## **Multistate Isomerization of Size-Selected Clusters**

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The electronic spectra of mass-specific dichloroanthracene  $Kr_N$  clusters were interrogated by resonant two-photon two-color ionization. A novel effect of abrupt spectral line narrowing with increasing cluster size at N=17 was observed, which signals the nonrigid-to-rigid, collective, three-dimensional, multistate isomerization in the heterocluster.

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Phase transformations in finite systems<sup>1,2</sup> are of considerable conceptual interest. While the monotonic decrease of the melting temperature with decrease of the particle size has long been predicted<sup>3</sup> and experimentally documented for (supported) metal clusters,<sup>4</sup> a satisfactory description of a "melting transition" in clusters<sup>5-14</sup> is In clusters of a method of the method of th synonymous to isomerization between a multitude of isomers, with the underlying physical processes exhibiting dynamic size effects.  $^{6-14}$  At the lower end of the size spectrum the phase space of the system is characterized by a small number of isomers between which isomerization proceeds in a diffusionless manner.<sup>6,11</sup> As the cluster size increases, the number of accessible isomers becomes frighteningly large (e.g., a lower limit of 988 isomers for  $Ar_{13}$ ), <sup>23</sup> resulting in hierarchical multistate isomerization, with the onset of the breakdown of the separation of time scales between interwell and intrawell motion.<sup>5,7-9</sup> Soft modes and diffusive intracluster motion set in  $^{7-9}$  with coexistence between different isomers for distinct clusters. Interphase (rigid-nonrigid) coexistence within the same cluster<sup>6-11</sup> is manifested for large clusters, which are characterized by a dense spectrum of accessible isomers separated by thermally surmountable barriers, whereupon the separability of time scales breaks down.

Experimental interrogation of cluster isomerization can rely on vibrational<sup>24</sup> or electronic<sup>19–22,25</sup> spectroscopy of a guest molecule in a heterocluster, which acts as a probe for the cluster nuclear dynamics.<sup>25</sup> Early studies of vibrational spectra of SF<sub>6</sub>· Ar<sub>N</sub><sup>24</sup> and electronic spectra of tetracene· Ar<sub>N</sub><sup>25</sup> clusters were not mass specific, being hampered by "trivial" inhomogeneous broadening, which originates from the cumulative absorption of clusters of a different size. Mass-selective spectroscopy is essential to explore the "intrinsic" inhomogeneous broadening due to different isomers of the same size. Leutwyler and Bösiger<sup>19–22</sup> pioneered the study of isomerization processes in 2D for mass-selected carbazole·Ar<sub>N</sub> heteroclusters by the resonant two-photon one-color ionization (R2P1CI) method. This method may be fraught with experimental difficulties because of the possibility of fragmentation of the cluster ion, which is produced with considerable excess vibrational energy.<sup>26</sup> R2P1CI mass-resolved spectra may be shifted and broadened because of the contribution from fragments of higher clusters. To overcome the difficulty inherent in the R2P1CI method a two-photon two-color ionization technique should be employed. By an appropriate choice of the energy of the second photon, the cluster ion is produced with low excess energy, resulting in fragmentation-free spectra.

We have utilized the resonant two-photon two-color ionization (R2P2CI) method to interrogate the  $S_0 \rightarrow S_1$ spectra of mass-specific heteroclusters of 9,10-dichloroanthracene (DCA) with Ar or Kr. The choice of DCA as the probe molecule in the heterocluster was motivated by the small external heavy-atom effect on intersystem crossing in DCA  $\cdot R_N$  (R = Ar, Kr, Xe) clusters,<sup>27</sup> which facilitates its study in heteroclusters of heavy atoms, e.g., Kr. The "soft" R2P2CI spectra of DCA  $Ar_N$ (N=1-55) and of DCA·Kr<sub>N</sub> (N=1-20) clusters (with excess vibrational energy of  $\leq 30$  cm<sup>-1</sup>) preclude any dissociative process and reflect the dynamics of these clusters at approximately constant temperature (vibrational temperature  $T_v = 20-30$  K). We wish to report on a new phenomenon of spectral line narrowing setting in at large cluster sizes, which signals the nonrigid-to-rigid transition in the 3D cluster,<sup>5-15</sup> and which is analogous to the freezing transition in an infinite system.

The cluster beam was generated in a three-chamber differentially pumped vacuum system. The first chamber contained a magnetically actuated pulse valve with a conical nozzle (0.5 mm diam, 30° angle).<sup>28</sup> The beam was skimmed and passed to the chamber containing a reflection time-of-flight mass spectrometer. The mass spectrometer, with a "Daley" ion detector for high masses sensitivity, was operated with a delayed pulsed extraction (2  $\mu$ sec), so that the ionization occurred in a field-free domain. Resolution of  $M/\Delta M = 500$  was achieved at masses up to 2000 amu. The cluster beam was probed by two-photon two-color threshold ioniza-

tion. An excimer laser (Lambda physik 150 msc) was used for pumping two dye lasers (Lambda physik). The two mildly focused (1-mm beam waist) laser beams, overlapping at the ionization volume of the mass spectrometer were aligned for counter propagation with the cluster beam, resulting in a relatively long ionization cylinder ( $\sim 5$  mm long). The pulse energy of 1 mJ for the first excitation step and 0.2 mJ for the second step were sufficient to generate a thousand ions per pulse of

the parent molecule and avoid power broadening (the laser pulse duration was  $\sim 20$  nsec). Independent wavelength tuning of each laser allowed us to selectively excite a given cluster and ionize it at its threshold so as to minimize the excess energy leading to fragmentation. No evidence for fragmentation was found near threshold ionization (with excess vibrational energy of 30 cm<sup>-1</sup>) as inferred from (i) the appearance of distinct spectral features for each N, (ii) the absence of ion fragments



FIG. 1. Optical absorption spectra of mass-selected DCA·Kr<sub>N</sub> clusters (N = 1-20) in pulsed supersonic jets (30% He and 70% Ne) obtained by resonant two-photon two-color ionization in conjunction with time-of-flight mass spectroscopy.

DCA·Ar<sub>M</sub> (M < N) upon R2P2CI of DCA·Ar<sub>N</sub>, and (iii) the ion signal was linear in each of the two laser beam intensities. The vibrational temperature  $T_v = 20$ -30 K of the DCA molecule in small clusters (N = 1-3)was estimated from the amplitude of hot vibrational bands in the spectrum.

The  $S_0 \rightarrow S_1$  transition of mass-selected DCA·Kr<sub>N</sub> heteroclusters (Fig. 1) exhibits diverse spectroscopic phenomena with increasing cluster size. "Small" clusters (N=1-4) show a sharp electronic origin together with a prominent intermolecular vibrational excitation of 40 cm  $^{-1}$ , which corresponds to the perpendicular motion of the Kr atom with respect to the DCA microsurface.<sup>29</sup> Each of these clusters exhibits a single predominant structure. "Medium"-sized DCA·Kr<sub>N</sub> clusters (N = 5-10) exhibit two following qualitative changes (Fig. 1): (1) N=5. The appearance of a complex but wellresolved structure, indicating coexistence of several isomers in distinct clusters. (2) N = 10. The disappearance of a spectral structure and appearance of "slushlike" broadening. These qualitative spectral changes, which were observed in DCA  $\cdot$  Ar<sub>N</sub> clusters, <sup>30</sup> were attributed <sup>30</sup> to (1) local isomerization and/or surface melting in 2D, <sup>19-22</sup> and (2) a wetting-nonwetting transition involving a transformation from 2D to 3D.<sup>22</sup>

A novel phenomenon on the onset of line narrowing with increasing N was observed for DCA  $\cdot$  Kr<sub>17</sub> clusters. In the range N = 10-16 the spectra of the DCA·Kr<sub>N</sub> clusters are structureless and broad with the linewidth (FWHM), and  $\Delta(N)$ , monotonically increasing with increasing N for  $\Delta(10) = 20$  cm<sup>-1</sup> to  $\Delta(16) = 85$  cm<sup>-1</sup> (Figs. 1 and 2). At N = 17 a discrete well-resolved spectral structure abruptly appears, being accompanied by pronounced line narrowing (Figs. 1 and 2). In the same size range the red spectral shift exhibits a monotonically slow increase with increasing N (Fig. 2). A qualitatively similar phenomenon is observed for  $DCA \cdot Ar_N$  clusters where the linewidth of the structureless spectral feature reaches a maximum at N=20 and decreases with further increasing N. An effect of line narrowing in benzene  $Ar_N$  clusters has very recently been observed by Hahn and Whetten,<sup>31</sup> where R2P1C spectra exhibit a narrowing onset around N = 17-19. Unfortunately, these R2P1CI experiments<sup>31</sup> result in benzene Ar<sub>N</sub><sup>+</sup> clusters with a high excess internal (vibrational) energy of 4300 cm<sup>-1</sup>, which considerably exceeds both the benzene-Ar binding energy  $(370 \text{ cm}^{-1})^{32,33}$  and the Ar-Ar interaction  $(98 \text{ cm}^{-1})^{34}$  whereupon extensive cluster ion fragmentation occurs. Our "soft" R2P2CI method is fragmentation free.

Our results for the onset of line narrowing in heteroclusters exhibit an abrupt reduction of the number of isomers in DCA·Kr<sub>N</sub> from N=16 to N=17 at constant temperature. These results provide the spectroscopic manifestation of the nonrigid (disordered) to rigid (ordered) multistate isomerization in a 3D heterocluster,



FIG. 2. Size dependence of the red spectral shift and the width (FWHM) of the prominent lowest-energy spectral feature of the  $S_0 \rightarrow S_1$  transition of DCA·Kr<sub>N</sub> clusters.

which is achieved by increasing the cluster size (N) at (approximately) constant temperature. In medium sized 3D clusters characterized by "soft" interactions, the number of isomers increases exponentially with increasing N.<sup>23</sup> Multistate isomerization is exhibited between the most stable rigid isomer and a large number of excited nuclear configurations. The onset temperature of isomerization at a fixed N is expected to increase with increasing N.<sup>7-12</sup> The nonrigid-rigid transition is accomplished by increasing N at a fixed temperature in the 3D system. The dimensionality (3D) of the system (in the size range N = 15-20) is inferred from spectroscopic information as the two-sided growth of these clusters,<sup>29</sup> together with model calculations of potential surfaces of an aromatic molecule (rare gas)<sub>N</sub> cluster.<sup>31,32</sup> For a sufficiently large heterocluster, with a 3D structure, the rigid-nonrigid transition is analogous to multistate isomerization in a neat rare-gas cluster.<sup>1,7-9,11-14</sup> This isomerization is expected to be "collective" involving all cluster atoms.

Heteroclusters consisting of an aromatic molecule doped in a rare-gas cluster exhibit a complex pattern of 2D and 3D isomerization processes, which provide the microscopic precursors of surface at bulk phase changes. While some of the 2D isomerizations in carbazole· $Ar_N$ <sup>19-22</sup> and DCA· $R_N$  (R=Ar, Kr) may be system specific, the nonrigid-rigid isomerization in the 3D heterocluster, which is documented by us, is universal and constitutes the microscopic analog of the freezing transition in macroscopic systems.

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