

Progress on inner-shell excitations of molecular van der Waals clusters

E. Rühl,^{a*} R. Flesch,^a W. Tappe^a and A. A. Pavlychev^b

^aFachbereich Physik, Universität Osnabrück, Barbarastr. 7, 49069 Osnabrück, Germany, and ^bInstitute of Physics, St Petersburg State University, St Petersburg 198904, Russia.
E-mail: ruehl@uos.de

Recent progress on core-level excitation of molecular van der Waals clusters is reported. Resonant excitation near element *K* edges of isolated and clustered molecules gives rise to small spectral shifts that can only be detected with high spectral resolution. This requires the use of state-of-the-art storage-ring facilities along with insertion devices and high-resolution soft X-ray monochromators. Selected experimental results on carbon monoxide clusters are reported. For the vibrationally resolved C 1s → π* (*v* = 0) band of clustered CO, these indicate characteristic line broadening as well as a small red shift of 2 ± 1 meV compared with the isolated molecule. The results are discussed within the framework of the quasi-atomic approach with respect to intermolecular interactions, freezing of molecular rotations in clusters, and dynamic localization of resonant core-to-valence excitations.

Keywords: molecules; clusters; near-edge spectra; quasi-atomic approach.

1. Introduction

Core-level excitation of clusters has recently become a field of research that has been shown to provide unique information on size effects of matter (Rühl *et al.*, 1993; Federmann *et al.*, 1994; Rühl, 2000). The element-selective excitation process, which is obtained from resonant excitation of core levels in the soft and hard X-ray regime (Stöhr, 1992), requires the use of tunable light sources, which are most suitably synchrotron radiation sources.

Excitations in the near-edge regime are most sensitive to size- and composition-dependent changes in the electronic structure of variable-size atomic clusters (Pavlychev *et al.*, 1995; Björneholm *et al.*, 1995; Knop *et al.*, 1998). This becomes evident when the absorption cross section of an atomic rare gas is compared with that of the corresponding solid (Haensel *et al.*, 1973; Steinberger *et al.*, 1999). Considerable size-dependent changes in electronic structure occur in these systems, since the atomic Rydberg states are converted into the corresponding surface and bulk excitons of the solid. The gas-to-solid shift is for most core-excited rare gases of the order of several hundreds of millielectronvolts, so that this quantity is easily detected, even by low-resolution soft X-ray monochromators (Rühl *et al.*, 1993; Knop & Rühl, 1996). More recently, high-resolution near-edge spectroscopy of variable-size krypton clusters has revealed small spectral shifts that are as small as 20 meV (Knop *et al.*, 1998). Various blue-shifted features were identified, where characteristic spectral shifts were assigned to individual geometric sites, such as corners, edges, faces and sub-surface layers. This work also indicated that the clusters are dominated by edge sites, which was rationalized in terms of imperfect cluster structures that are formed by jet expansion techniques. This result agrees well with previous results from extended X-ray absorption fine structure (EXAFS) spectroscopy applied to rare-gas clusters (Kakar *et al.*, 1997).

Various molecular cluster systems have been investigated to date in the core-excitation regime (Rühl, 2000). Most of these studies made use of low ($E/\Delta E \leq 500$) or medium energy resolution ($500 \leq E/\Delta E \leq 5000$) in the soft X-ray regime, where *K*- or *L*-shell excitations of light elements occur. In these works, significant spectral changes in size-dependent near-edge structure were only observed in cluster systems with strong chemical or intermolecular bonds, such as in sulfur clusters (Teodorescu *et al.*, 1998) or in water clusters (Björneholm *et al.*, 1999). By contrast, earlier work on molecular van der Waals clusters has shown that the pre-edge core-to-valence transitions of gas-phase molecules and their clusters are almost identical in energy (Rühl, 1992). More recently, a substantial blue shift of the order of 1 eV relative to the isolated molecule was found for the 1s → σ* shape-resonance regime of nitrogen clusters and the solid (Pavlychev & Rühl, 2000). By contrast, no such shifts were observed in the case of CO clusters. These results were rationalized in terms of the quasi-atomic approach (QA) (Pavlychev *et al.*, 1993) by considering the effect of the low symmetric cluster field on strongly localized molecular excitations with respect to their dynamic symmetry (Pavlychev *et al.*, 1998; Pavlychev & Rühl, 2000).

The present paper focuses on recent progress on near-edge absorption of variable-size molecular van der Waals clusters. We discuss carbon monoxide and its clusters as simple model systems. We review recent work on low-spectral-resolution experiments and compare these results with high-resolution work that requires the use of high-brilliance synchrotron radiation sources, insertion devices and high-resolution soft X-ray monochromators.

2. Experimental

The experimental setup has been described in detail earlier (Rühl *et al.*, 1991). Briefly, it consists of the following major components.

(i) A continuous supersonic jet expansion is used for cluster production, where neat CO is expanded through a 50 μm nozzle. The cluster jet is shaped by a 500 μm skimmer before it is excited by monochromatic synchrotron radiation. Typically, the stagnation pressure p_0 and the stagnation temperature T_0 are varied in the following regimes: $100 \leq p_0$ (kPa) ≤ 500 and $150 \leq T_0$ (K) ≤ 300 , 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 clusters, one obtains smaller values of $\langle N \rangle$ than for atomic clusters. This is mostly a result of the additional cooling of the internal degrees of freedom, so that $\langle N \rangle \simeq 150$ is estimated to be reached under the present conditions, assuming that the clustering behaviour of CO is similar to that of N₂ (*cf.* Vostrikov *et al.*, 1994).

(ii) Synchrotron radiation is obtained from the storage rings BESSY-I and BESSY-II. Experiments at low or moderate energy resolution ($E/\Delta E$) were performed at the HE-TGM-II beamline at BESSY-I [$150 \leq E$ (eV) ≤ 600 , $300 \leq E/\Delta E \leq 500$ (Pavlychev & Rühl, 2000)]. High-resolution experiments were carried out at the U49-SGM beamline at BESSY-II, where $E/\Delta E > 10^4$ is reached (Senf *et al.*, 1999).

(iii) 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 (TOF-MS). This device is used in a pulsed mode to separate and detect the cluster cations and their fragments. Typically 300 V pulses of 1–2 μs length were used at a repetition rate of 20–50 kHz in order to accelerate the cations from the ionization region onto the channel-plate detector. Yields of mass-selected cations are obtained by selecting a mass channel while scanning the photon energy. Total ion yields (TIY) are

measured either by running the TOF-MS in a continuous mode or by using a channeltron that is mounted opposite to the TOF-MS. The latter device can alternatively be used to measure total electron yields by inverting the voltages. 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 was calibrated by comparison with electron energy loss data (Sodhi & Brion, 1984).

The sample gas was of commercial quality (Messer-Griesheim; purity > 99.99%). It was used without further purification.

3. Results and discussion

Fig. 1 shows a comparison of the total ion yield of molecular carbon monoxide with the photoion yield of $(\text{CO})_2^+$ in the C 1s excitation regime (280–330 eV). This spectrum is recorded at $\langle N \rangle \simeq 150$. However, the photoionization mass spectrum shows only dominant mass lines in the cluster regime of $(\text{CO})_n^+$, with $n \leq 10$. This discrepancy between the estimated neutral size distribution, corresponding to $\langle N \rangle$, and the final products of ionic fragmentation, corresponding to $(\text{CO})_n^+$, mostly arises from efficient fragmentation of large singly and multiply charged clusters, formed upon core-level excitation. Therefore, photoion yields of small cluster fragments, such as $(\text{CO})_2^+$, are suitable to obtain information on changes in electronic structure of larger neutral precursors.

The C 1s excitation regime is governed by an intense resonance at 287.40 eV, which is caused by the C 1s $\rightarrow \pi^*$ transition (Wight *et al.*, 1973; Sodhi & Brion, 1984). The energy position of this resonance is found to be identical in the $(\text{CO})_2^+$ yield (Pavlychev & Rühl, 2000) as well as in the solid (Rosenberg *et al.*, 1985). When the cluster spectrum is compared with the molecular total-ion yield, minor changes are found, which are mostly caused by transitions that involve Rydberg excitations: (i) the lowest Rydberg transition in the molecular spectrum (C 1s $\rightarrow 3p$) occurs near 293.3 eV; this feature is

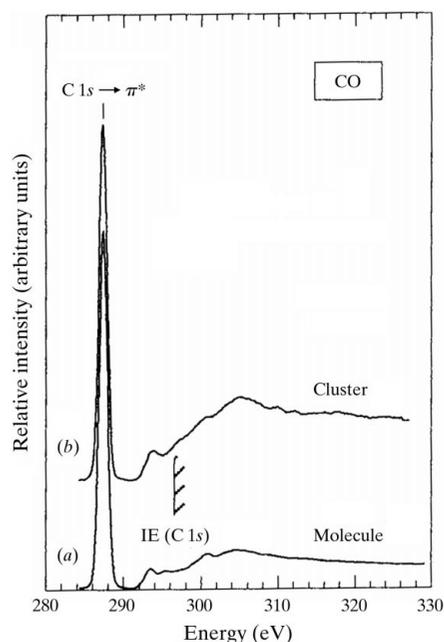


Figure 1 (a) Total cation yield of neat CO recorded in the C 1s excitation regime. (b) Photoion yield of $(\text{CO})_2^+$ recorded at $\langle N \rangle \simeq 150$. The vertical dashed line corresponds to the C 1s ionization energy [IE(C 1s) = 296.19 eV (Jolly *et al.*, 1984)].

slightly blue-shifted by ~ 0.3 eV in the $(\text{CO})_2^+$ yield; (ii) another weak feature found near 295 eV is not observed in the dimer yield; and (iii) a double excitation feature that occurs at 300.7 eV is considerably damped in intensity in the $(\text{CO})_2^+$ yield. These changes are similar to findings for atomic clusters, where the exciton bands are blue-shifted relative to the Rydberg transitions in a bare atom (Rühl *et al.*, 1993; Pavlychev *et al.*, 1995). We note that the energy position of the broad C 1s $\rightarrow \sigma^*$ transition remains unchanged. This result has been discussed recently in terms of dynamic properties of $1s \rightarrow \sigma^*$ resonances (Pavlychev & Rühl, 2000). It has been shown that substantial energy shifts ($\Delta E \simeq 1$ eV) of $1s \rightarrow \sigma^*$ resonances occur in clusters and solids of homonuclear diatomic molecules, such as nitrogen. This has been rationalized in terms of dynamic core-hole localization and core-hole symmetry breaking in the low-symmetry cluster potential, leading to incoherent intramolecular interferences of the photoelectron waves in the $1s \rightarrow \sigma^*$ regime. By contrast, no such changes are expected to occur in clusters and solids of heteronuclear diatomic molecules, such as CO, which is in agreement with the present experimental results (*cf.* Fig. 1).

Fig. 2 shows a comparison of the C 1s $\rightarrow \pi^*$ ($\nu = 0$) resonance of molecular and clustered carbon monoxide, where the expansion conditions are similar to those of the spectra shown in Fig. 1. However, the spectral resolution is considerably enhanced ($E/\Delta E > 10^4$). The two spectra were recorded simultaneously in order to avoid any energy-calibration errors, so that spectral shifts of >1 meV could be detected. Properties of the isolated molecule are obtained from the C^+ yield, since this mass channel is exclusively populated by molecular fragmentation. Electronic properties of clusters are probed by the $(\text{CO})_2^+$ yield, similar to low-resolution work (see Fig. 1). The molecular spectrum is dominated by an intense resonance at 287.40 eV (Sodhi & Brion, 1984), corresponding to the C 1s $\rightarrow \pi^*$ ($\nu = 0$) transition. Excited vibrational states ($\nu > 0$) are observed with considerably lower intensity as a result of unfavourable Franck-Condon factors of a molecular system that undergoes little change in geometrical structure upon core-level excitation (Domke *et al.*, 1990). The weak $\nu = 1$ level is found at 287.656 eV, which is in agreement with previous work (Floreano *et al.*, 1999).

The spectral line shape of the molecular C 1s $\rightarrow \pi^*$ ($\nu = 0$) transition is approximated by a Voigt profile. A spectral deconvolution produces a Lorentzian line width of 85 ± 1 meV, which is primarily the result of the core-hole lifetime, and a Gaussian width of 41 ± 1 meV, which is at least partially the result of the band width of the

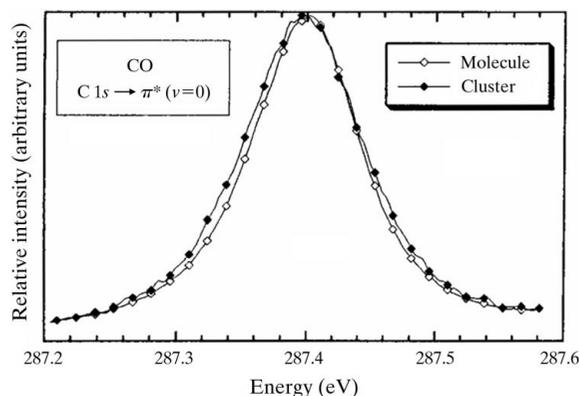


Figure 2 Photoion yields of C^+ (molecule) and $(\text{CO})_2^+$ (cluster) recorded at $\langle N \rangle \simeq 150$ in the C 1s $\rightarrow \pi^*$ ($\nu = 0$) regime. The lines connect the experimental data points. For clarity, every fifth data point is indicated by a diamond (molecule: open diamonds; clusters: filled diamonds).

X-ray monochromator. Both contributions yield the total width of the Voigt profile of 102 ± 1 meV FWHM (full width at half-maximum). These results are in good agreement with the recent work of Floreano *et al.* (1999), who found an identical Lorentzian width of 85 ± 1 meV and a somewhat larger Gaussian contribution of 54 meV, which mostly arises from an enhanced bandwidth of their X-ray monochromator. The spectral line shape also contains a minor asymmetry, where the cation intensity is slightly increased at the low-energy part of the line profile. This is an indication of asymmetric broadening effects, which are likely caused by thermal excitation of molecular rotations.

The spectral shape of the $C 1s \rightarrow \pi^*$ transition of the $(CO)_2^+$ yield is remarkably similar to that of the isolated molecule (*cf.* Fig. 2). The Franck–Condon factors are essentially unchanged and only minor spectral changes occur, indicating that the $C 1s \rightarrow \pi^*$ transition is primarily governed by intramolecular properties rather than by intermolecular interactions. However, there are characteristic differences between the molecular and cluster $C 1s \rightarrow \pi^*$ transition. The $(CO)_2^+$ yield shows a characteristically broadened $C 1s \rightarrow \pi^*$ ($\nu = 0$) transition, with 113 ± 1 meV FWHM (*cf.* Fig. 2). It can also be represented by a Voigt profile; however, the Lorentzian and Gaussian line widths are increased to 90 ± 1 and 50 ± 1 meV, respectively. This cannot be the result of an increased spectral band width of the monochromator. We rather assume that there are other contributions to changes in the spectral line shape of clusters that are related to intermolecular vibrations (*cf.* Anderson *et al.*, 1970). In addition, we observe a small, but clearly identifiable red shift of 2 ± 1 meV of the maximum of the $C 1s \rightarrow \pi^*$ ($\nu = 0$) transition in clusters relative to the bare molecule.

The wavefunction of a clustered molecule is represented by $\Psi(\mathbf{r}, \mathbf{R}, \mathbf{X}) = \psi(\mathbf{r}, \mathbf{R})\varphi(\mathbf{X} - \mathbf{X}_0)$, where \mathbf{r} and \mathbf{R} are coordinates of the electrons and the nucleus in the molecule, and \mathbf{X} and \mathbf{X}_0 give its centre of gravity and equilibrium position in the cluster, respectively. The changes in spectral line widths and energy positions upon clustering are rationalized in terms of changes in intermolecular interaction which controls the φ function. Therefore, a Voigt profile is evidently not well suited to model the spectral line shape. Nevertheless, the increased Lorentzian line width is unlikely to be the result of changes in core-hole lifetime. It is rather expected that the line widths of the $C 1s \rightarrow \pi^*$ ($\nu = 0$) transition are efficiently affected by fast cluster decay dynamics of the final states accessed in clusters as a result of the intermolecular coordinate, and are partially affected by the presence of intermolecular vibrations Ω_N . As $N \rightarrow \infty$, the conventional picture of Gaussian broadening of X-ray transitions in solids is approached, with the standard deviation $\sigma = [S(\Omega) \cotan(\Omega/kT)]^{1/2}$, where the coupling constant S is equal to mean number of phonons Ω created in the transition, k is the Boltzmann constant, and T is the absolute temperature. The increase of the Gaussian width by $\sim 20\%$ provides evidence for phonon-like broadening in clusters.

In general, X-ray transitions in clusters are strongly localized within the excited molecule so that the spectral shift can either be assigned to efficient freezing of molecular rotations or to a polaron-like shift of the Frank–Condon transition in defect centres. Considering the molecular constants of CO (Huber & Herzberg, 1979), one finds for the $C 1s \rightarrow \pi^*$ transition of CO that the thermal distribution of the rotational branches is not entirely symmetric around the origin of the band, so that freezing of molecular rotations in clusters is expected to give rise to a blue shift of 2 ± 1 meV. On the other hand, a polaron-like shift (see *e.g.* Harrison, 1970) can also account for dynamic stabilization, corresponding to a spectral red shift, of core-excited molecules in clusters (Flesch *et al.*, 2001). This effect results from self-trapping in displaced positions with $\mathbf{X} - \mathbf{X}_0 \neq 0$ in a

deformable cluster, which is caused by changes in the radius of interaction between the core-excited molecule and its neighbours in clusters and the solid. Hence, an increase in dynamic stabilization on intramolecular vibrational bands is expected to occur if the interaction of the core-excited molecule with its neighbours increases. In particular, previous results on $1s$ -excited nitrogen clusters provide evidence for strong dynamic localization of the core hole in one of the equivalent atomic sites, since the dynamic dipole momentum of N_2^* will dominate the interaction with its neighbours (Flesch *et al.*, 2001). The magnitude of the red shift is expected to be related to the stabilization that occurs *via* excitation of intermolecular vibrations. In the case of CO clusters, there are no equivalent atomic sites so that such a stabilization effect should be small. As a result, the excitation energies of core-to-valence transitions ($1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$) remain practically unchanged (Pavlychev & Rühl, 2000).

4. Conclusions

Recent experimental progress in high-resolution spectroscopy in the near-edge regime is reported. We have shown that high spectral resolution is required in order to observe, in the pre-edge regime of molecular clusters, small energy shifts and changes in the line shape of core-to-valence transitions that reflect changes in electronic structure, compared to the free molecule, and the occurrence of intermolecular interactions. This work has been stimulated by the availability of state-of-the-art soft X-ray monochromators, insertion devices and high-brilliance synchrotron radiation facilities. It is anticipated that these results will also stimulate theoretical work, so that the quantitative understanding of size effects of matter will develop further.

Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. We thank the Messer-Griesheim GmbH for the gift of the carbon monoxide sample.

References

- Anderson, A., Sun, T. S. & Donkersloot, M. C. A. (1970). *Can. J. Phys.* **48**, 2265–2271.
- Björneholm, O., Federmann, F., Fössing, F. & Möller, T. (1995). *Phys. Rev. Lett.* **74**, 3017–3020.
- Björneholm, O., Federmann, F. & Möller, T. (1999). *J. Chem. Phys.* **111**, 546–550.
- Domke, M., Xue, C., Puschmann, A., Mandel, T., Hudson, E., Shirley, D. A. & Kaindl, G. (1990). *Chem. Phys. Lett.* **173**, 122–128.
- Federmann, F., Björneholm, B., Beutler, A. & Möller, T. (1994). *Phys. Rev. Lett.* **73**, 1549–1552.
- Flesch, R., Pavlychev, A. A., Neville, J. J., Blumberg, J., Kuhlmann, M., Tappe, W., Senf, F., Schwarzkopf, O., Hitchcock, A. P. & Rühl, E. (2001). To be published.
- Floreano, L., Naletto, G., Cvetko, D., Gotter, R., Malvezzi, M., Marassi, L., Morgante, A., Santaniello, A., Verdini, A., Tommasini, F. & Tondello, G. (1999). *Rev. Sci. Instrum.* **70**, 3855–3864.
- Haensel, R., Kosuch, N., Nielsen, U., Rössler, U. & Sonntag, B. (1973). *Phys. Rev. B*, **7**, 1577–1591.
- Harrison, W. (1970). *Solid State Theory*. New York: McGraw Hill.
- Huber, K. P. & Herzberg, G. (1979). *Molecular Spectra and Molecular Structure*, Vol. 4. New York: Van Nostrand.
- Jolly, W. L., Bomben, K. D. & Eyer mann, C. J. (1984). *At. Data Nucl. Data Tab.* **31**, 433–493.
- Kakar, S., Björneholm, O., Weigelt, L., deCastro, A. R. B., Tröger, L., Frahm, R., Möller, T., Knop, A. & Rühl, E. (1997). *Phys. Rev. Lett.* **78**, 1675–1678.
- Knop, A. & Rühl, E. (1996). *Structures and Dynamics of Free Clusters*, edited by T. Kondow, K. Kaya, A. Terasaki, pp. 235–243. Tokyo: Universal Academy Press.

- Knop, A., Wassermann, B. & Rühl, E. (1998). *Phys. Rev. Lett.* **80**, 2302–2305.
- Pavlychev, A. A., Fominykh, N. G., Watanabe, N., Soejima, K., Shigemasa, E. & Yagishita, A. (1998). *Phys. Rev. Lett.* **81**, 3623–3626.
- Pavlychev, A. A. & Rühl, E. (2000). *J. Elec. Spectrosc. Relat. Phenom.* **106**, 207–220. (Erratum: *J. Elec. Spectrosc. Relat. Phenom.* **107**, 203.)
- Pavlychev, A. A., Semenova, E. V., Hitchcock, A. P. & Rühl, E. (1995). *Physica*, **208/209**, 187–189.
- Pavlychev, A. A., Vinogradov, A. S., Stepanov, A. P. & Shulakov, A. S. (1993). *Opt. Spectrosc.* **75**, 327–341.
- Rosenberg, R. A., Love, P. J., LaRoe, P. R. & Rehn, V. (1985). *Phys. Rev. B*, **31**, 2634–2642.
- Rühl, E., Schmale, C., Jochims, H. W., Biller, E., Simon, M. & Baumgärtel, H. (1991). *J. Chem. Phys.* **91**, 6544–6550.
- Rühl, E. (1992). *Ber. Bunsenges. Phys. Chem.* **96**, 1172–1179.
- Rühl, E. (2000). *Theory and Experiments on Clusters*, edited by T. Kondow. Singapore: World Scientific. In the press.
- Rühl, E., Heinzel, C., Hitchcock, A. P. & Baumgärtel, H. (1993). *J. Chem. Phys.* **98**, 2653–2663.
- Senf, F., Eggenstein, F., Feikes, J., Follath, R., Hartlaub, S., Knuth, T., Lammert, H., Noll, T., Schmidt, J. S., Reichardt, G., Schwarzkopf, O., Weiss, M., Zeschke, T. & Gudat, W. (1999). *BESSY Annual Report*, pp. 512–514.
- Sodhi, R. N. S. & Brion, C. E. (1984). *J. Elec. Spectrosc. Relat. Phenom.* **34**, 363–372.
- Steinberger, I. T., Teodorescu, C. M., Gravel, D., Flesch, R., Wassermann, B., Reichardt, G., Huchings, C. W., Hitchcock, A. P. & Rühl, E. (1999). *Phys. Rev. B*, **60**, 3995–4004.
- Stöhr, J. (1992). *NEXAFS Spectroscopy*. Berlin: Springer.
- Teodorescu, C. M., Gravel, D. & Rühl, E. (1998). *J. Chem. Phys.* **109**, 9280–9287.
- Vostrikov, A. A., Dubov, D. Y. & Samoilov, I. V. (1994). *Tech. Phys.* **39**, 1267–1268.
- Wight, G. R., Brion, C. E. & van der Wiel, M. J. (1973). *J. Elec. Spectrosc. Relat. Phenom.* **1**, 457–469.