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Vibrational-state-dependent decay of the CO C(1s) excitation

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Molecular ionization and ionic fragmentation of core excited CO valence and Rydberg states are studied by partial-ion-yield spectroscopy at vibrational resolution. The vibrational intensities of the Rydberg excitations differ significantly depending on the ionization and/or fragmentation channel. The observed intensity variations are explained by nondissociative excited final ionic states of the subsequent molecular Auger decay. The vibrational levels of these final states become selectively depopulated due to interaction with dissociative decay channels leading to ionic fragmentation.

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Vibrational structures of core excited valence and Rydberg states of molecules have recently become a subject of rapidly increasing interest [1]. Vibrationally resolved spectroscopy allows detailed studies of the vibrational and geometrical properties of core excited molecules. In particular, it should be possible to use the vibrational structures as a local probe of molecular vibrations. All this information has been solely based on the analysis of absorption or photoionization spectra, both representing the total ionization cross section. Partial cross sections and fragmentation-specific ion yields were also studied extensively in the core-level region, but not with vibrational resolution [2,3].

It was assumed that the relative intensities of the partial and total yield measurements would not vary because of the high energy released in the core excitation. Furthermore, owing to the dominance of dissociative ionization in the core-level region, little attention was drawn to the nondissociative ionization channels, in particular for Rydberg excitations. These excitations decay predominantly via spectator transitions into two-hole one-electron final states because of the small overlap between the Rydberg electron and the 1s hole [4]. The potential curves of these states were assumed to be basically of repulsive nature, quenching the production of unfragmented molecular ions such as CO^+ and CO^{2+}. Previous core-level photoionization studies performed on CO [2,3] did not observe indeed any clearly enhanced CO^+ and particularly CO^{2+} signal in the partial ion yield of Rydberg excitations, corroborating the assumed complete fragmentation of the Rydberg excited molecules. We show in this Rapid Communication that, in contrast to this, nondissociative ionization also takes place in the decay of Rydberg excitations. Moreover, in the case of CO this nondissociative ionization channel displays a vibrational intensity pattern, which differs dramatically from that of the dissociative channels and total ionization yield. We explain the existence of these nondissociative channels through population of metastable Rydberg-satellite states in the inner-valence region via subsequent Auger decay of the Rydberg excitations. These metastable Rydberg-satellite states were examined more closely by threshold photoelectron spectroscopy (TPES) in order to study their possible interaction with dissociative inner-valence states as a possible cause for the unusual intensity variations in the CO^+ and CO^{2+} channels.

The first studies on the vibrational structure of core excitations in small molecules were performed using electron energy loss spectroscopy, e.g. [5]. The breakthrough in studying these phenomena via photoionization came after the development of high-resolution soft-x-ray monochromators [1]. Following the first pioneering experiments [6], new beamlines with similar resolution and to some extent higher photon flux [7,8] came into operation, extending the vibrationally resolved studies, in particular for CO [9,10]. The results showed the validity of the equivalent core model, which considers the electronic structure of a core excited molecule (CO, N_2) as being equivalent to that of the corresponding valence excited molecule with a nuclear charge of $Z+1$ (NO). Only one major discrepancy remains, and this is that none of the $ns\sigma$ states with $n>3$ of CO are visible, whereas these states are clearly exhibited in the N_2 excitation spectrum. This is in marked contrast to the $np\pi$ states, which appear almost at the same position in the core excitation spectra of these two molecules. Despite the achieved improvements in resolution and photon flux, vibrationally resolved studies have still been restricted to absorption or total yield measurements, supplemented by electron spectrometry measurements at selected photon energies [11]. Other measurements determining vibrationally resolved partial ionization yields across core excitations have not to our knowledge been reported.

Our experiments were performed at beamline BW3 of the Hamburger Synchrotronstrahlungslabor (HASYLAB) of DESY [12]. This beamline is a triple N-pole undulator beamline ($N=21,33,44$) equipped with a high-resolution SX700 plane grating monochromator modified for high photon throughput. This instrument routinely achieves a resolution of 3000 with a photon flux of 10^{12}photons/sec. In order to record different partial ionization yields simultaneously during the photon energy scan a newly developed time-of-flight (TOF) mass spectrometer was used. The spectrometer consists of a McLaren type space charge focusing instrument of 42 mm length with an extraction field of 1000 V/cm and a multihit anode. This makes it possible to measure all pairs

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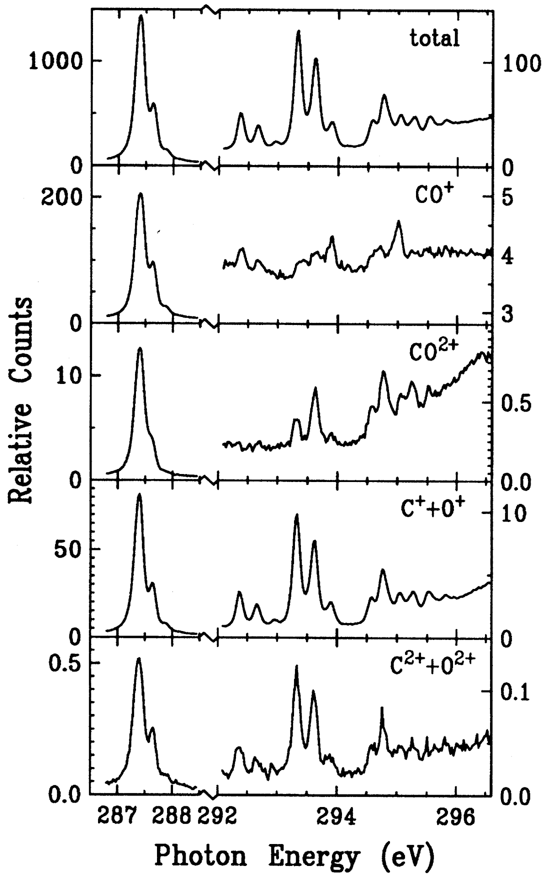

FIG. 1. Total and selected partial ion yields recorded in the C(1s) valence and Rydberg excitation region of CO.

of charged particles in coincidence, independent of their charge state and initial kinetic energy. The flight times of the ions were measured with respect to the bunch marker of the storage ring, which was operated in a double-bunch mode with a time window of 480 nsec, yielding intrinsic branching ratios of fragment ions. The spectrometer was set at an angle of 54.7° with respect to the electric vector of the photon beam in order to remove the effect of anisotropic fragmentation in the peak shapes [13]. The background pressure was better than 3×10^{-6} mbar during the measurements. The details of this TOF mass spectrometer will be described elsewhere [14]. In order to avoid possible distortions of the scans, all coincident and noncoincident ionization channels (23) were measured simultaneously during one photon energy scan, including the monitoring of the background in the time spectra. This capability is crucial for the comparison of photon-energy-dependent details in the different spectra. In order to examine the possible final states of the decaying Rydberg excitations more closely, the ion yield measurements were supplemented by a threshold photoelectron spectrum in the inner-valence region taken as described in a previous publication [15].

Figure 1 shows 5 out of 11 partial ionization yields for the C(1s) excitation of CO between 287 and 296.5 eV. This region covers the C(1s)$\rightarrow\pi^*$ excitation (287–289 eV) and all of the stronger Rydberg series up to $n=7$ (292–296 eV). The figure shows that, despite the large variation in relative counting rate covering more than three orders of magnitude, the relative line intensities in most of the dissociative ionization channels are indeed quite similar. Our results confirm the predominance of the C$^+$ and O$^+$ dissociation channel, as already inferred from the sum of all vibrational components in the lower-resolution measurements [2,3]. The observed branching ratios are in good accord with the most recent low-resolution measurement [3]; however, the present measurements reveal many more dissociative and nondissociative channels than observed before, most of them still awaiting a theoretical explanation. Here we will concentrate on the behavior of the nondissociative channels. These differ markedly from the rest of the ionization channels, which behave mostly in accord with the total ionization yield.

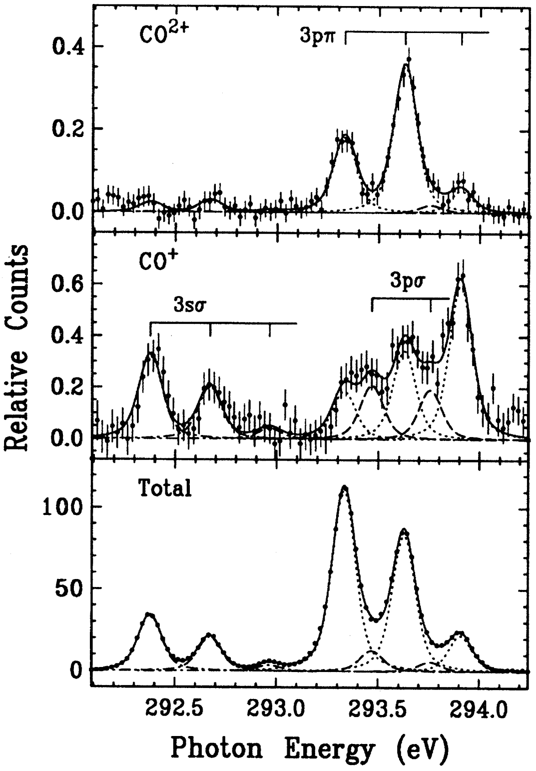

FIG. 2. CO^{2+}, CO$^+$, and the total ion yield for the C(1s)-Rydberg excitation for $n=3$. The fitted curves represent the different vibrational components of these excitations.

The nondissociative ionization channels yielding CO$^+$ and CO^{2+} molecular ions show a vibrational pattern in the Rydberg excitations that appears partly inverted when compared to the total ionization yield. Furthermore, additional Rydberg series seem to appear. To examine these differences in more detail, Figs. 2 and 3 show the two nondissociative ionization channels along with the total ion yield on an enlarged scale for different Rydberg excitations with $n=3$ and $n\geqslant3$, respectively. Contributions from valence ionization and ionization by stray and higher order light in the yield curves have been subtracted. The experimentally obtained yields (dots) were reproduced by a least-squares computer analysis in which the peaks were assumed to have Voigt profiles. The positions of the peaks in the total ion yield spectra are compared to the results of Domke *et al.* [9], giv-

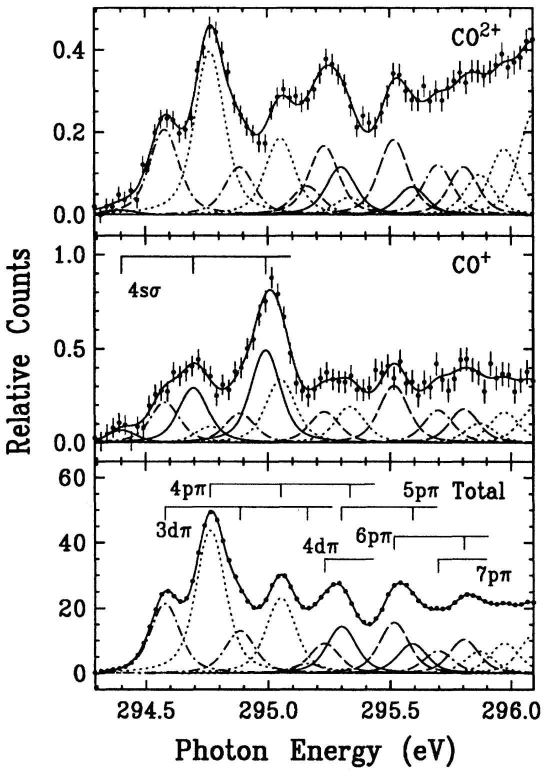

FIG. 3. CO^{2+} and CO^+ in comparison to the total ion yield for all Rydberg excitations with $n \geqslant 3$, including the "missing" $4s\sigma$ series. The different vibrational components of the various series are obtained by a fitting procedure and depicted by corresponding curves.

ing peak intensities in good agreement with their data. A linear contribution due to continuum ionization is not shown in Fig. 3.

Indications of changing vibrational patterns are already exhibited in the vibrational spectrum of the $C(1s) \rightarrow \pi^*$ resonance. The higher vibrational components are relatively enhanced in CO^+, with respect to the total ionization yield, whereas in CO^{2+} they are slightly reduced. This redistribution of oscillator strengths within vibrational progressions becomes clearly apparent when Rydberg excitations are considered. In Fig. 2, the $3p\pi$ vibrational intensities become completely inverted in CO^+ compared with the total ion yield, whereas in CO^{2+} the $\nu = 1$ vibrational component shows up as the strongest, giving rise to three different vibrational patterns in each channel. In addition, the $3s\sigma$ series between 292.3 and 293 eV seems to be largely suppressed in CO^{2+}, whereas in CO^+ this series closely follows the total yield behavior. The situation becomes even more complicated when the higher Rydberg series, shown in Fig. 3, are examined. Close inspection reveals that even so far unidentified series, such as the $4s\sigma$ series, are clearly exhibited in the CO^+ spectrum. This "*missing series*" appears at the position expected by the theoretical calculations of Padial *et al.* [16] and Iwata *et al.* [17].

The observed intensity variations in the partial ion yields cannot be explained by properties of the excited initial state or the strength of the Auger transition, as in total yield spectroscopy, because these are determined entirely by the absorption strength. Consequently, if one considers the possibility of selective depopulation via curve crossings these variations must depend on the behavior in the final states. The final states of our resonant Auger process are two-hole one-electron states in the binding energy range of the inner-valence states, a region characterized by the breakdown of the molecular orbital picture and dominated by repulsive energy curves. However, despite the predominance of dissociative behavior in these states [18], there are very recent indications for the existence of high lying metastable Rydberg states in this energy region. A high-resolution photoelectron spectroscopy (PES) study of Baltzer *et al.* [19] revealed a whole variety of narrow satellite lines assigned tentatively as nondissociative Rydberg-excited shakeup states. This interpretation is corroborated by observation of highly excited quasistable states of neutral CO converging to valence and Rydberg-excited satellite states [20]. In order to examine these states also at their production threshold a comparison is made with a threshold photoelectron spectrum taken in the photon energy region of the corresponding binding energies. Figure 4 shows the high-resolution inner-valence PES spectrum along with the corresponding TPES spectrum. The analogy is obvious, showing that these states are populated from threshold over a wide energy range. However, both spectra show also the degeneracy of these states with very broad

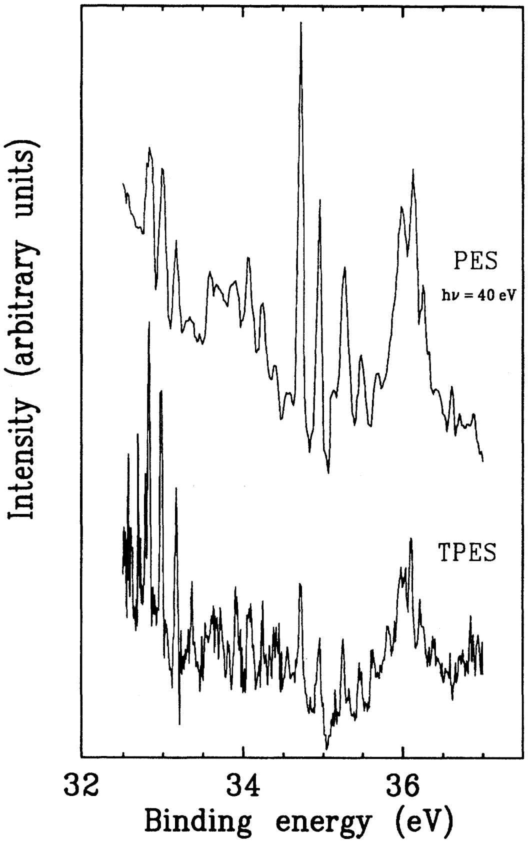

FIG. 4. Inner-valence threshold photoelectron spectrum (TPES) compared to a corresponding high-resolution photoelectron spectrum (PES) of CO by Baltzer *et al.* [19].

dissociative features, indicating the possibility for strong interaction between both groups of states, dissociative and nondissociative.

If we consider these Rydberg-excited satellite states as potential final states of the resonant Auger decay of our Rydberg-excited core hole states,

$$h\nu + \mathrm{CO} \rightarrow \mathrm{CO}^*(1s^{-1}nl\lambda) \rightarrow \mathrm{CO}^+(n'\lambda'^{-1}n''\lambda''^{-1},nl\lambda) + e^-,$$

the observed variations in the vibrational patterns of these excitations can be explained easily in terms of interacting final states of the decay process, in particular between dissociative and nondissociative final states. The coexistence of metastable and repulsive potential curves in a certain energy range gives rise to curve crossings and avoided curve crossings. These are both a potential source for vibrational redistribution between dissociative and nondissociative channels via selective depopulation of certain channels, as observed in our partial-ion-yield spectra. These effects may be expected to be exhibited in the Rydberg excitations of other molecules with a similar complex inner-valence structure such as N_2, O_2, and NO; however, it is still unclear whether this delicate balance between metastable and repulsive final states is a more general phenomenon of the inner-valence region of those molecules or a characteristic feature of CO because of the particularly pronounced breakdown of the orbital picture in this molecule.

In summary, we have reported on vibrationally resolved partial-ion-yield measurements covering relative intensities over more than three orders of magnitude in the C($1s$) core excitation region of CO. Our results show clearly the existence of nondissociative ionization channels for the different Rydberg series that exhibit unexpected variations in their vibrational patterns. The most dramatic difference compared to the absorption spectrum is for the CO^+ partial ion yield in which the missing $4s\sigma$ series becomes apparent. The intensity variations are explained by interacting dissociative and nondissociative final states of the subsequent resonant Auger process. The vibrational levels for the nondissociative final states are selectively depopulated.

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[1] C.T. Chen, Nucl. Instrum. Methods A **256**, 595 (1987); C.T. Chen and F. Sette, Rev. Sci. Instrum. **60**, 1616 (1989); Phys. Scr. **T31**, 119 (1990).

[2] W. Eberhard, T. K. Sham, R. Carr, S. Krummacher, M. Strongin, S. L. Weng, and D. Wesner, Phys. Rev. Lett. **50**, 1038 (1983).

[3] A. P. Hitchcock, P. Lablanquie, P. Morin, E. Lizon, A. Lugrin, M. Simon, P. Thiry, and I. Nenner, Phys. Rev. A **37**, 2448 (1988).

[4] W. Eberhardt, in *Applications of Synchrotron Radiation*, edited by W. Eberhardt, Springer Series in Surface Sciences Vol. 35 (Springer, Berlin, 1995).

[5] M. Tronc, G.C. King, and F.H. Read, J. Phys. B **12**, 137 (1979); A.P. Hitchcock and C.E. Brion, J. Electron Spectrosc. Relat. Phenom. **18**, 1 (1980).

[6] C. T. Chen, Y. Ma, and F. Sette, Phys. Rev. A **40**, 6737 (1989).

[7] K. J. Randall, J. Feldhaus, W. Erlebach, A. M. Bradshaw, W. Eberhardt, Z. Xu, Y. Ma, and P. D. Johnson, Rev. Sci. Instrum. **63**, 1367 (1992).

[8] M. Domke, T. Mandel, A. Puschmann, C. Xue, D. A. Shirley, G. Kaindl, H. Petersen, and P. Kuske, Rev. Sci. Instrum. **63**, 80 (1992).

[9] M. Domke, C. Xue, A. Puschmann, T. Mandel, E. Hudson, D.A. Shirley, and G. Kaindl, Chem. Phys. Lett. **173**, 122 (1990); **174**, 668(E) (1990).

[10] K. J. Randall, A. L. D. Kilcoyne, H. M. Köppe, J. Feldhaus, A. M. Bradshaw, J.-E. Rubensson, W. Eberhardt, Z. Xu, P. D. Johnson, and Y. Ma, Phys. Rev. Lett. **71**, 1156 (1993).

[11] M. Neeb, J.-E. Rubensson, M. Biermann, and W. Eberhardt, J. Electron Spectrosc. Relat. Phenom. **67**, 261 (1994).

[12] A.R.B. de Castro and R. Reininger, Rev. Sci. Instrum. **63**, 1317 (1992); C.U.S. Larsson, A. Beutler, O. Björneholm, F. Federmann, U. Hahn, A. Rieck, S. Verbin, and T. Möller, Nucl. Instrum. Methods A **337**, 603 (1994).

[13] E. Shigemasa, T. Hayaishi, T. Sasaki, and A. Yagishita, Phys. Rev. A **47**, 1824 (1993); O. Hemmers, F. Heiser, J. Eiben, R. Wehlitz, and U. Becker, Phys. Rev. Lett. **71**, 987 (1993); J.D. Bozek, N. Saito, and I.H. Suzuki, J. Chem. Phys. **100**, 393 (1994).

[14] F. Heiser, K. Wieliczek, N. Saito, and U. Becker (unpublished).

[15] F. Heiser, U. Hergenhahn, J. Viefhaus, K. Wieliczek, and U. Becker, J. Electron Spectrosc. Relat. Phenom. **60**, 337 (1992).

[16] N. Padial, G. Csanak, B. V. McKoy, and P. W. Langhoff, J. Chem. Phys. **69**, 2992 (1978).

[17] S. Iwata, N. Kosugi, and O. Nomura, Jpn. J. Appl. Phys. **17**, Suppl. **17-2**, 105 (1978).

[18] U. Becker, O. Hemmers, B. Langer, A. Menzel, R. Wehlitz, and W. B. Peatman, Phys. Rev. A **45**, R1295 (1992).

[19] P. Baltzer, M. Lundqvist, B. Wannberg, L. Karlsson, M. Larsson, M. A. Hayes, J. B. West, M. R. F. Siggel, A. C. Parr, and J. L. Dehmer, J. Phys. B **27**, 4915 (1994).

[20] A. Dadouch, G. Dujardin, L. Hellner, M.J. Besnard-Ramage, and B.J. Olsson, Phys. Rev. A **43**, 6057 (1991); T. Masuoka and E. Nakamura, *ibid.* **48**, 4379 (1993); P. Erman, E. Rachlew-Källne, and S.L. Sorensen, Z. Phys. D **30**, 315 (1994).