

Line shapes of  $1s \rightarrow \pi^*$  excited molecular clustersA. A. Pavlychev,<sup>1</sup> R. Flesch,<sup>2</sup> and E. Rühl<sup>2</sup><sup>1</sup>*Institute of Physics, St. Petersburg State University, St. Petersburg 198904, Russian Federation*<sup>2</sup>*Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany*

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The line shapes of  $1s \rightarrow \pi^*$ -excited molecular Van der Waals clusters are compared to those of the corresponding isolated molecules. Small, but distinct spectral changes are observed, such as spectral shifts, line broadening, and changes in intensity. These are assigned in terms of variations in motion of the core-excited molecule within the molecular clusters using a simple model. Contributions from intra- and inter-molecular vibrations in core-excited clusters, which contribute to the experimentally observed spectral changes, are discussed.

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Core level excitation of molecules and molecular clusters provides specific information on electronically excited molecular states and their dynamics [1]. This is a result of strong spatial localization of the excited atom, which allows site- and element-selective excitations in variable size free clusters [2]. Therefore, clusters allow to investigate specifically size effects of matter, since the surface-to-bulk ratio can be easily varied [1,3,4]. Core-to-valence transitions, such as  $1s \rightarrow \pi^*$ -transitions, dominate the near-edge regime of molecules and molecular clusters [5–7], as well as the corresponding molecular solids [8]. These transitions may show vibrational fine structure, which can be described by Franck-Condon transitions. Moreover, substantial line broadening may also occur. This is essentially due to the femtosecond lifetime of the core-excited states. Furthermore, strong dynamic localization and temporary trapping of the ejected photoelectron occurs in the narrow region at the core-ionized atom [7]. Recent high resolution studies on Van der Waals clusters indicate that there is further broadening compared to the bare molecules, small spectral shifts of the vibrationally resolved transitions, and small changes in Franck-Condon factors [5,7]. These works already show that localized molecular modes have no importance to the dynamics of Van der Waals systems. However, it is not clear yet to what extent they affect photoexcitation and de-excitation processes in core-excited Van der Waals clusters and the corresponding solids.

In the present paper we examine in a systematic way the effect of intermolecular interactions on the vibrational fine structure of  $1s \rightarrow \pi^*$ -excitations in free and clustered carbon monoxide and nitrogen. We develop a concept that allows us to rationalize changes in line widths, line intensities, as well as changes in energy position upon cluster formation of  $1s \rightarrow \pi^*$ -excited molecular clusters. We also provide experimental results on O  $1s \rightarrow \pi^*$ -excited carbon monoxide clusters  $[(\text{CO})_n]$ , which are discussed along with a theoretical model and previous results on C  $1s \rightarrow \pi^*$ -excited CO clusters and N  $1s \rightarrow \pi^*$ -excited nitrogen clusters  $[(\text{N}_2)_n]$  (cf. Refs. [5,7]).

The experimental setup has been described before [1,9]. Briefly, a continuous supersonic jet expansion is used for cluster production, where pure molecular gases are expanded

through a 50  $\mu\text{m}$  nozzle. Variable size clusters are formed under conditions, where the stagnation pressure  $p_0$  and stagnation temperature  $T_0$  are varied in the following regimes:  $1 \text{ bar} \leq p_0 \leq 5 \text{ bar}$  and  $150 \text{ K} \leq T_0 \leq 300 \text{ K}$ , leading at low  $T_0$  and high  $p_0$  to the efficient formation of clusters. The average cluster size  $\langle N \rangle$  characterizes the size distribution of the neutral cluster jet. In the case of CO- and  $\text{N}_2$ -clusters, one obtains  $\langle N \rangle \leq 150$  under the present expansion conditions (cf. Ref. [10]). The gases are of commercial quality (Messer-Griesheim; purity >99.99%). The cluster jet is shaped by a 500  $\mu\text{m}$  skimmer. The experiments are carried out at the U49-SGM- and UE52-SGM-beam lines [BESSY (Berlin, Germany)], where an energy resolution  $E/\Delta E > 10^4$  is reached [11]. The cluster jet is crossed by the beam of monochromatic synchrotron radiation under collision free conditions in the ionization region of a time-of-flight mass spectrometer. Yields of mass-selected cations are obtained by selecting a mass channel while scanning the photon energy. The spectra are normalized to the photon flux by using either the photocurrent of a gold mesh or the total ion yield of rare gases. The photon energy scale is calibrated by comparison with high-resolution electron energy loss data [12].

The energy of a molecular core-to-valence transition from the vibrational ground state  $v''=0$  into the  $1s \rightarrow \pi^*$ -excited state with vibrational levels  $v'$  can be described in the framework of the Born-Oppenheimer approximation

$$E_x^{\text{gas}}(v') = E_{1s \rightarrow \pi^*} + \hbar\omega_e \left( v' + \frac{1}{2} \right) - \hbar\omega_e x_e \left( v' + \frac{1}{2} \right)^2 + E_{v',N'} - E_{v'',N''}. \quad (1)$$

The total excitation energy  $E_x^{\text{gas}}(v')$  is well-known from experiments. It consists of the following components [cf. Eq. (1)]: (i) The energy of the  $1s \rightarrow \pi^*$ -transition ( $E_{1s \rightarrow \pi^*}$ ); (ii) the vibrational energy  $[\hbar\omega_e(v' + 1/2)]$ ; (iii) the anharmonicity energy  $[\hbar\omega_e x_e(v' + 1/2)^2]$ , where  $\hbar\omega_e x_e$  is the anharmonicity constant; and (iv) the rovibrational energy  $E_{v',N'} - E_{v'',N''}$ , where  $E_{v,N}$  takes the coupling of vibrational and rotational motions into account. Usually, the rovibrational term is ignored in the analysis of x-ray absorption spectra, because of substantial line broadening. In the case of molecular Van

der Waals clusters the molecular wave function is replaced by a superposition of the wave functions  $\Psi_m^{(j)}$ , corresponding to those of the molecules bound in the cluster, where  $j=1,2,\dots,n$  and  $n$  is the number of molecules bound in the cluster. The function  $\Psi_m^{(j)}$  is represented by  $\psi_{el}^{(j)}(\mathbf{r},\mathbf{R})\chi_{vib}^{(j)}(\mathbf{R})\chi_\lambda^{(j)}(\mathbf{X}-\mathbf{X}_0)_j$ . In addition to the molecular variables  $\mathbf{r}$  and  $\mathbf{R}$ , corresponding to the coordinates of the electrons and the nuclei, we introduce the coordinate  $\mathbf{X}_j$ , which describes the motion of the molecular center of mass  $j$  relative to the equilibrium position  $\mathbf{X}_{0j}$  in a cluster.  $\chi_\lambda^{(j)}$  describes librations of the molecular unit  $j$  relative to the equilibrium position. In addition to the intramolecular  $v''\rightarrow v'$  transitions there are intermolecular  $\lambda''\rightarrow\lambda'$  transitions.  $\lambda''$  and  $\lambda'$  describe the vibrational levels in the cluster potential of the ground-state and core-excited state, respectively. Then, the energy of a  $1s(v''=0)\rightarrow\pi^*(v')$ -transition in a cluster is given by

$$E_x^{\text{cluster}}(v') = E_{1s\rightarrow\pi^*} + \hbar\omega_e\left(v' + \frac{1}{2}\right) - \hbar\omega_e x_e\left(v' + \frac{1}{2}\right)^2 + \delta\varepsilon, \quad (2)$$

where  $\delta\varepsilon$  is the average energy of intermolecular  $\lambda''\rightarrow\lambda'$ -transitions.  $E_{1s\rightarrow\pi^*}$ ,  $\hbar\omega_e$ , and  $\hbar\omega_e x_e$  are the electronic excitation energy, the harmonic vibrational spacing, and anharmonicity constant of intramolecular vibrations in clusters, respectively. Equation (2) shows that the direct application of the Franck-Condon analysis to the vibrational fine structure may encounter difficulties in clusters, because of the uncertainty in the term that originates from the different energies of the molecular motions in their respective environments:

$$\Delta = E_{v'N'} + E_{v''N''} - \delta\varepsilon. \quad (3)$$

Equation (3) contains contributions from: (i) freezing of molecular rotations upon cluster formation, corresponding to  $E_{v'N'} - E_{v''N''}$ , assuming that the Van der Waals clusters are solid and (ii) changes in the intermolecular potential from the neutral ground state cluster to the core-excited cluster, corresponding to  $\delta\varepsilon$ . These are conditioned by changes in molecular librations, which are due to the formation of a core-hole-electron pair, corresponding to spatial localization. The rovibrational and librational effects in molecular motions cannot be neglected when a Franck-Condon analysis of the experimental vibrational fine structure of core-to-valence transition is performed [7]. The importance of intermediate core-hole state effects on core-to-valence transitions of clusters is discussed in the following: First the intermediate cluster state is presented by a superposition of degenerate or quasidegenerate core-excited cluster states:  $U^*(X) = n^{-1}\sum_{(j=1)}^n U^{*(j)}(X)$ . The potential  $U^{*(j)}$  refers to a cluster that contains a  $1s\rightarrow\pi^*$ -excited molecule, which is centered at  $X_{0j}$ . For  $n \gg 1$  the potential is obtained from shifting the ground state potential  $U$  upward by the photon energy  $E_0$ , i.e.,  $U^*(X) \approx U(X) + E_0$ . Figure 1(a) serves to illustrate the expected spectral changes in x-ray transition within this statistic model of core-excited clusters. The vertical  $\lambda''\rightarrow\lambda'$ -transitions, which accompany the  $1s(v''=0)$

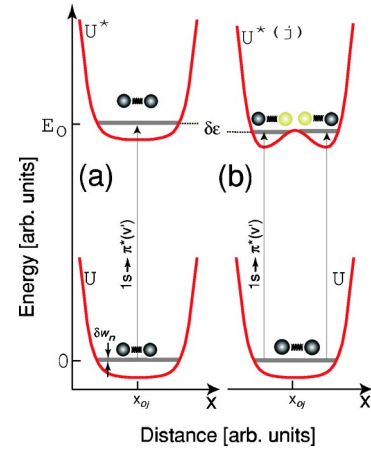


FIG. 1. Cluster potentials and N  $1s(v''=0)\rightarrow\pi^*(v')$  transition in a linear chain of nitrogen molecules within (a) statistic ( $U^*$ ) and (b) dynamic ( $U^{*(j)}$ ) models of the intermediate core-ionized cluster state (for details see text).

$\rightarrow\pi^*(v')$ -excitation, are represented by phononlike bands. Their widths  $\delta w_n$  account for the presence of intermolecular motions with considerably lower energies  $\Omega_n$  ( $\sim$ few meV) than the intramolecular vibrations  $\omega_e$  ( $\sim$ hundreds of meV), corresponding to  $\Omega_n \ll \omega_e$ . The center of molecular mass oscillates around the equilibrium position, practically without any changes before and after the x-ray transition. The intensities of the intramolecular vibrational transitions are governed by Franck-Condon factors and no energy shift of the core-to-valence  $v'$ -bands will appear. There is just an additional symmetric broadening of the  $v'$ -bands. The width of each line is  $w_{v'} + 2\delta w_n$ , where  $w_{v'}$  is the width of  $v'$ -band in an isolated molecule and the magnitude of  $\delta w_n$  can be estimated from the intermolecular ground state vibrations. This statistic model does not allow us to account for a correlation between molecular librations and strong dynamic localization of a  $1s\rightarrow\pi^*(v')$ -excitation within a molecular unit. The potential  $U^{*(j)}$  is used to account for this correlation effect in cluster excitations. The individual line shapes of the core-excited molecules are superimposed to all degenerate or quasidegenerate molecular sites in a cluster to obtain the line shape of core-excited molecular clusters (see, Ref. [2]). Figure 1(b) indicates that local changes of the potential at  $X_{0j}$  are observed for a linear chain of nitrogen molecules, where the intermolecular separation  $|X_{0j} - X_{0j\pm 1}|$  is set to the value in solid nitrogen. This already shows that it is possible to observe significant spectral changes, even if a oversimplified cluster geometry is used. The potential  $U^{*(j)}$  differs strongly from  $U^*$  at  $X_{0j}$ .  $U^{*(j)}$  becomes deeper and two distinct minima appear, which are separated by a potential barrier at  $X_{0j}$ . This double minimum potential is caused by the increased attraction of the core-excited molecule ( $j$ ) to the neighbors centered at  $X_{0j\pm 1}$  in the linear chain model. This additional attraction is caused by a dynamic dipole moment  $d_j$  of the core-excited molecule due to dynamic core-hole localization on one of the equivalent atoms [2]. As a result one finds

$$U^{(j)} \approx U + E_0 + U_{d_j} = U^* + U_{d_j}. \quad (4)$$

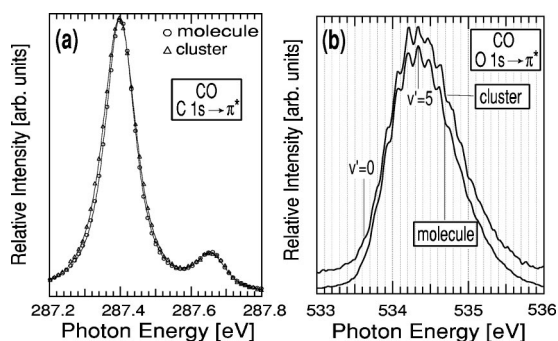


FIG. 2. Near edge spectra of C  $1s$  and O  $1s$  excited CO and clusters near the  $1s \rightarrow \pi^*$ -transition: (a) C  $1s$ -regime; (b) O  $1s$ -regime. See text for further details (cluster: recorded at  $\langle N \rangle \approx 150$ ).

The additional potential ( $U_{d_i} < 0$ ) is responsible for the attraction that appears between  $j$  and  $j \pm 1$  bound units. This potential considers the spectral changes that occur upon cluster formation in the case of strong dynamic core-hole localization on the molecular unit  $j$  (cf. Ref. [13]). The redshift ( $\delta\epsilon < 0$ ) of the  $1s \rightarrow \pi^*(v'=0)$ -band in clusters [see Fig. 1(b)] originates from the coupling of the core-excited molecule with its neighbors and reflects the correlation of the molecular motion with dynamic core-hole localization in clusters. This correlation effect, corresponding to  $U^*(j) < U^*$  at  $X_{0j}$ , can be described in terms of *dynamic stabilization* [5]. This is due to the temporary self-trapping of a core-excited molecule at new, displaced intermolecular positions ( $X_{0j}^*$ ) in a deformable core-excited cluster. This dynamic model leads to intensities of  $v'' \rightarrow v'$ -transitions that are primarily governed by Franck-Condon factors, additional symmetric broadening of the  $v'$ -bands, and a redshift  $\delta\epsilon < 0$  of the core-to-valence  $v'$ -band in comparison with the gas phase. For low  $v'$  the  $\delta\epsilon$ -shift can be approximately described as  $v'$ -independent. The widths ( $w_{v'}$ ) of the individual  $v'$ -bands are mostly determined by the inverse core-hole lifetime ( $\tau_{1s}$ ). Fast molecular dissociation may also contribute to line broadening [14]. Such channels of fast molecular dissociation are possibly blocked by the presence of a potential barrier in the intramolecular potential when  $R$  approaches the radius of the intermolecular potential well. The intramolecular channels can assist in Auger and radiative core-hole decay processes, as discussed for atomic clusters [15]. Thus, one may expect that intramolecular Auger decay channels lead to broadening of the molecular  $v'$ -bands, whereas the stabilization of dissociation channels may even lead to line narrowing.

Figure 2 shows high-resolution spectra of molecular ( $C^+$  yield) and clustered CO [ $(CO)_2^+$  yield] in the narrow spectral regime the C and O  $1s \rightarrow \pi^*$ -resonance. The vibrational fine structure of the C  $1s \rightarrow \pi^*$ -resonance of CO is dominated by an intense resonance at 287.400 eV, [16] corresponding to the C  $1s \rightarrow \pi^*(v'=0)$ -transition [cf. Fig. 2(a)]. The weak  $v' = 1$  level is found at 287.656 eV. The spectral shape of the  $1s \rightarrow \pi^*$ -transition in clusters is remarkably similar to that of the isolated molecule. The Franck-Condon factors are essentially unchanged and only minor spectral changes occur, in-

dicating that the C  $1s \rightarrow \pi^*$ -transition is primarily governed by intramolecular properties. However, there are characteristic differences between the transitions of neat and clustered CO. The C  $1s \rightarrow \pi^*(v'=0)$ -band in clusters is broadened (full width at half maximum  $113 \pm 1$  meV) relative to  $102 \pm 1$  meV in the isolated molecule. These line profiles can be represented by a Voigt fit [16,17]. It is found that the increased width of the C  $1s \rightarrow \pi^*(v'=0)$ -band in clusters is mostly due to an increase of both, the Gaussian and the Lorentzian line width to  $50 \pm 1$  meV and  $90 \pm 1$  meV, respectively. Assuming, that the contribution to the Gaussian line width from the bandwidth of the x-ray monochromator is a constant quantity, then there must be other reasons which are related to the properties of clusters. In addition, we observe a small, but clearly identifiable redshift of  $2 \pm 1$  meV of the maximum of the C  $1s \rightarrow \pi^*(v'=0)$ -transition in clusters relative to the neat molecule, similar to previous work [6,7]. These spectral changes are discussed below. Figure 2(b) shows the vibrational fine structure of the O  $1s \rightarrow \pi^*$ -resonance in CO and in CO-clusters. This band is well-known in the isolated molecule [17–19]. It is characterized by a progression of transitions to vibrational levels and unfavorable Franck-Condon factors of transitions into low  $v'$  levels. This is mostly due to the increase of the internuclear separation in O  $1s \rightarrow \pi^*$ -excited CO. There is no energy shift between the vibrational maxima of isolated and clustered molecules [cf. Fig. 2(b)]. We also observe for the O  $1s \rightarrow \pi^*$ -band no changes in vibrational spacing upon cluster formation. This result is consistent with previous work, where we have shown that dynamic stabilization following core-level excitation will preferentially occur in clusters of homonuclear molecules, leading to substantial energy shifts of core-to-valence transitions in the  $1s \rightarrow \sigma^*$ -regime [2]. In addition, the following spectral changes are observed upon cluster formation:

(i) The relative intensities of the individual vibrational transitions are slightly changed in clusters compared to the bare molecule [see Fig. 2(b)]. We note that the relative intensities of the vibrational transitions above the Franck-Condon maximum ( $v' > 5$ ) are somewhat enhanced in the case of clusters. This indicates that the change in C  $\equiv$  O-bond length upon O  $1s \rightarrow \pi^*$ -excitation is slightly larger in clusters than in the isolated molecule. Using the  $Z+1$ -core analogy, one can assume that CF, corresponding to O  $1s$ -excited CO, has a slightly longer intramolecular bond length, if it is solvated by CO. This is likely due to the permanent dipole moment of the solvent molecules, which destabilize the core-excited molecule. In contrast, a bond shortening by  $\sim 100$  fm is observed, in N  $1s \rightarrow \pi^*$  excited nitrogen clusters, where the solvent shell evidently stabilizes the core-excited molecule. [7] In the case of CO, the full spectral deconvolution of the O  $1s \rightarrow \pi^*$ -band has been performed for molecular CO [16,18]. It is by far more complicated than in the case of nitrogen and bears some ambiguities. Therefore, we have not attempted to perform a Franck-Condon analysis for CO-clusters. In contrast to nitrogen clusters the redshift is in the case of C  $1s$ -excited CO-clusters weaker because of small changes of the intermolecular interaction upon core level excitation. As a result, a double minimum potential, similar to that shown in Fig. 1(b), does not describe this



situation properly. We rather assume that Fig. 1(a) models CO clusters suitably, since dynamic localization cannot efficiently occur in this system.

(ii) Possible changes in line shape of the individual vibrational transitions cannot be quantitatively inferred from the experimental data shown in Fig. 2(b). The features are blended as a result of the small vibrational spacings, corresponding to 166 meV, and substantial line broadening of 143 meV [18]. At least the top of the O  $1s \rightarrow \pi^*$ -band shows that there are no substantial changes in line width upon cluster formation, so that the final states in clusters do not change the dynamics in this spectral regime. The increase of the Gaussian widths by 20% of the  $\nu'$ -bands of C  $1s \rightarrow \pi^*$ -excited CO-clusters relative to neat CO gives evidence for phononlike broadening. This effect is less clear for the O  $1s \rightarrow \pi^*$ -band. By increasing the number of molecules, that are bound in a cluster, the broadening of the  $\nu'$ -band approaches the conventional picture of Gaussian broadening, which dominates x-ray transitions in solids [20]. The in-

creased Lorentzian linewidths found in C  $1s \rightarrow \pi^*$ -excited CO clusters are unlikely the consequence of a decreased core hole lifetime. It is rather expected that this broadening is efficiently affected by fast cluster decay dynamics of the final states that are accessed in clusters. These occur as a result of the intermolecular coordinate and in addition, at least in part, by the presence of librations.

In conclusion, we have developed a qualitative model that allows us to rationalize the variety of different experimental results that occur in the regime of core-to-valence transitions of molecular Van der Waals clusters. Recent and previous experimental results indicate that this model is suitable to explain small spectral shifts as well as changes in line shape compared to the isolated molecules.

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