

Biexcitonic Autoionization in Naphthalene Trimer Clusters

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Exciton annihilation processes involving biexcitonic interactions are known to efficiently ionize molecular and semiconductor crystals and large molecular clusters. We present the first spectroscopic evidence for biexcitonic two-photon ionization of small molecular clusters. In this case the process resembles resonant multiphoton autoionization of two-electron atoms.

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Atomic and molecular cluster spectroscopy 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 co-workers⁸ concluded that large benzene clusters ($n > 20$) ionize by an exciton annihilation mechanism, involving sequential excitation of two or more molecules in the cluster. They described the ionization process in terms of diffusion and annihilation involving a pair of excitonic states. This accounted for the anomalously high efficiency observed for cluster photoionization. Previously, biexcitonic annihilation was identified in bulk molecular crystals⁹ and indirect evidence was obtained for biexcitonic autoionization in gallium arsenide.^{10,11} Whereas biexcitons in semiconductor crystals are characterized by the large dimensions of Wannier excitons, tightly bound Frenkel excitons in molecular crystals are comparable to the size of small molecular clusters. In this Letter we present the first direct spectroscopic evidence in support of a biexcitonic autoionization process for the naphthalene trimer cluster.

The exciton annihilation mechanism shares some characteristics of resonant multiphoton excitation of autoionizing two-electron atoms, such as strontium¹² and barium.¹³ In barium, for example, highly efficient ionization occurs when two $6s^2$ electrons are sequentially excited in the overall three-photon process $6s^2-6p^1s^1-20s^16s^1-20s^16p^1$, 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 $6s-6p$ character associated with the third photon resonance, although this resonance is shifted by configuration interaction and broadened relative to the ground-state-based resonance. This leads to a characteristic power-dependent spectral signature. However, ionization excitation spectra for large molecular clusters

and bulk crystals are dominated by the one-photon ground-state absorption spectra, because the majority of second photon interaction events occur at a substantial distance from the original site.

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.^{14,15} Resonant (1+1) ionization^{16,17} [Fig. 1(a)] is commonly used for spectroscopy of these systems because it provides the sensitivity required for mass-resolved detection of low-density clusters formed in a supersonic expansion. The electronic spectra of trimer clusters of benzene¹⁴ and naphthalene¹⁵ are characterized by excitonlike 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 related to the parent monomer vibronic state. Resonant interaction (multipolar and possibly higher-order effects) induce splittings (related to factor group splittings of molecular crystals) of from 1 to 20 cm^{-1} between relat-

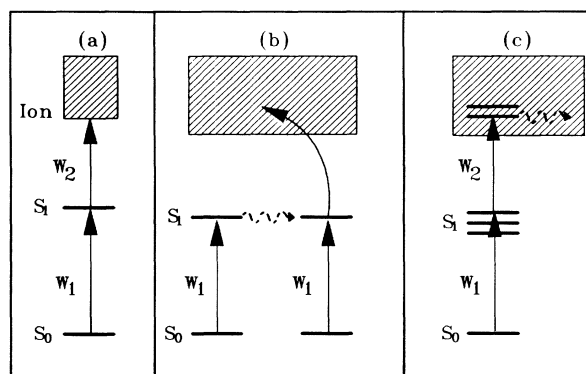


FIG. 1. Two-photon ionization processes include (a) resonant (1+1) ionization; (b) exciton annihilation, where the wiggly arrow represents exciton transport and the curved arrow represents ionization subsequent to exciton encounter; and (c) resonant two-photon autoionization, where the multiplet of levels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

ed components. The one-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_{3g} symmetry in the S_1 state) is shown in Fig. 2, curve *a*. Only one component is observed for this transition because the monomer transition moments are all parallel in the trimer structure (shown in the inset in Fig. 2, as derived¹⁵ from a dipolar interaction analysis of the trimer spectrum). The trimer ionization potential (IP) is not yet established; however, two photons in resonance with $\bar{8}_0^1$ are expected to exceed the trimer IP (which is below the monomer IP of 65665 cm^{-1} , Ref. 18).

Our experimental investigations are based on two-color pump-probe spectroscopy. Naphthalene clusters, cooled below 100 K rotational and vibrational temperature in a supersonic expansion (experimental details appear elsewhere¹⁵), 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 , time delayed by 10 ns (W_1 and W_2 pulse widths are 5 ns), is scanned across the S_1 - S_0 spectrum and the region of the IP- S_1 threshold. The combined-beam ionization signals are analyzed for ionization in excess of the sum of independent W_1 and W_2 beam signals. This represents processes requiring 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. The signal of interest was improved by implementing a difference technique whereby an oscillating

optical wedge deflected beam overlap on every other pulse. Signals for the nonoverlapped condition were electronically subtracted from overlapping beam signals.

In Fig. 2 the one-color spectrum of $\bar{8}_0^1$ for the isotopically pure *h*-8 cluster (curve *a*) is compared to the directly recorded two-color spectrum (curve *b*) and to the W_1+W_2 difference spectrum (curve *c*). The difference spectrum is centered near the one-color transition, and it is substantially broadened relative to the one-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 resonance (1+1) ionization is not important. However, it should be noted that the signal-to-noise ratio 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.] Ionization is enhanced whenever both W_1 and W_2 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- S_1) observed for the monomer. In this case the signal rises abruptly to a plateau when the total energy exceeds the ionization potential. The new spectral characteristics suggest the ionization mechanism involves two ground-state-based S_1 - S_0 transitions.

One-color and two-color spectra are presented for the isotopically mixed DHD trimer in Fig. 3, curves *a* and *b*. The one-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 (there is

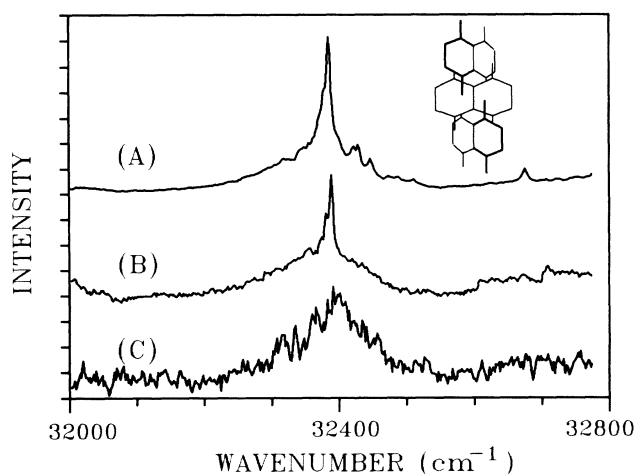


FIG. 2. Observed cluster ionization spectra for $\bar{8}_0^1$ of the isotopically pure protonated trimer (HHH) recorded (curve *a*) with W_1 only (one color), (curve *b*) two color with overlapping beams, and (curve *c*) the difference spectrum, where the nonoverlapping beam spectrum is subtracted from the overlapping beam spectrum.

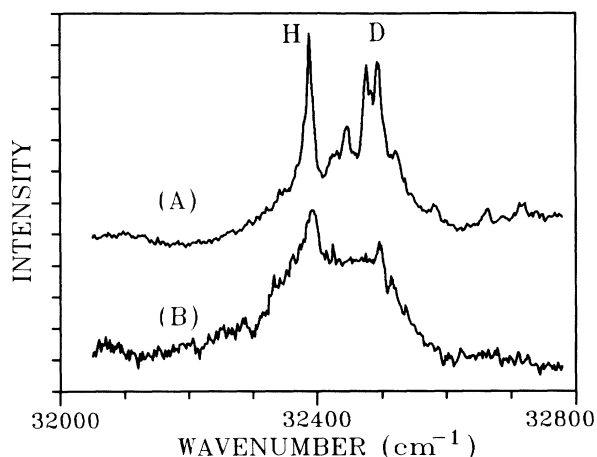


FIG. 3. Observed cluster ionization spectra for $\bar{8}_0^1$ of the mixed isotope trimer (DHD) recorded (curve *a*) with W_1 only (one color) and (curve *b*) two color with overlapping beams. Transitions to states primarily associated with protonated molecules are labeled H and those derived from deuterated molecules are labeled D.

no evidence of multiple permutational isotopic conformers such as DHD and HHD¹⁵). In the two-color experiment, all three sharp components are attenuated when W_1 is resonant with the H transition. The presence of W_1 clearly alters the W_2 spectrum, revealing broadening and a small redshift.¹⁹ The enhancement always occurs near the corresponding one-color transition. The reduction in all three DHD components demonstrates the coupled nature of the trimer transitions. These effects were observed under all molecular-beam expansion, at all excitation intensities, and for all transitions observed. In no case was there direct evidence of spectral hole burning²⁰ and fragmentation into monomer and dimer ions was not significantly enhanced in the presence of W_1 excitation.

The two-color ionization spectra were modeled by incoherent population rate equations,^{16,21} with provision made for excitation by a W_1 beam at a constant excitation rate, combined with a spectrally varying excitation rate for the W_2 beam. Use of the incoherent kinetic master-equation treatment is justified on the basis of 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 monomer²³) 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 Fig. 4 the simulated two-color spectra are shown for various W_1 intensities. These predicted

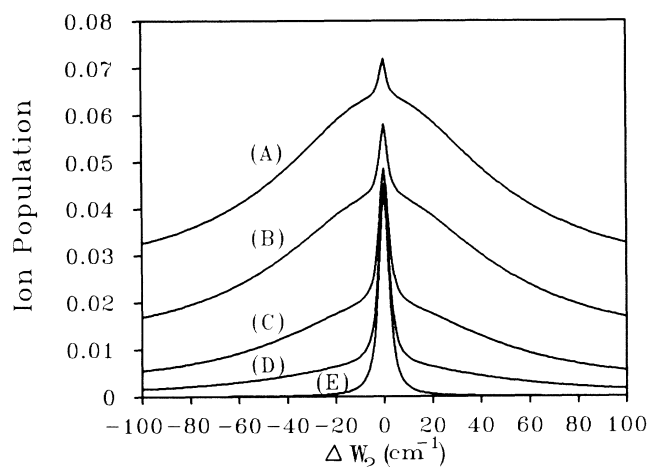


FIG. 4. Simulated spectrum for the autoionizing two-photon cluster excitation mechanism, calculated for various intensities of the fixed frequency W_1 beam corresponding to one-color excitation rates: curve a, 0; curve b, $3 \times 10^7/\text{s}$; curve c, $1 \times 10^8/\text{s}$; curve d, $3 \times 10^8/\text{s}$; and curve e, $6 \times 10^8/\text{s}$. The intensity chosen for the scanned W_2 beam provides a one-color excitation rate of $1 \times 10^9/\text{s}$ at line center.

spectral profiles closely simulate the observed two-color spectra. At low W_1 and W_2 fluences, sharp spectra are predicted, and broadening occurs as W_2 increases. With increased W_1 fluence, the amplitude of the sharp transition decreases 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 base line. The amplitude of the base line would increase relative to the sharp component as W_1 fluence increases. Therefore, these results provide strong support for the autoionization model.

Rudimentary 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 (vs 317 ns for $\bar{8}_0^1$ in the monomer). Fluorescence lifetime measurements were attempted; however, it was not possible to identify signals arising from the trimer. (Fluorescence signal strength relative to the monomer was substantially less than observed by ionization methods.)

The above considerations support the resonant two-photon autoionization mechanism 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 $1.6 \times 10^{-19} \text{ cm}^2$ (Ref. 24) for the monomer S_1 ionization transition (IP- 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 100 fs, which is comparable to autoionization rates measured for Rydberg states of the monomer²⁵ that are isoenergetic with cluster biexcitonic states. The redshift indicates excitonic interactions are attractive as in semiconductor biexcitonic states; however, the lifetime determined molecular biexciton width is as large as the binding, in contrast to semiconductors, where binding exceeds linewidth.¹¹ 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. 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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