# Dynamic Stabilization in $1\sigma_u \rightarrow 1\pi_g$ Excited Nitrogen Clusters

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High-resolution $1s$ near-edge spectra of molecular nitrogen and variable size nitrogen clusters obtained using monochromatic synchrotron radiation from the high brilliance BESSY-II storage ring facility are reported. The vibrationally resolved $1\sigma_u \rightarrow 1\pi_g$ core-to-valence excitation band of clusters shows a distinct redshift of $6 \pm 1$ meV relative to the isolated molecule, but the vibrational structure and linewidths are essentially unchanged. This shift is assigned to dynamic stabilization of $1\sigma_u \rightarrow 1\pi_g$ excited molecules in clusters, arising from the dynamic dipole moment generated by core-hole localization in the low-symmetry cluster field. This leads to changes in intermolecular interactions compared to the ground-state cluster. Such spectral shifts are expected to occur generally in molecular clusters and in the corresponding condensed phase.

Free clusters have received considerable attention recently since they are known to bridge the gap between the gas and condensed phases of matter [1]. The geometry and electronic structure of variable size clusters reflect size-dependent properties of matter, which are suitably investigated by inner-shell excitations [2–5]. The conversion of atomic Rydberg states into the corresponding surface and bulk core excitons was observed earlier for rare gas clusters [3–5]. These changes in electronic structure are also accompanied by size-dependent structural changes [2]. Spatial localization of nonequivalent atomic sites determines size- and site-dependent spectral shifts of core excitons in variable size clusters [3,6].

The x-ray absorption spectra of molecules and molecular clusters are dominated by core electron excitations into valence-type unoccupied states, which can be located either below or above the core ionization threshold [7]. The $1s$-excitation spectrum of molecular nitrogen is characterized by an intense $1\sigma_u \rightarrow 1\pi_g$ band at 400.84 eV [7,8], which has vibrational fine structure when studied at high resolution [9–11]. The N $1s$ spectrum of condensed nitrogen also exhibits a vibrationally resolved $1\sigma_u \rightarrow 1\pi_g$ transition at high resolution, which is similar in shape to the molecular band [12–14].

We focus in this paper on nitrogen clusters with the emphasis on the vibrational fine structure of the $1\sigma_u \rightarrow 1\pi_g$ transition. For such cases, it is expected that cluster dynamics controls the spectral changes in the core level excitation regime relative to the isolated molecule. This allows one to probe intermolecular interactions of element–selectively excited moieties. This issue has not been previously addressed in the context of core-excited molecular clusters. The present work takes advantage of the new high brilliance light source BESSY-II that

offers sufficient photon flux at low photon bandwidth. For the first time this allows investigations of small spectral shifts in vibrationally resolved core $\rightarrow$ valence transitions in variable size molecular clusters. Size effects in $1s$-excited nitrogen clusters were investigated earlier, but the spectral resolution was not sufficient to observe any distinct changes of the resonant features in the pre-edge regime [15].

The experimental setup was described earlier [3,15]. Briefly, nitrogen clusters are produced by expanding the neat gas through a nozzle of 50 $\mu$m diameter at typically $p_0 = 5$ bar and $150 \leq T_0 \leq 300$ K. The jet is skimmed and transferred into a chamber, where a time-of-flight mass spectrometer is located. Molecules and clusters are excited by a beam of monochromatic x rays from the U49-SGM beamline at the storage ring BESSY-II [16]. The monochromator is operated in first order of a 1200 lines/mm spherical grating with a typical energy resolving power $E/\Delta E \gtrsim 10^4$ at 400 eV photon energy. Photoion yields of mass-selected cations are measured as a function of photon energy. The present setup allows one to measure up to three cation masses simultaneously, so that photoion yields of the isolated molecule and cluster cations are measured under *entirely* identical conditions. Therefore, small spectral shifts are obtained with high precision. Results on the bare molecule are either obtained from total ion yields, under conditions where no clusters are present in the jet, or by selecting $N^+$, since this mass channel is primarily due to molecular fragmentation [15]. The $(N_2)_2^+$ mass channel is selected to investigate properties of variable size clusters. This approach is suitable for the N $1s$ regime, where double ionization is an efficient process [15]. Thus, the $(N_2)_2^+$ yield is primarily a result of fission of doubly charged clusters that

are smaller than the critical size of stable dications $n_{crit}$, with $n_{crit}\left((N_2)_n^{++}\right) = 99$ [17]. As a result, properties of large clusters $[(N_2)_n$, with $n \gtrsim 100]$ are not efficiently probed by $(N_2)_2^+$ yields. The average cluster size $\langle n \rangle$ is determined according to previous estimates [18], reaching $\langle n \rangle \approx 150$ at $T_0 = 150$ K and $p_0 = 5$ bar. Further support for this size estimate comes from photoion yields of $(N_2)_2^+$ that were recorded in the Rydberg excitation regime (406–409 eV). These results will be discussed in detail elsewhere [19]. Briefly, the $(N_2)_2^+$ photoion yield is dominated in the Rydberg regime by surface excitons for $\langle n \rangle \approx 150$, which are blueshifted by $\gtrsim 200$ meV relative to the corresponding molecular Rydberg transitions. This finding is similar to earlier work on variable size rare gas clusters [3]. The average cluster size estimated from the blueshift of the excitons [19] is found to be consistent with the estimate that is based on the expansion conditions.

Figure 1 shows the $1\sigma_u \rightarrow 1\pi_g$ resonance in the isolated molecule and for clusters at $\langle n \rangle \approx 150$. The molecular energy positions and the spectral profiles for the vibrational levels are in agreement with previous work [9–11,20]. The FWHM of the Voigt profiles used for deconvolution of the vibrational progression is 123 meV. Similar results are obtained for the $1\sigma_u \rightarrow 1\pi_g$ transition in the $(N_2)_2^+$ yield spectrum, where neither a noticeable spectral broadening of the vibrational levels nor changes in vibrational spacings are found. However, we do observe a fixed redshift of the maxima by $6 \pm 1$ meV relative to the isolated molecule (cf. Fig. 2) and small but statistically significant changes in the intensity ratios of the individual vibrations, where the Franck-Condon factors
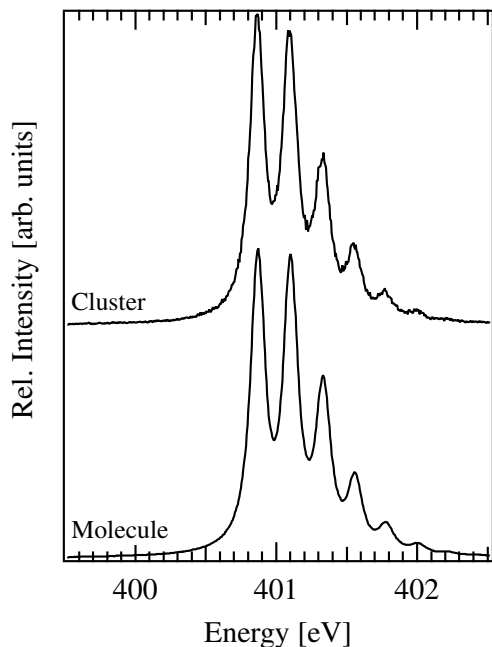
of $v > 0$ are slightly reduced in clusters. Minor changes in Franck-Condon factors are modeled by using a Morse potential (cf., e.g., [10]). The Franck-Condon analysis yields that the change in intramolecular $N \equiv N$ distance of $1\sigma_u \rightarrow 1\pi_g$ excited nitrogen clusters is smaller by 100 fm than in the bare molecule.

Changes in chemical bonding, molecular rotations, and photoexcitation dynamics are the main candidates to rationalize the small redshift of the $1\sigma_u \rightarrow 1\pi_g$ band in clusters relative to the isolated molecules. However, as we argue systematically in the following paragraphs, only a dynamic stabilization of the nitrogen clusters following photoexcitation satisfactorily explains the experimental observations.

The correlation of the energy position of the $1\sigma_u \rightarrow 1\pi_g$ resonance with a decrease in the antibonding character of the $1\pi_g$ molecular orbital in clustered nitrogen is inconsistent with the fact that both $\omega_e$ and $\omega_e x_e$ remain unchanged. Moreover, one encounters insuperable difficulties if one adopts a quasistationary treatment of the vibrational fine structure in a short-lived highly excited state. Considering that $\Gamma = 118 \pm 5$ meV and $\omega_e \approx 235.2$ meV [10], the lifetime of the $1\sigma_u \rightarrow 1\pi_g$ excitation corresponds to two classical periods $2t_{vib} \approx 36$ fs of intramolecular vibrations. These are accompanied



FIG. 1.   $1\sigma_u \rightarrow 1\pi_g$ transition of molecular nitrogen ($N^+$ yield, bottom) and clustered nitrogen $[(N_2)_2^+$ yield, $\langle n \rangle \approx 150$, top].
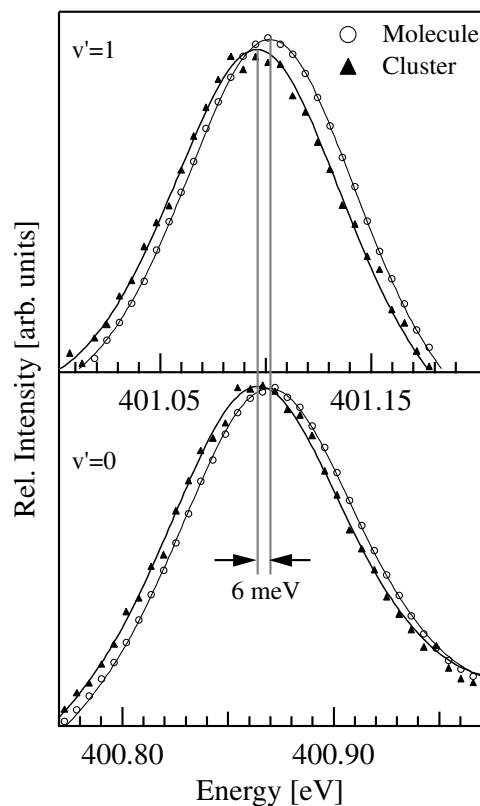


FIG. 2.   $1\sigma_u \rightarrow 1\pi_g$ transition of molecular (circles) and clustered (triangles) nitrogen at $\langle n \rangle \approx 150$ in the $v = 0$ and $v = 1$ regimes. The solid lines are obtained from the spectral deconvolution.

by a nonadiabatic change in equilibrium $N \equiv N$ distance $r_e$, increasing from 1.09768 Å in the $^1\Sigma_g$ ground state [21] to 1.1641 Å in the intermediate core-excited $(N^*N1s_\sigma^{-1}2p_\pi^1)^1\Pi$ state [10]. The bond length increases to 1.1749 Å in the $N_2^+ A\,^2\Pi_u$-state that is efficiently formed after electronic relaxation [11,21]. Such changes in $r_e$ represent one of various possible channels of core level excitation and subsequent electronic relaxation.

Freezing of rotational degrees of freedom of molecules that are bound in clusters is also discounted, since the $^1\Sigma \rightarrow {}^1\Pi$ transition [10,22] gives rise to a rotational profile that is shaded to the red, where the $R$ branch corresponds to the bandhead. Therefore, complete freezing of molecular rotations starting from $T = 300$ K is expected to yield a slight blueshift of $\approx 5$ meV that is accompanied by negligible changes in spectral line shapes.

Vibronic coupling is known to dominate $1s \rightarrow \pi^*$ transitions of polyatomic linear molecules [23,24]. The present results indicate that it is of no importance in $1s$-excited nitrogen clusters. Even though coupling of the electronic wave function to cluster modes cannot be entirely excluded, one expects a blueshift as well as spectral broadening of the vibrationally resolved $1\sigma_u \rightarrow 1\pi_g$ transition. This spectral shift is mainly a result of the dipole forbidden $1\sigma_g \rightarrow 1\pi_g$ transition of the isolated molecule, which is calculated to be blueshifted by 70 meV relative to the $1\sigma_u \rightarrow 1\pi_g$ transition [25].

Thus, the small redshift of $6 \pm 1$ meV cannot be a result of changes in the rotational or vibrational intramolecular dynamics. Rather, the spectral shift is assigned to intermolecular dynamics of core-excited molecules in clusters.

The linkage of photoexcitation dynamics to spectral [6] and angular [26] dependences of photoexcitation processes is provided by superimposing quasiatomic time-dependent excitations $c_1(N_{1s \rightarrow 2p} \equiv N) + c_2(N \equiv N_{1s \rightarrow 2p})$ with respect to the anisotropic and radial deformation of the N $2p$ function by the potential of the surroundings as well as the time relation between core-hole hopping and core-hole Auger relaxation and radiative decays [6]. Earlier work indicates that the $1\sigma_u \rightarrow 1\pi_g$ transition contains a substantial amount of localization [25]. Localization and delocalization of core holes in homonuclear diatomic molecules has been investigated in recent work on core-excited $O_2$ [23]. Hence, the resonant features are mainly assigned to the quasiatomic doubly degenerate $N^*N\,^1\Pi$-state with $C_{\infty v}$ symmetry. The inversion symmetry is broken in clustered molecules, as any changes in vibrational fine structure in clusters are revealed.

Neglecting molecular rotations yields that the molecular wave function $\Phi(\mathbf{r}, \mathbf{R}, \mathbf{X})$ is $\Psi(\mathbf{r}, \mathbf{R})\exp(i\mathbf{k}\mathbf{X})$, where $\mathbf{r}$ and $\mathbf{R}$ are radius vectors of electrons and the nuclei in the molecule, $\mathbf{X}$ gives its center of gravity, and $\mathbf{k}$ is the wave vector. In clusters $\Phi \cong \Psi(\mathbf{r}, \mathbf{R})\varphi(\mathbf{X} - \mathbf{X}_0)$, where $\varphi$ describes molecular librations of low frequencies $\Omega_n$ and large amplitudes $\Delta\mathbf{X}_n$ of displacement relative to the equilibrium position $\mathbf{X}_0$. The quantity $\varphi$ is determined

by the strength of the intermolecular interaction, and its self-energy $\varepsilon_n$ differs for the initial and final states in photoexcitation. Assuming that $\Psi$ remains unchanged in free and clustered molecules, resonant photoabsorption in clusters is expressed by

$$I(\omega) \sim |\langle \Psi_{\pi_g} |\mathbf{d}| \Psi_0 \rangle|^2 \delta(\hbar\omega - E_{00} - \hbar\omega_e \upsilon' - \Delta\varepsilon),$$

where lifetime broadening is ignored, $|\langle \Psi_{\pi_g} |\mathbf{d}| \Psi_0 \rangle|^2$ is the dipole matrix element of the $1\sigma_u \rightarrow 1\pi_g$ transition, $E_{00}$ is the molecular value of the 0-0 transition, $\omega_e$ is the intramolecular vibrational frequency in the equilibrium position, and $\Delta\varepsilon$ gives the gas-to-cluster shift of the vibrationally resolved $1\sigma_u \rightarrow 1\pi_g$ transition. The core-excited molecule is assumed to be fixed at the position $\mathbf{X}_0 + \Delta\mathbf{X}$. It is expected, as a result of strong dynamic $1s$ hole localization, that the dynamic dipole moment of the $^1\Pi$-excited molecule within a cluster increases the coupling to its neighbors. Therefore, the effective radius of intermolecular interactions is reduced and a variety of different metastable positions are available for the core-excited $N^*N$ moieties, which are bound at different low-symmetry ($\mathbf{X}_0^* \neq \mathbf{X}_0$) sites of lower potential energy compared to the vertical core-to-valence transition with frozen ground-state geometry. This is equivalent to a dynamic stabilization of the core-excited molecule in a cluster, resulting from its self-trapping in displaced positions with $\Delta\mathbf{X} \neq 0$ in a deformable cluster, similar to a polaron shift of Franck-Condon transitions in defect centers of solids [27]. The net result is that clusters as well as solids have core-excited valence states which are redshifted by $\Delta\varepsilon$ relative to the bare molecule. The magnitude of $\Delta\varepsilon$ can be estimated to be of the order of the intermolecular vibrations in the electronic ground state $\Omega (32 \leq \Omega \leq 80$ cm$^{-1}$ [28]). The redshift can also be rationalized in terms of the $(Z + 1)$ equivalent core analogy [9,10], implying that dynamic stabilization in core-excited $(N_2)_n$ can be modeled by ground-state properties of $(N_2)_{n-1}NO$. To the best of our knowledge, intermolecular dynamics properties of such heteroclusters have not been reported, so that the magnitude of $\Delta\varepsilon$ is not exactly known from this approach.

In addition, specific differences between the intramolecular and intermolecular dynamics may occur upon core-hole creation. Unlike stabilization of intermolecular vibrations, the $1\sigma_u \rightarrow 1\pi_g$ excitation contributes to the population of intramolecular vibrations which persist after the core-hole decay [11]. The intermolecular vibrations may interfere with the intramolecular ones. However, the analysis of the experimental results clearly indicates that such interference can be ignored on short time scales, where $t_{intra} \ll t_{inter}$. These time scales can be estimated from the vibrational frequencies [10,28], with $t_{intra} \sim 18$ fs and $420 \leq t_{inter} \leq 1060$ fs. In these cases, the excitation occurs in a nearly fixed molecule, where

$t_{inter}$ corresponds to the energy transfer from vibrational levels of the core-excited molecule to its neighbors, which is evidently slow compared to the intramolecular vibrations.

We assign the small energy shift of the $1\sigma_u \rightarrow 1\pi_g$ transition in nitrogen clusters relative to bare molecule to dynamic stabilization that follows photoexcitation, rather than to changes in chemical bonding. The absolute magnitude of the spectral shifts will depend on changes in intermolecular interactions occurring in the core-excited system. Dynamic core hole localization also occurs near core exciton/Rydberg transitions, but its observation is hindered due to the strong size and site dependence of these transitions. The present results indicate that dynamic stabilization is of general relevance to core-excited van der Waals systems without permanent dipole moments. Moreover, high-resolution x-ray absorption is a suitable probe of dynamical aspects of intermolecular interactions in molecular clusters and in the condensed phase.

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