excitation and to exciton fusion in larger clusters.

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PROGRESS REPORT

Molecular Detection Using Rydberg, Autoionizing, and Cluster States

1. Introduction

The primary objective of this program is to study multiphoton ionization processes in large aromatic molecules and molecular clusters in order to elucidate their excitation processes. This work is directed toward development of detection methods with improved sensitivity and selectivity. Currently we are exploring new cluster ionization processes. Whereas, molecular monomers ionize by a sequential process described as resonant $(1 + 1)$ ionization, where the first photon interacts with the ground to intermediate state transition normally associated with 1-photon absorption, and the second photon ionizes the intermediate state,^{1,2} our results indicate that trimer clusters of naphthalene ionize by a bimolecular excitonic mechanism. It resembles the exciton fusion process recently discovered by Whetten and coworkers³ for the case of large benzene clusters. However, in the case of small clusters such as naphthalene, the mechanism is actually more closely related to the multiphoton resonant 2-electron autoionization mechanism that induces ionization in 2-electron atoms such as strontium and barium.⁴ Nonetheless, the net result is greatly increased ionization efficiency relative to the monomer, different spectral signatures, and altered intensity dependences.

Ionization processes of monomers have been studied extensively.^{1,2} Figure 1a summarizes the typical 2-color experiment used to probe resonant $(1 + 1)$ ionization. A pulsed laser source is adjusted to wavelength W_1 in resonance with an allowed ground state

to intermediate state transition of the molecule. A second laser beam of wavelength W_2 is scanned over wavelengths spanning the ionization potential. In the most simple case, an onset step, as shown in Figure 2 for the naphthalene monomer, is observed in the spectrum, corresponding to the threshold energy where total photon energy exceeds the lowest ionization potential of the molecule. Below this energy there is little ionization because the overall interaction requires 3 or more photons. Above the energy the ionization signal is relatively constant until the total energy exceeds the energy needed to excite an optically active vibrational state of the ion. In the past, significant deviations were observed from this most basic behavior. Transitions to Rydberg states can occur below the ionization potential. This often results in a series of weak discrete lines that converge to the ionization potential. We observed extensive structure above the ionization potential for naphthalene.⁵ This was explained on the basis of autoionizing Rydberg series converging to higher vibrational ionization limits. These features were highly dependent on the specific vibronic states excited. Spectral features are also observed above the ionization limit corresponding to spectroscopic transitions of the ions formed in the ionization process.⁶ Under appropriate conditions, W_2 induces ion fragmentation in addition to ion formation. The spectra are usually recorded by monitoring the parent ion, therefore fragmentation results in a loss of signal, causing dips in the spectrum. Dips are observed below the ionization threshold due to excitation of dark spectroscopic states. These states are ionized less efficiently than the directly excited states, thus decreasing ionization. Previously, we observed this type of transition for aniline and iodine.

In the case of clusters, several factors are relevant to understanding ionization processes. The ion could have geometry significantly different from the neutral. Whereas the naphthalene monomer ion spectroscopy indicates that monomer ion geometry is little changed from the ground and S_1 states, the dimer S_1 spectra shown in Figure 3 suggest a strong tendency for excimer formation. The evidence is a broad spectral envelope, suggesting a long unresolved vibrational progression in the intermolecular mode, and an anomalously large red shift of the transition. Both of these factors imply formation of an excimer state with stronger intermolecular binding. This effect could occur in the dimer ion as well, and would cause the W_2 ionization spectrum to shift and to greatly broaden. Therefore it would be difficult to observe the ionization threshold, and there would be no evidence of Rydberg or autoionizing levels. The trimer S_1 -- S_0 spectrum is sharp, transitions involving intermolecular vibrational modes are weak, and the energy shift is normal. Thus, there is no evidence of excimer formation. Prior studies suggest that a geometrical barrier or the delocalization of excitation may account for the absence of excimer formation in the trimer and tetramer.⁷ If this is the case, then the trimer should have a simple step function W_2 ionization spectrum, and the threshold would be expected to occur in the low energy portion of the S_1 -- S_0 spectrum.

2. EXPERIMENTAL

The experimental approach is based on 2-color pump probe spectroscopy. Cooled naphthalene clusters are excited to the S_1 states by interaction with a photon of wavelength W_1 . This wavelength is selected to coincide with a strong discrete cluster transition. A probe beam with a time delay greater than the pulse

widths is scanned across the region of the S_1 -- S_0 spectrum and the IP-- S_1 threshold transition. The combined-beam ionization signals are analyzed for ionization in excess of that obtained from the sum of independent W_1 and W_2 beams. This difference represents the processes that require a photon from each of the two sources. It was possible to directly observe signal enhancement as the two beams were moved into spatial overlap, providing the lasers were tuned to appropriate wavelengths. However, it was difficult to maintain stable signal amplitude over the long duration of spectral scans. Therefore, a difference technique was implemented, whereby an oscillating optical wedge deflected beams from overlap on every other pulse. Signals for the nonoverlapped condition were electronically subtracted from overlapping beam signals on a pulse-by-pulse basis, resulting in the difference spectrum.

In Figure 4 the 1-color spectrum of $\bar{8}_0^1$ for the isotopically pure h-8 cluster (a), is compared to the directly recorded 2-color spectrum (b) and to the $W_1 + W_2$ difference spectrum, (c). The difference spectrum is centered near the 1-color transition, however it is substantially broadened relative to the 1-color spectrum. An extensive search for increased trimer ionization in the region corresponding to the monomer ionization transition IP-- S_1 revealed no discernible difference signal. This indicates that resonant (1 + 1) ionization is not important. However, it should be noted that signal-to-noise for the trimer is considerably less than for the monomer, therefore we cannot exclude the possibility that some direct (1 + 1) ionization contributes to the cluster signal. An alternative explanation is that the ion has different geometry from the neutral S_1 trimer, thus the threshold for onset of ionization could be spread over a broad wavelength range, such that it is

unobservable, given the relatively poor available signal-to-noise ratio.

Ionization is clearly enhanced by the combined presence of W_1 and W_2 , when W_2 is scanned in the vicinity of S_1 -- S_0 vibronic transitions. The trimer ionization spectrum does not resemble the monomer S_1 ionization spectrum. Direct 2-color spectra for the HHH and DHD trimers are presented in Figures 4b and 5b. These are to be compared with the corresponding difference spectra of Figures 4c. In each case, the presence of W_1 clearly alters the spectrum recorded by W_2 , revealing broadening and a small red shift, however the enhancement always occurs near the corresponding 1-color transition. These effects were observed under all molecular beam expansion conditions, at all excitation intensities, and for all transitions observed. In no case was there direct evidence of spectral holeburning and there was no apparent tendency to form dimer and monomer species as a result of W_1 excitation.

The isotopically mixed trimer transitions $\bar{8}_0^1$ is particularly interesting. The 1-color spectrum consists of three principal sharp components that are related to the monomer transition: a component derived from the pure protonated molecule (H) at 32372 cm^{-1} and the split pair of components, related to the deuterated pair of molecules (DD), at 32461 and 32478 cm^{-1} . In the 2-color experiment, all three sharp components are attenuated in the presence of W_1 , which is resonant with the H transition. The reduction in all three components demonstrates the coupled nature of the trimer transitions.

Preliminary time dependence studies were performed in order to test the consistency of the model. The combined $W_1 + W_2$ signal was maximum when W_2 followed W_1 by 2 to 10 ns. The signal was less than

noise for longer delays. This observation is consistent with the proposed model, provided the lifetime of the electronically excited cluster is approximately 10 ns (The monomer lifetime for $\bar{8}_0^1$ is 317 ns).

3. DISCUSSION

Holeburning is a competing process which could influence the ionization spectra recorded in 2-color experiments. In this process, the inhomogeneous subset of clusters resonant with W_1 would be depleted by the W_1 exciting beam. Then the W_2 signal would decline as W_2 is scanned over W_1 . The situation could be relatively complex, with a distribution of inhomogeneous widths for clusters of different initial temperatures. Inhomogeneous holeburning spectra were simulated for parameters appropriate to the naphthalene clusters, resulting in the spectra presented in Figure 6. The model includes two sets of molecules, one cool, and the other at elevated temperature. Fluence, homogeneous relaxation rates, and temperature parameters were varied in order to test for the spectral signature of holeburning. The simulated spectra always displayed evidence of a dip at line center. This was not observed under any conditions. Therefore, holeburning is not important under our experimental conditions.

The 2-color ionization spectra were modeled by incoherent population rate equations,^{1,8} with provision made for excitation by a W_1 beam at constant excitation rate combined with the spectrally varying excitation rate for the W_2 beam. Justification for use of the incoherent kinetic master equation treatment is based on the chaotic temporal characteristics of the pulsed laser source.⁹ Lorentzian line shapes were assumed, with characteristic half widths

at half height of 1 cm^{-1} for the first $S_1 \rightarrow S_0$ absorption and 50 cm^{-1} for the second autoionizing step. The cross section for the first step was assumed to be 10^{-13} cm^2 (calculated for the ultracold cluster, assuming a 10 ns nonradiative lifetime and Franck-Condon factors appropriate to the monomer) and for the second step, the cross section was reduced by a factor equal to the ratio of linewidths of the first to second steps. In Figure 7 the simulated 2-color spectra are shown for various ratios of intensities of the W_1 to W_2 beams. These predicted spectral profiles closely simulate the observed 2-color spectra. (It was difficult to control the relative intensities in the experimental measurements, however it is clear from a review of the extensive data, that observed spectra are well described by the predicted profiles.) At low W_1 and W_2 fluences, sharp spectra are predicted, and as W_2 increases, simple broadening is predicted. As W_1 fluence increases, the sharp transition is predicted to decrease in amplitude, and rounded shoulders appear on the wings, extending approximately 30 cm^{-1} from line center. Experimental results fully demonstrate these predicted characteristics. If this model is applied to conventional resonant $(1 + 1)$ ionization, it predicts the spectra would consist of a sharp component superimposed on a flat baseline. The amplitude of the baseline would increase relative to the sharp component as W_1 fluence increases.

The above considerations support the resonant 2-photon autoionization model for trimer ionization. The ground state based vibronic transitions are strong, with optical cross sections on the order of 10^{-13} cm^2 , versus a cross section of $1.6 \times 10^{-19} \text{ cm}^2$ for the monomer S_1 ionization transition (denoted $\text{ion} \rightarrow S_1$). Thus, the ionization step limits the overall rate of $(1 + 1)$ ionization in the

monomer, whereas large cross sections govern the transitions in the case of trimer autoionization. The broadening and shift of the combined $W_1 + W_2$ spectrum is also in accord with the model, implying an autoionization lifetime on the order of 50 fs. The red shift indicates increased intermolecular interaction relative to the neutral excited states, and this is consistent with expectations for long range intermolecular interactions. The results have important implications for 1-color 2-photon ionization spectroscopy of clusters. Spectra obtained by this technique are governed by a convolution of spectra for the first and second photon. Since the second photon interacts with a broadened, shifted transition, the excitation spectrum for the overall process will be appropriately modulated by this component, leading to intensity dependent broadening. The implications of these results is that small size homomolecular van der Waals clusters will ionize by the autoionization mechanism, provided the intermediate state is stable on the time scale of the excitation pulse.

REFERENCES

1. V. S. Letokhov, "Laser Photoionization Spectroscopy", Academic Press, Orlando 1987.
2. S. H. Lin, Y. Fujimura, H. H. Neusser, and E. W. Schlag, Multiphoton Spectroscopy of Molecules, Academic Press, Orlando, 1984.
3. K. E. Schriver, M. Y. Hahn, and R. L. Whetten, Phys. Rev. Lett. 59,1906 (1987).
4. W. E. Cooke, T. F. Gallagher, S. A. Edelstein, and R. M. Hill, Phys. Rev. Lett. 40, 178 (1978); W. E. Cooke and T. F.

- Gallagher, Phys. Rev. Lett., **41**, 1648 (1978); R. S. Berry, Phys. Rev. **A31**, 3059 (1984); W. Vassen, Zeitschrift f. Physik, **8**, 149 (1988); P. Lambropoulos, Phys. Rev. **A** Dec (1988); W. Cooke, Phys. Rev. **A** May, (1989).
5. J. A. Syage and J. E. Wessel, J. Chem. Phys. **87**, 6207 (1987).
 6. J. A. Syage and J. E. Wessel, J. Chem. Phys. **87**, 3313 (1987); J. A. Syage and J. E. Wessel, Appl. Opt. **26**, 3573 (1987).
 7. J. A. Syage and J. E. Wessel, J. Chem. Phys. **89**, 5962 (1988); J. Wessel and J. A. Syage, J. Phys. Chem. **XXX** (1989).
 8. P. M. Johnson, M. R. Berman, and D. Zakheim, J. Chem. Phys. **62**, 2500, (1975); M. B. Robin, Appl. Opt. **19**, 3941 (1980).
 9. I. Schek and J. Jortner, Chem. Phys. **97**, 1 (1985).
 10. U. Boesl, H. J. Neusser, and E. W. Schlag, Chem. Phys. **55**, 193 (1981).

FIGURES

1. 2-photon ionization processes include (a) resonant ($1 + 1$) ionization, (b) exciton fusion where the wiggly arrow represents diffusion and the curved arrow represents ionization subsequent to exciton encounter, and (c) 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.
2. Resonance 2-color ionization spectrum of naphthalene monomer. The W_1 laser is in resonance with $\bar{8}_0^1$, and the W_2 laser is

scanned across the vibrationless ionization threshold at 301 nm.

3. Resonance 2-photon ionization spectrum of the naphthalene dimer.
4. Observed cluster ionization spectra for $\bar{8}_0^1$ of the isotopically pure protonated trimer (HHH) recorded (a) with W_1 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.
5. Observed cluster ionization spectra for $\bar{8}_0^1$ of the mixed isotope trimer (DHD) recorded (a) with W_1 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.
6. Simulated inhomogeneous hole burning spectra. Two inhomogeneous thermal distributions are considered, one with a temperature of 10 K and a second 50 K distribution. A laser at $W_1 = 0$ burns holes in the distributions and a low intensity laser at W_2 is scanned over the resultant distribution, generating the signal intensity represented on the vertical axis. The different curves correspond to increasing products of W_1 fluence times removal cross section (P) (a) $P = 24.3$, (b) $P = 8.1$, (c) $P = 2.7$, (d) $P = 0.9$, (f) $P = 0.3$, and (g) $P = 0.1$.
7. Simulated spectrum for the autoionizing 2-photon cluster excitation mechanism, calculated using incoherent population rate equations for various transition rates induced by the W_1 beam: (a) 0, (b) 3×10^7 , (c) 1×10^8 , (d) 3×10^8 , and (e) 1×10^9 /s.

PUBLICATIONS

J. A. Syage and J. E. Wessel, "Resonance Interactions in Naphthalene Clusters," (accepted by J. Phys. Chem.)

J. Wessel, "Bimolecular Autoionization in the Naphthalene Trimer Cluster," (to be submitted to Phys. Rev. Lett.) included as an appendix

PRESENTATIONS

J. E. Wessel and J. A. Syage, "Resonant Two-Photon Ionization Spectroscopy of Naphthalene Clusters," International Laser Science Conference, Atlanta, Georgia October, 1988.

J. E. Wessel, "Resonance Interactions in Naphthalene Clusters," University of Pennsylvania Chemistry Department, Philadelphia, Pennsylvania, December, 1988. (invited)

J. E. Wessel, "Resonance Interactions in Naphthalene Clusters," Informal Conference on Photochemistry, Santa Monica, California, January, 1989. (invited)

J. E. Wessel, "Resonance Interactions in Naphthalene Clusters," Quantum Electronics and Laser Science Conference, Baltimore, April, 1989.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

BIMOLECULAR AUTOIONIZATION IN THE NAPHTHALENE TRIMER CLUSTER

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Spectroscopy of atomic and molecular clusters is currently receiving intense scientific attention because it provides direct insight into the evolution of properties from atomic scale to bulk crystalline systems.¹⁻³ It impacts disciplines ranging from metallurgy and semiconductor physics to molecular biology. Problems addressed by cluster spectroscopy include properties of the long range intermolecular potential,⁴ the nature of critical phenomena,⁵ the dynamics of phase transitions,⁶ and the relationship between surface states and bulk states of matter.⁷ Recently, Whetten and coworkers⁸ concluded that large benzene clusters ionize by an exciton fusion mechanism, involving diffusion and bimolecular annihilation of excitonic states to form ions. This mechanism was found to be far more efficient than conventional resonance (1 + 1) ionization of monomer benzene. It is essentially the same as the exciton annihilation mechanism previously identified in bulk crystals.⁹⁻¹¹ This letter presents direct spectroscopic evidence in support of a bimolecular excitonic ionization process in the naphthalene trimer cluster. In this case, the participating excitonic states are spectroscopically resolved.

The exciton fusion mechanism shares some characteristics of resonant multiphoton excitation of autoionizing 2-electron atoms, such as strontium¹² and barium.¹³ In this case, highly efficient ionization occurs when the two $6s^2$ electrons are excited ($6s^2 \rightarrow 6p^1 s^1 \rightarrow 20s^1 6s^1 \rightarrow 20s^1 6p^1$) in the overall 3-photon process, leading to a final state above the lowest ionization potential. Configurational mixing with the lower energy ionization continua results in rapid autoionization, however the mixing is insufficient to destroy the discrete spectrum associated with absorption of the third photon. Therefore the cross section for the third interaction remains large, even though the final state is above the ionization limit. The atomic process, which has been used extensively in fundamental

studies,¹²⁻¹⁵ is similar to the recently discovered autoionizing biexcitons in semiconductor crystals.⁹

In this letter we present evidence that suggests small homomolecular van der Waals clusters ionize by a process analogous to 2-photon autoionization of the 2-electron atom. The process enhances ionization efficiency and strongly modulates the resonance (1 + 1) ionization spectra. Weakly bound van der Waals molecular clusters are attractive subjects for fundamental studies because the cluster states are closely related to well understood monomer molecular states.^{16,17} Resonant (1 + 1) ionization (Figure 1a) is commonly used for spectroscopy of these systems because it provides the requisite sensitivity to conduct mass resolved detection on low density clusters formed in a supersonic expansion. Resonant (1 + 1) ionization is well understood for monomer atomic and molecular systems.^{18,19}

The electronic spectra of trimer clusters of aromatic hydrocarbons are now well established. Both benzene¹⁶ and naphthalene¹⁷ trimer spectra are characterized by exciton-like splittings in electronic transitions between the ground (S_0) and first excited electronic state (S_1) of the neutral clusters. Each parent monomer state contributes a cluster state energetically near the parent monomer vibronic state. Resonant interaction (multipolar and possibly higher order effects) induce splittings of 1 to 20 cm^{-1} between related components. Each excited cluster state extends over the monomer units of the cluster. The 1-color spectrum of the isotopically pure protonated naphthalene trimer (HHH) measured in the region of the strong vibronically induced transition (denoted $\bar{8}_0^1$, corresponding to excitation of one quantum of vibrational mode 8 of b_{1g} symmetry in the S_1 state) is shown in Figure 2a. Only one component is observed for this transition because the monomer transition moments are all parallel in the trimer structure. Under these conditions, only the lowest energy component carries oscillator strength in ground state based transitions. This component is displaced 16 cm^{-1} below the bandcenter energy for the vibronic level. The sharp spectral transitions indicate that rapid dynamics do not occur in the S_1 state, and the lack of prominent intramolecular vibrational transitions indicates that the cluster geometry does not change substantially between ground and excited states.

The naphthalene trimer ionization potential is not well established. Ionization occurs at 8.142 eV in the monomer,²⁰ therefore $\bar{7}_0^1$ is the first monomer vibronic band which leads to direct (1 + 1) ionization. In the case of the trimer, $\bar{8}_0^1$ is the first strong (1 + 1) ionization transition.

Spectroscopic results presented below indicate that optical transitions in molecules of the trimer are relatively weakly coupled, and thus resemble the barium autoionizing transition cited above, in which the $s^2-s^1p^1$ transition is weakly coupled to $s^1p^1-p^2$. Cluster transitions with monomer ground state parentage provide large cross sections for interaction with the second photon. If the ionization potential is exceeded when two photons are absorbed, then autoionization will occur. The second transition is subject to spectral shifts as a result of the altered intermolecular interactions, in the same way that configurational interaction in barium alters $s^1p^1-p^2$ relative to $s^2-s^1p^1$ or bandgap renormalization influences nonlinear spectroscopy in semiconductors.

In the cases of benzene, naphthalene, and anthracene clusters, the 2-photon annihilation energy can exceed the cluster ionization potential. Whetten et al.⁸ conclude that the encounter rate should be on the subnanosecond time scale in benzene clusters with $n > 20$, thus accounting for rapid ionization. These authors recognized that ground to excited state discrete transitions have cross sections orders of magnitude larger than cross sections for intermediate state to ionization continuum absorption. Thus, they concluded that exciton fusion ionization should be far more efficient than direct resonance (1 + 1) ionization.

The experimental approach is based on 2-color pump probe spectroscopy. Cooled naphthalene clusters are excited to the S_1 states by interaction with a photon of wavelength W_1 . This wavelength is selected to coincide with a strong discrete cluster transition. A probe beam of wavelength W_2 with a time delay greater than the pulse widths is scanned across the S_1-S_0 spectrum and the IP- S_1 threshold transition. The combined-beam ionization signals are analyzed for ionization in excess of that obtained from the sum of independent W_1 and W_2 beams. This difference represents the processes that require a photon from each of the two sources. It was possible to directly observe signal enhancement as the two beams

were moved into spatial overlap, providing the lasers were tuned to appropriate wavelengths. However, it was difficult to maintain stable signal amplitude over the long duration of spectral scans. Therefore, a difference technique was implemented, whereby an oscillating optical wedge deflected beam overlap on every other pulse. Signals for the nonoverlapped condition were electronically subtracted from overlapping beam signals on a pulse-by-pulse basis, resulting in the difference spectrum.

In Figure 2 the 1-color spectrum of $\bar{g}_0^1$ for the isotopically pure h-8 cluster (a), is compared to the directly recorded 2-color spectrum (b) and to the $W_1 + W_2$ difference spectrum, (c). The difference spectrum is centered near the 1-color transition, however it is substantially broadened relative to the 1-color spectrum. An extensive search for increased trimer ionization in the region corresponding to the monomer ionization transition $IP \rightarrow S_1$ revealed no discernible difference signal. This indicates that resonance $(1 + 1)$ ionization is not important. However, it should be noted that signal-to-noise for the trimer is considerably less than for the monomer, therefore we cannot exclude the possibility that some direct $(1 + 1)$ ionization contributes to the cluster signal. An alternative explanation is that the ion has different geometry from the neutral S_1 trimer, thus onset of ionization could be spread over a broad wavelength range, such that it is unobservable, given the relatively poor available signal-to-noise ratio.

Ionization is clearly enhanced by the combined presence of W_1 and W_2 , when W_2 is scanned in the vicinity of $S_1 \rightarrow S_0$ vibronic transitions. The trimer ionization difference spectrum does not resemble the monomer S_1 ionization spectrum. Direct 2-color spectra for the isotopically pure trimer HHH and the mixed isotope DHD trimer are presented in Figures 2b and 3b. These are to be compared with the corresponding difference spectra of Figures 2c and 3c. In each case, the presence of W_1 clearly alters the spectrum recorded by W_2 , revealing broadening and a small red shift, however the enhancement always occurs near the corresponding 1-color transition. These effects were observed under all molecular beam expansion conditions, at all excitation intensities, and for all transitions observed. In no case was there direct evidence of spectral holeburning and fragmentation into monomer and

dimer ions was not significantly enhanced in the presence of W_1 excitation.

The isotopically mixed trimer transitions $\bar{8}_0^1$ is particularly interesting. The 1-color spectrum consists of three principal sharp components that are related to the monomer transition. A component corresponding to the H molecule occurs at 32372 cm^{-1} and a pair of components at 32461 and 32478 cm^{-1} correspond to the two D molecules. In the 2-color experiment, all three sharp components are attenuated in the presence of W_1 , which is resonant with the H transition. The reduction in all three components demonstrates the coupled nature of the trimer transitions.

Holeburning is a competing process which could influence ionization spectrum recorded in 2-color experiments. In this process, the inhomogeneous subset of clusters resonant with W_1 would be depleted by the W_1 exciting beam. Then the W_2 signal would decline as W_2 is scanned over W_1 . The situation could be relatively complex, with a distribution of inhomogeneous widths for clusters of different initial temperatures. Inhomogeneous holeburning spectra were simulated for parameters appropriate to the naphthalene clusters, resulting in the spectra presented in Figure 4. The model includes two sets of molecules, one cool, and the other at elevated temperature. Fluence, homogeneous relaxation rates, and temperature parameters were varied in order to test for the spectral signature of holeburning. The simulated spectra always displayed a characteristic dip at line, whereas this was not observed. Therefore holeburning was not important under prevailing experimental conditions.

The 2-color ionization spectra were modeled by incoherent population rate equations,^{18,21} with provision made for excitation by a W_1 beam at constant excitation rate combined with the spectrally varying excitation rate for the W_2 beam. Justification for use of the incoherent kinetic master equation treatment is based on the chaotic temporal characteristics of the pulsed laser source.²² Lorentzian line shapes were assumed, with characteristic half widths at half height of 1 cm^{-1} for the first S_1 -- S_0 absorption and 50 cm^{-1} for the second autoionizing step. The cross section for the first step was assumed to be 10^{-13} cm^2 (calculated for the ultracold cluster, assuming a 10 ns nonradiative lifetime and Franck-Condon factors appropriate to the monomer) and for the second step, the cross

section was reduced by a factor equal to the ratio of linewidths of the first to second steps. In Figure 5 the simulated 2-color spectra are shown for various ratios of intensities of the W_1 to W_2 beams. These predicted spectral profiles closely simulate the observed 2-color spectra. (It was difficult to control the relative intensities in the experimental measurements, however it is clear from a review of the extensive data, that observed spectra are well described by the predicted profiles.) At low W_1 and W_2 fluences, sharp spectra are predicted, and as W_2 increases, simple broadening is predicted. As W_1 fluence increases, the sharp transition is predicted to decrease in amplitude, and rounded shoulders appear on the wings, extending approximately 30 cm^{-1} from line center. Experimental results fully demonstrate these predicted characteristics. If this model is applied to conventional resonance ($1 + 1$) ionization, it predicts the spectra would consist of a sharp component superimposed on a flat baseline. The amplitude of the baseline would increase relative to the sharp component as W_1 fluence increases. Therefore these results provide strong support for the autoionization model.

Preliminary time dependence studies were performed in order to test the consistency of the model. The combined $W_1 + W_2$ signal was maximum when W_2 followed W_1 by 2 to 10 ns. The signal was less than noise for longer delays. This observation is consistent with the proposed model, provided the lifetime of the electronically excited cluster is approximately 10 ns (versus 317 ns for $\bar{B}_0^1$ in the monomer).

The above considerations support the resonant 2-photon autoionization model for trimer ionization. The ground state based vibronic transitions are strong, with optical cross sections on the order of 10^{-13} cm^2 , versus a cross section of $1.6 \times 10^{-19}\text{ cm}^2$ for the monomer S_1 ionization transition (denoted ion-- S_1). Thus, the ionization step limits the overall rate of $1 + 1$ ionization in the monomer, whereas large cross sections govern the transitions in the case of trimer autoionization. The broadening and shift of the combined $W_1 + W_2$ spectrum is also in accord with the model, implying an autoionization lifetime on the order of 50 fs. The red shift indicates increased intermolecular interaction relative to the neutral excited states, and this is consistent with expectations for long range

intermolecular interactions. The results have important implications for 1-color 2-photon ionization spectroscopy of clusters. Spectra obtained by this technique are governed by a convolution of spectra for the first and second photon. Since the second photon interacts with a broadened, shifted transition, the excitation spectrum for the overall process will be appropriately modulated by this component, leading to intensity dependent broadening. The implications of these results is that small size homomolecular van der Waals clusters will ionize by the autoionization mechanism, provided the intermediate state is stable on the time scale of the excitation pulse.

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REFERENCES

1. S. Sugano, Y. Nishina, and S. Ohnishi, *Microclusters*, Springer-Verlag, New York, 1987.
2. A. W. Castleman, Jr., R. G. Keese, *Science*, **241**, 36 (1988).
3. see review issues: *Chem Rev.* **86**, No. 3 (1986); *J. Phys. Chem.* **91**, No. 10 (1987).
4. A. D. Buckingham, P. W. Gowler, and J. M. Hutson, *Chem. Rev.* **88**, 963 (1988).
5. F. F. Abraham, *Homogeneous Nucleation Theory*, Academic Press, New York, 1974.
6. K. Binder and M. H. Kalos, in *Monte Carlo Methods in Statistical Physics*, Ch. 1; H. Muller-Krumbhaar, *ibid*, Ch. 5.
7. S. M. Beck, *J. Chem. Phys.* **XXX** (1989).
8. K. E. Schriver, M. Y. Hahn, and R. L. Whetten, *Phys. Rev. Lett.* **59**, 1906 (1987).
9. M. Combescot and R. Combescots, *Phys. Rev. B* **15** Aug., 1989,
10. W. Knox, *Theory of Excitons*, Wiley, New York.

11. M. Pope and C. E. Swenberg, *Ann. Rev. Phys. Chem.* **36**, 613 (1985).
12. W. E. Cooke, T. F. Gallagher, S. A. Edelstein, and R. M. Hill, *Phys. Rev. Lett.* **40**, 178 (1978).
13. W. E. Cooke and T. F. Gallagher, *Phys. Rev. Lett.*, **41**, 1648 (1978).
14. R. S. Berry, *Phys. Rev.* **A31**, 3059 (1984); W. Vassen, *Zeitschrift f. Physik*, **8**, 149 (1988).
15. P. Lambropoulos, *Phys. Rev.* **A** Dec (1988); W. Cooke, *Phys. Rev.* **A** May, (1989).
16. K. O. Bornsen, S. H. Lin, H. L. Selzle, and E. W. Schlag, *J. Chem. Phys.* **90**, 1299 (1989).
17. J. A. Syage and J. E. Wessel, *J. Chem. Phys.* **89**, 5962 (1988); J. Wessel and J. A. Syage, *J. Phys. Chem.* **XXX** (1989).
18. V. S. Letokhov, *Laser Photoionization Spectroscopy*, Academic Press, Orlando 1987.
19. S. H. Lin, Y. Fujimura, H. H. Neusser, and E. W. Schlag, *Multiphoton Spectroscopy of Molecules*, Academic Press, Orlando.
20. M. A. Duncan, T. G. Dietz, and R. E. Smalley, *J. Chem. Phys.* **75**, 2118 (1981).
21. P. M. Johnson, M. R. Berman, and D. Zakheim, *J. Chem. Phys.* **62**, 2500, (1975); M. B. Robin, *Appl. Opt.* **19**, 3941 (1980).
22. I. Schek and J. Jortner, *Chem. Phys.* **97**, 1 (1985).
23. U. Boesl, H. J. Neusser, and E. W. Schlag, *Chem. Phys.* **55**, 193 (1981).

FIGURES

1. 2-photon ionization processes include (a) resonant ($1 + 1$) ionization, (b) exciton fusion where the wiggly arrow represents diffusion and the curved arrow represents ionization subsequent to exciton encounter, and (c) 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.

2. 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.
3. Observed cluster ionization spectra for $\bar{8}_0^1$ of the mixed isotope trimer (DHD) 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.
4. Simulated inhomogeneous hole burning spectra. Two inhomogeneous thermal distributions are considered, one with a temperature of 10 K and a second 50 K distribution. A laser at $W1 = 0$ burns holes in the distributions and a low intensity laser at W2 is scanned over the resultant distribution, generating the signal intensity represented on the vertical axis. The different curves correspond to increasing products of W1 fluence times removal cross section (P) (a) $P = 24.3$, (b) $P = 8.1$, (c) $P = 2.7$, (d) $P = 0.9$, (f) $P = 0.3$, and (g) $P = 0.1$.
5. Simulated spectrum for the autoionizing 2-photon cluster excitation mechanism, calculated using incoherent population rate equations for various transition rates induced by the W1 beam: (a) 0, (b) 3×10^7 , (c) 1×10^8 , (d) 3×10^8 , and (e) 1×10^9 /s.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5