Vibrationally selective resonant Auger spectroscopy of the $3p$ core-to-Rydberg excitation in CO

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The Auger decay of the C $1s \rightarrow 3p$ excitation in CO has been studied by means of vibrationally selective angle-resolved electron spectroscopy. It is shown that for these highly excited Rydberg states the strict spectator model works excellently in describing the Auger decay. Consequently, all the spectral features have been identified by comparison to previous normal Auger studies. Intense lines belonging to $3p \rightarrow 4p$ shakeup also accompany the main lines; together with the total absence of any participator contribution, this reveals the atomiclike nature of the $3p$ Rydberg orbital. Remarkably large differences between the decay spectra recorded on the $3p(v'=0)$ and the $3p(v'=1)$ resonance reveal the spatial differences in the decay paths. For transitions to the final state with the lowest binding energy in the spectator region, an angular anisotropy dependent upon the vibrational quantum number of the final state is observed. We observe different angular anisotropy for transitions to different vibrational levels of the same electronic final state in resonant Auger spectroscopy. [S1050-2947(97)07107-2]

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I. INTRODUCTION

For the CO molecule, the majority of the resonant Auger or Auger resonant Raman studies have so far concentrated upon the Auger decay resulting from core excitation to the first unoccupied $2\pi^*$ valence level [1–4]. There has also been a considerable interest in the shape resonance [1,2,5], where the excited core electron can be considered to be temporarily trapped in an orbital of σ^* symmetry. Both of these resonances have been shown to yield nonisotropic Auger electron emission [1,2]. Together with normal Auger studies [6–8], where the excitation energy is far above the ionization threshold, considerable insight into the vibrational lifetime interference influence on the Auger decay as well as on the coupling strength between the excited electron and valence electrons has been obtained. Selective excitation to distinct Rydberg levels in connection with electron spectroscopy of the resulting decay has recently become possible for small molecules, such as N_2 and HCl [9–11]. These studies have revealed the usefulness of the strict spectator model and an almost total absence of any participator contribution to the decay for core-to-Rydberg excitations. However, these molecular studies have often suffered from moderate monochromator and spectrometer resolution, making detailed information about molecular vibrational progression difficult or impossible to obtain. For CO, the majority of the earlier synchrotron-radiation-based measurements of the decay processes from core-to-Rydberg excitations have concentrated on ion yield measurements [12–14]; from these studies considerable insight into the molecular orientation caused by the excitation process has been reached. Recently, a vibrationally selective x-ray emission study of both the $3s$ and the $3p$ resonance was performed [15]. A large difference be-

tween the x-ray emission spectra, depending on the vibrational quantum number of the excited state, was observed. A similar effect is thus expected for the corresponding Auger decay, due to the similarities between the nonradiative and the radiative decay.

For small diatomic molecules, the energy splitting between the vibrational levels of the intermediate state may exceed the natural lifetime width of the $1s$ core hole state. If the exciting photon bandwidth is sufficiently narrow, distinct vibrational levels of the intermediate state can be selectively excited. Together with high-resolution electron decay spectra, it makes it possible to obtain detailed knowledge about the transition between the excited neutral intermediate state and the singly ionized final state. In addition, if high resolution is combined with angle-resolved measurements, important complementary information can be obtained. The aim of this work is thus to study the Auger decay of the core-to-Rydberg excited state with angular resolution, and incorporate high resolution in both the exciting photon flux and the electron decay spectra.

Within the dipole approximation the angular distribution of the emitted electrons for completely linearly polarized light is expressed as [16]

$$I(\sigma,\varphi) = \frac{\sigma}{4\pi}\left[1 + \frac{\beta}{2}\left(\frac{1}{2} + \frac{3}{2}\cos 2\varphi\right)\right]. \quad (1)$$

Here σ is the total cross section, β is the parameter describing the angular dependence of the specific transition studied, and φ is the angle between the polarization plane and the direction of the emitted electron. Neglecting interference effects, the angular distribution of Auger electrons is within the two-step model described as the product $\beta = A c_a$, where A is the photon-energy-dependent molecular alignment parameter, and c_a the parameter characterizing the intrinsic anisotropy of the Auger decay [17]. The selectivity in the alignment is caused by the dipole selection rule for

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photoexcitation, i.e., for a $1s \rightarrow np$ transition the photoabsorption is expected to be enhanced for molecules that have the molecular axis perpendicular to the electric field vector. For molecules, the asymmetry of the Auger electron decay is in turn caused by the nonisotropic charge distribution [17]. An estimate of the alignment parameter can be obtained indirectly from the angular dependence of an Auger group. By studying the angle-resolved Auger electron spectra at photon energies corresponding to the π^* resonance and the σ^* shape resonance for N_2, the effect of the A parameter on the asymmetry of the Auger decay was recently shown by Kivimäki et al. [18].

II. EXPERIMENT

The experiment was carried out at the MAX I storage ring in Lund, Sweden, at beamline 51 (BL51) [19]. The beamline uses radiation from a short period undulator giving reasonable photon flux in the 60–600 eV range. BL51 is provided with a modified SX-700 plane grating monochromator. In this study a photon bandwidth of approximately 150 meV at 293 eV photon energy was used. Recently, an end station with the possibility of rotating the SES-200 electron energy analyzer in a plane perpendicular to the direction of the incoming photon beam was installed at BL51 [20]. The transmission of this spectrometer decreases rather slowly with increasing kinetic energy, making it possible to record electrons with high initial kinetic energy at reasonable intensity. This is of crucial importance for studies of weak resonant processes, such as the one presented here. For this particular study, a constant analyzer pass energy of 75 eV, resulting in an electron spectrometer resolution of around 150 meV was used. Due to the high kinetic energy of the Auger electrons, a small but non-negligible Doppler broadening of approximately 40 meV must also be taken into account. This yields a total experimental resolution of approximately 210 meV, arising from the monochromator, Doppler and spectrometer broadening. The CO gas was commercially obtained from Alfax with a purity of $\approx 99.9\%$; valence electron spectra were measured to check for possible contamination of the sample, and the photon flux was measured by a photodiode in the end of the gas cell.

To account for differences in transmission between different analyzer angles, Ne $2p$ photoelectron spectra were recorded at similar experimental conditions. This line was chosen since the β parameter and the cross sections for Ne $2p$ are well known [21]. From measurements of the Ne $2s$ photoelectron line together with the Ne $2p$ photoelectron line the degree of linear polarization was determined to be greater than 96% at ≈ 290 eV photon energy. Transmission correction was also made from measurements of the CO valence photoelectron lines using known β parameters [22], although the accuracy is not as high as in the case of Ne $2p$. Furthermore, it was found that the participator contribution to the total decay was negligible. Therefore, the 4σ, 1π, and 5σ photoelectron lines can be used as an inherent transmission correction for spectra recorded at different angles. To eliminate errors induced by instabilities in the absolute intensity of the photon flux, for instance, due to mechanical instabilities of the spectrometer or fluctuations of the position of the electron beam in the storage ring, such an inherent transmis-
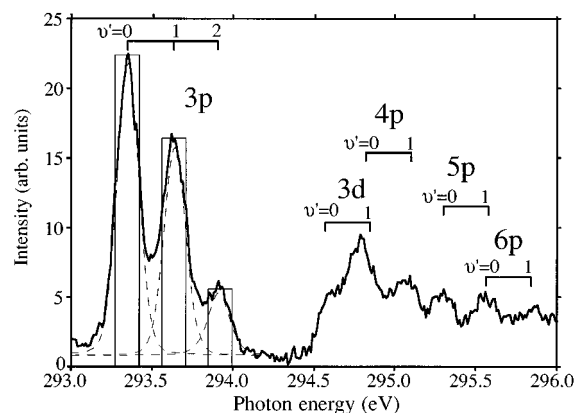

FIG. 1. Partial electron yield spectrum covering the photon energy region of all the $(1h\text{-}1e)$ singly excited Rydberg states except the $3s$ level.

sion correction from peaks in the decay spectra corresponding to final states with holes in the 4σ, 1π, or 5σ orbital is very helpful. These three methods resulted in similar corrections for the transmission difference between different analyzer angles.

It has also been shown that the angular anisotropy of the Auger decay may vary across resonances [1]. Efforts have consequently been made to keep track of the accurate photon energy calibration during the recordings.

III. RESULTS AND DISCUSSION

The ground-state valence electron configuration of CO is $(\text{core})^4(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2$. From earlier studies of the Auger decay of Rydberg excitations for small molecules [9,15], it is known that the participator contribution to the total decay is small or negligible. Due to the fact that the participator transitions correspond to final states that also can be reached via the direct photoionization, it is difficult to obtain an accurate estimate of the participator decay contribution. In the present study, the direct photoionization contribution has been estimated by recording photoelectron spectra of the three valence lines 4σ, 1π, and 5σ with a nonresonance photon energy close to the first Rydberg resonance, where the participator contribution can be considered to be negligible. Comparison to the spectra recorded at the $3p$ resonance revealed that the valence electron lines in the off-resonance spectrum have about the same intensity as the corresponding lines in the resonant Auger spectra. Therefore the resonant population of valence single-hole (participator) final states must be of very low probability. This immediately indicates a weak coupling between the excited Rydberg electron and the core hole as well as the valence electrons [11].

The absorption spectrum covering the photon energy region for all the singly core excited $(1h\text{-}1e)$ Rydberg states except the $3s$ state is shown in Fig. 1. The peak assignments are taken from a study by Domke et al. [13]. From earlier measurements on the $2\pi^*$ resonance of CO [3], it is well known that interference effects may greatly influence the structure of the Auger spectrum. To be able to distinguish between lifetime vibrational interference and angular dependence effects, efforts were made to cancel out the possible

interference effects. Firstly, the energy of the exciting photons was precisely controlled by a regular recording of the absorption spectrum. In this way, the decay spectra can be recorded at exactly the same photon energy at both angles, resulting in identical interference contributions. Secondly, decay spectra from the C $1s \rightarrow 3p(v'=0)$ and C $1s \rightarrow 3p(v'=1)$ excitations were recorded with a photon energy slightly off resonance maxima. These measurements showed that even with a photon energy detuning of several tens of meV, it was not possible to reproduce the angular-dependent effects observed between spectra recorded at 0° and 55°. We are thus confident that the angular dependence could be isolated.

The photon bandwidth of approximately 150 meV is represented by the boxes shown in Fig. 1, which is clearly narrower than the vibrational spacing of approximately 300 meV. The absorption spectrum was fitted with Voigt profiles in order to evaluate the role of lifetime vibrational interference (LVI). LVI is caused by the overlap of the exciting photon energy distribution and the Lorentzian tails of the adjacent vibrational intermediate states. In the case of excitation to the first vibrational state $v'=0$, the contribution from the second vibrational state was found to be less than 5%, so practically only the $v'=0$ level is populated in the intermediate state. Since it is known that the strength of the interference contribution to the decay spectra is of the same order of magnitude as the population of adjacent intermediate states [3], the interference is very weak in the $v'=0$ case. For the second vibrational level, $v'=1$, the overlap with adjacent vibrational levels is stronger, about 8% from the $v'=0$ level and 2% from the $v'=2$ level. Thus, in the case of $v'=1$ the vibrational interference contribution, together with the direct part from adjacent vibrational intermediate states, should play a minor role and is hence assumed to have a small impact on the decay spectra for the C $1s \rightarrow 3p(v'=1)$ excitation. When exciting the $v'=2$ intermediate vibrational state, the overlap with the other two vibrational levels is larger than for the previous two cases. From the absorption spectrum the contribution from the $v'=0$ and $v'=1$ intermediate states to the total intensity of the $v'=2$ level can be estimated to about 20%.

Electronic state-state interference may also occur in the decay from the $3p(v'=0,1,2)$ intermediate states, since the $3p$ states of π symmetry overlap with the corresponding $3p$ states of σ symmetry. In a study by Domke *et al.* [13], it was found that the photoexcitation probability of $3p$ states of σ symmetry is substantially lower than the corresponding states of π symmetry. In addition, the $3p\sigma$ resonances were found to be shifted approximately 0.15 eV towards higher photon energy. Due to this shift and the narrow exciting photon bandwidth used to excite the $3p$ vibrational states, any contribution to the decay spectra from intermediate states of σ symmetry should be very low, and will be neglected in the following discussion.

The assignment of the structures in the decay spectra from the $3p(v'=0)$, $3p(v'=1)$, and $3p(v'=2)$ intermediate states has been carried out by comparison to the normal Auger decay spectra of CO [6–8]. To justify such a comparison, the $v'=0$, $v'=1$, and $v'=2$ decay spectra were added, after normalization to the intensity of the valence photoelectron lines. In Fig. 2 the sum spectrum is shown together with a
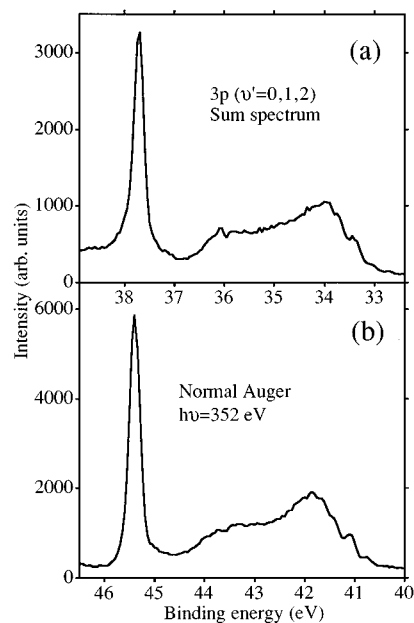

FIG. 2. Lower part: the normal Auger spectrum recorded at 352 eV photon energy. The binding energy scale was calibrated using the C $1s$ ionization energy of 296.08 eV [13]. Upper part: the spectrum obtained by a weighted summation of the decay spectra from the $3p(v'=0,1,2)$ intermediate states.

normal Auger decay spectrum. As seen, the sum spectrum strongly resembles the CO normal Auger spectrum. This is expected if the spectator electron located in a Rydberg orbital does not couple with the outermost valences electrons and, instead, just acts by screening due to the Coulomb interaction. In the strict spectator model, the $(2h\text{-}1e)$ decay spectrum associated with a core excited Rydberg state should be the same as for the $2h$ Auger decay spectrum, but shifted towards lower binding energy (by about 7.7 eV). Thus, structures in the decay spectra from different core excited vibrational intermediate states can be identified by comparison to the normal Auger spectrum, provided that the average over vibrational levels is made as described above. The close resemblance between the normal Auger decay spectrum and the sum $3p(v'=0,1,2)$ decay spectrum in Fig. 2 also suggests a moderate interference contribution to the normal Auger decay. This is supported by the theoretical study of Correia *et al.* [8], in which the interference contribution showed significant effects only in the finer details of the decay spectrum. This further supports the conclusion that the interference contributions to the vibrationally selectively excited resonant Auger spectra reported here are small.

A. Auger decay of the C $1s \rightarrow 3p(v'=0)$ state

The resonant Auger decay following excitations to the intermediate vibrational Rydberg states $v'=0$, $v'=1$, and $v'=2$ were recorded for both 0°, i.e., the electron emission direction parallel to the polarization plane, and for the magic angle of 55°. In Fig. 3(a), the spectator part of the $3p(v'=0)$ decay spectrum is shown. After subtraction of the intensity of the 3σ valence line, which lies in this binding energy region, an average β value of ≈ -0.2 for the whole considered spectator group was determined using Eq. (1). Ion yield
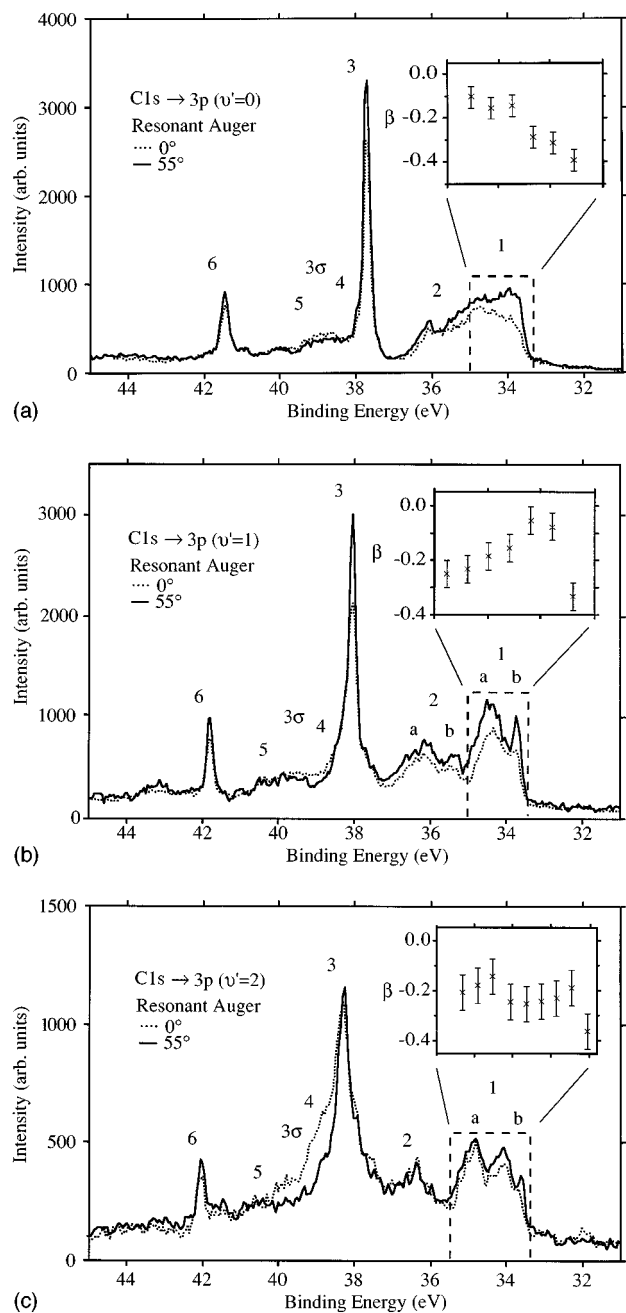
FIG. 3. (a) Spectator part of the Auger decay spectra from the photoexcited C $1s^{-1}3p(v'=0)$ intermediate states. Solid lines represent the spectra recorded at 55° and dotted lines the spectra recorded at 0°. The variation of the β parameter over the $X+3p$ final state is shown as an inset. (b) The spectator part of the Auger decay spectra from the photoexcited C $1s^{-1}3p(v'=1)$ intermediate states. The variation of the β parameter over the $X+3p$ final state is shown as an inset. (c) The spectator part of the Auger decay spectra from the photoexcited C $1s^{-1}3p(v'=2)$ intermediate states. The variation of the β parameter over the $X+3p$ final state is shown as an inset.

studies of the excitation to the first unoccupied valence level in CO have shown that the C $1s\rightarrow 2\pi^*$ excitation selects molecules with an axis preferentially oriented perpendicular to the polarization plane [2]. For this excitation, the majority of the Auger transitions have been found to have β values around -0.5 [23], i.e., more than a factor of two lower than

for the spectator part of the $3p$ decay. This implies that a similar, but weaker alignment of the intermediate state should also occur for the C $1s\rightarrow 3p\pi$ excitation. For a diatomic molecule a direct estimate of the alignment parameter A can be obtained from the angular dependence parameter (β_i) of the emitted ions in an ion yield measurement. In an ion yield study by Bozek $et\ al.$ [14] it was found that the $3p$ resonance revealed $\beta_i=-0.44$, which should be compared to the $\beta_i=-0.95$ found for the $2\pi^*$ resonance [2].

The decay of the C $1s\rightarrow 3p(v'=0)$ excitation is dominated by one sharp peak [labeled 3 in Fig. 3(a)]. A similar dominant and sharp peak is also seen in the normal Auger decay spectrum [6–8], and was assigned to transitions to the dicationic B final state. Consequently, the sharp peak in the decay spectra from the C $1s\rightarrow 3p(v'=0)$ excitation should be due to the same final-state configuration as in the normal Auger case, but shifted in energy due to the presence of a spectator electron in the $3p$ orbital. For this $(2h\text{-}1e)$ $3p$ spectator final state, we introduce the notation $B+3p$. The $B+3p$ final state is a doublet with a leading configuration of $(\text{core})^4(3\sigma)^2(4\sigma)^1(1\pi)^4(5\sigma)^1(3p)^1$ [7]. The characteristic sharpness of the structure associated with the B state is, in the case of normal Auger, explained by the fact that transitions between vibrational levels with the same vibrational quantum number is an order of magnitude stronger than the other possible transitions [6]. This is because the dicationic B state has an equilibrium internuclear distance $(R_e=1.097$ Å) similar to that of the C $1s$ core ionized state $(R_e=1.073$ Å) [8,24]. Thus, the presence of a spectator electron has a minor or at least comparable effect on the bond length for both the intermediate state and the final state, as expected for a Rydberg orbital with nonbonding character. This has also been observed in absorption spectroscopy wherefrom an equilibrium internuclear distance of 1.073(1) Å has been estimated for the C $1s\rightarrow 3p\pi$ excitation [13].

At the high binding energy side of peak 3 there is a similarly sharp but weaker structure, peak 6, located 3.73 eV from the $B+3p$ peak. Peak 6 is interpreted as belonging to a $B+4p$ final state, i.e. $3p\rightarrow 4p$ shakeup accompanying the Auger decay. To test this identification, a resonant Auger spectrum was recorded at the C $1s\rightarrow 4p$ resonance. From the latter spectrum, the $4p$ main lines were found at the same binding energies as the lines associated with the $3p\rightarrow 4p$ shakeup in Fig. 3(a), strongly supporting the shakeup interpretation. The $B+4p$ shakeup structure is about four to five times weaker than the $B+3p$ main line. The observed ratio is comparable to the ratio predicted by Armen in a study of the response of an electron in a hydrogenic orbital to a sudden change in central charge from Z to $Z+1$ [25]. To allow such a straightforward comparison the quantum defect for CO (0.775) [13] was implemented. In addition, in Ref. [25] it is predicted that the $3p\rightarrow 4p$ should be the only allowed shakeup transition, as we observe in this study. The relative intensity of the shakeup transition is somewhat lower than predicted by Armen, but the discrepancy can most certainly be explained by a weak but larger valence character of the $3p$ Rydberg orbital than that of the $4p$ orbital, giving rise to a smaller overlap between the two Rydberg orbitals than would be the case for two pure atomiclike orbitals.

The $B+4p$ shakeup state is found to have nearly the same β as the $B+3p$ main line, Table I. In the ion yield study by

TABLE I. Binding energies and angular anisotropy parameters (β) for transitions from the $3p(v' =0,1,2)$ intermediate states to ceertain electronic final states. The binding energies were determined as the center of gravity of the spectral structure.

Assignments in Fig. 3.	Identification	Binding energy (eV)			β
		$3p(v'=0)$	$3p(v'=1)$	$3p(v'=2)$	
Spectator group					$-0.22(5)$
1	$X+3p$	34.3	34.12	34.3	$-0.24(10)$
2	$A+3p$	35.8	35.97	36.4	$-0.16(10)$
3	$B+3p$	37.70	37.97	38.26	$-0.29(7)$
4	$X+4p$	38.3	38.0	38.2	
5	$A+4p$	39.7	40.0	40.3	
6	$B+4p$	41.43	41.73	42.02	$-0.24(7)$

Bozek *et al.* [14], the molecular orientation parameter of the $4p$ resonance was found to have almost half the strength of the $3p$ resonance, -0.25 and -0.44, respectively. Such a large difference is not observed in the present experiment. The discrepancy is most probably due to the fact that the molecules are selectively aligned in the C $1s \rightarrow 3p$ excitation, and the following shakeup has consequently a small or negligible effect on the molecular alignment.

The rest of the structures in Fig. 3(a) can be assigned in a similar manner with the aid of the normal Auger decay. The structures on the low-binding-energy side of the characteristic $B+3p$ peak, labeled 1 and 2, should be analogous to the transitions to the X and A final states in normal Auger decay; we thus denote these states as $X+3p$ and $A+3p$. In normal Auger decay, the X state has a leading $(\text{core})^4(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^0$ configuration and the A state has a leading $(\text{core})^4(3\sigma)^2(4\sigma)^2(1\pi)^3(5\sigma)^1$ configuration [7]. On the high-energy side of the $B+4p$ peak weak structures are just seen; these are interpreted as being due to transitions to the electronic final state of the $(\text{core})^4(3\sigma)^2(4\sigma)^2(1\pi)^2(5\sigma)^2$ configuration [26] plus the $3p$ spectator electron. Energetically this structure could also be due to shakeup to Rydberg orbitals with a higher main quantum number than 4, but in that case the shape of the structure should reflect the overall shape of the $3p$ spectator Auger decay; thus this explanation may be ruled out.

Comparing Figs. 2 and 3(a), one observes that the number of vibrational levels observed in the $3p(v'=0)$ resonant Auger decay is, as expected, fewer than in the case of normal Auger decay. This is simply due to the difference in vibrational envelopes for the intermediate state of the $3p(v' =0)$ resonant Auger decay compared to the core-ionized Auger decay. However, it is still difficult to discern structures belonging to transitions to the $A+3p$ state versus the $X+3p$, since the vibrational progressions for these two states overlap. For this reason the binding energies of the $X+3p$ and $A+3p$ states in Table I are not as accurately determined as those for the $B+3p$ and $B+4p$ states. The structures on the high-binding-energy side of the $B+3p$ state [labeled 4 and 5 in Fig. 3(a)] are interpreted as belonging to $A+4p$ and $X+4p$ states, using the same arguments as for the $B+4p$ state. The shakeup to main line intensity ratios of these transitions seems to be comparable to that of the $B +4p$ state, but the energy separation from the corresponding main lines is slightly higher, around 3.9 eV. This difference

is most probably due to a weak valence character of the $3p$ Rydberg orbital, indicating the possibility of a spin and angular momentum coupling of the electron in the $3p$ Rydberg orbital and the valence holes that depends upon the final state. However, interpretation of these shakeup states is aggravated by the presence of the 3σ valence photoelectron line, which is located in this energy region.

In the normal Auger decay [6,7,24], structures belonging to transitions to triplet final states have also been claimed to exist in the energy region of interest. However, the intensities of these triplet states, which should correspond to quartet states in resonant Auger decay, have been found to be very low compared to the intensity of the singlet states. Therefore, the intensity from transitions to quartet final states in the present resonant Auger decay spectra should be insignificant, and consequently no attempt to identify such states has been made.

Comparison between the structure belonging to transitions to the $X+3p$ final state for 55° and 0° shows some very interesting features. The transitions to the lower vibrational levels of the $X+3p$ final state, labeled 1 in Fig. 3(a), show angular dependence that differs from the other transitions in the $X+3p$ group. Our data show a trend towards a lower β parameter with decreasing vibrational quantum number of the $X+3p$ final state. For the $X+3p$ final state, this is a strong indication that the β parameter varies with the vibrational quantum number of the final state. Any influence from the structure associated with the $A+3p$ state, labeled 2, can be ruled out, since the angular dependence of the transitions to the $A+3p$ state is similar to the average angular dependence of the transitions to the $X+3p$ final state, as shown in Table I. In addition, the vibrational width of the structure belonging to the A state in normal Auger decay is 1.18 eV [7]. As already discussed, the number of decay paths should be fewer in the vibrationally selective resonance Auger decay than in the normal Auger decay. Thus the influences from structure associated with the $A+3p$ state should be very weak at the energy position for the lowest vibrational levels of the $X+3p$ state. For direct photoelectron lines [27] this effect of different β parameters for different vibrational transitions is well known, but for resonant Auger this is the first observation of such an angular-dependent effect. In addition, to our knowledge this is also the first observation of this effect for transitions corresponding to a final state with a spectator electron in a Rydberg orbital.

For CO, there have been many attempts to identify transitions to final states with an electron in a Rydberg orbital [27–29]. Independent of the presence of an intermediate state, transitions between the same ground and final states must have the same energy due to energy conservation. This holds despite differences in line profile, due to relaxation and lifetime broadening effects [8]. For this reason, a comparison between the present study and earlier inner valence photoelectron studies is possible. However, agreement between the inner valence photoelectron results and the resonant Auger results is poor. The binding energies of $3p$ Rydberg shakeup states reported in the inner valences studies [27–29] are consistently lower than the binding energies reported here. There is, however, a large scattering between values reported in different studies. This can probably be explained by the great difficulties in identifying the $3p$ shakeup states from inner valence spectra, arising from the very low cross section of the transitions and the presence of other spectral features in this energy region, such as inelastic scattering, transitions due to He II β radiation [27], and the broad 3σ valence photoelectron line. However, the present resonant Auger study does not suffer from any of the above mentioned drawbacks.

B. Auger decay of the C $1s \rightarrow 3p(v'=1)$ state

As for the excitation to the $3p(v'=0)$ intermediate state, the decay spectrum of the $3p(v'=1)$ excitation has been recorded at both 0° and 55°. Both spectra are displayed in Fig. 3(b), and the assignment therein is the same as for the decay spectra of the $3p(v'=0)$ state. For the structures associated with the transitions to electronic final states that have been assigned as $X+3p$ and $A+3p$, peak (1–2), we observe major differences in line shape when comparing the $3p(v'=0)$ and the $3p(v'=1)$ decay spectra. Particularly striking is the splitting of the Auger groups belonging to transitions to the $X+3p$ and the $A+3p$ final states into two subgroups in the $3p(v'=1)$ decay spectrum, labeled ''a'' and ''b'' in Fig. 3. This difference stems from the fact that the wave function for the $v'=0$ intermediate state is centered close to the minimum of the potential curve, whereas, for excitation to higher vibrational levels of the intermediate state, the wave function is mainly localized at the turning points of the potential curve. For the X and A final states, the equilibrium internuclear distance is larger than the equilibrium distance for the intermediate core ionized state. Transitions to the $X+3p$ and $A+3p$ are thus split into two spatially distinct decay paths, one taking place at the vicinity of the outer turning point and the other taking place at the vicinity of the inner turning point of the intermediate state potential curve. For the excitations to the $3p(v'=1)$ intermediate state, the outer turning point of the potential curve is closer to the equilibrium internuclear distance for the X and A final states. This suppresses the number of efficient decay paths and supports populations of lower vibrational levels in the final state. The enhanced population of lower vibrational levels is seen from the lower binding energy of the $X+3p$ state in the $3p(v'=1)$ decay, compared to binding energy of the $X+3p$ state in the $3p(v'=0)$ decay; see Table I.

The decay spectra of the C $1s \rightarrow 3p(v'=1)$ excitation have a novel angular dependence seen in the structure belonging to transitions to the $X+3p$ final state. For the transition belonging to the vibrational level with lowest binding energy the angular dependence is comparable to that in the $3p(v'=0)$ decay spectra; i.e., the β parameter is clearly lower ($\beta \approx -0.4$) than the average value for the rest of the lines corresponding to transitions to the $X+3p$ final electronic states ($\beta \approx -0.2$). However, for the structure at binding energies between 34 and 35 eV, a more complicated angular dependence pattern is observed. For this particular region, which contains transitions to four or five different vibrational levels of the $X+3p$ final state, the behavior of the structure in the decay spectra indicates that the β parameter decreases when the vibrational quantum number for the $X+3p$ state increases.

C. Auger decay of the C $1s \rightarrow 3p(v'=2)$ state

The decay spectra for the C $1s \rightarrow 3p(v'=2)$ excitation are recorded at both 0° and 55° as shown in Fig. 3(c). Due to the lower photon excitation probability of this resonance, it was not possible to achieve statistics comparable to the previous two resonances. There is a fairly close resemblance to the $3p(v'=1)$ decay spectrum, even though some differences, particularly for the $X+3p$ state, are seen. The similarity is expected, since the wave functions of the $3p(v'=1)$ and the $3p(v'=2)$ intermediate states are both preferentially localized at the turning points of the potential curve and should consequently yield similar decay spectra. For this decay spectrum, however, we expect to see a noticeable effect of interference and a direct contribution mainly arising from the $3p(v'=1)$ intermediate state, since from the absorption spectrum (Fig. 1) it was found that the contribution to the $v'=2$ excitation band from the $v'=0$ and $v'=1$ intermediate states is almost 20%. In addition, the relative contribution from the broad 3σ valence line to the $v'=2$ decay spectrum is also much larger than for the two above discussed decay spectra. This explains, to some extent, the broadness observed for the $B+3p$ Auger line in the $3p(v'=2)$ decay spectra. However, this broadness may partly come from the possibility of transitions between vibrational levels other than the dominating transition between the $v'=2$ levels of the final and intermediate states. Transitions to the $v'=0$ and $v'=1$ vibrational levels of the $B+3p$ final state, instead of the dominant transition, are then the candidates to explain the extra broadening. Particularly, we expect transitions from the $3p(v'=2)$ intermediate state to the $v'=1$ vibrational level of the $B+3p$ final state, since both the $v'=1$ and the $v'=2$ levels are located mainly at the turning points of the potential curve of the final state. Peaks arising from transitions between vibrational levels other than the dominating one must be located at the low-binding-energy side of the main peak, since the potential curve for the B final state in normal Auger decay has double minima and the highest vibrational level supported by the inner part is the $v'=2$ level [24]. On the low-binding-energy side the continuous distribution is also located, the continuous distribution is due to decay to the dissociative part of the potential curve of the final state.

Regarding the angular dependence for the $3p(v'=2)$ decay spectrum, we notice that for transitions to the $X+3p$ final state the observed anisotropy is similar to that observed in the $3p(v'=1)$ decay.

D. Angular anisotropy of the Auger decay

In the introduction we mentioned that in a two-step picture the Auger angular anisotropy can be described as the product of the molecular alignment parameter A and the intrinsic anisotropy parameter of the Auger decay c_a. In that way an estimate of c_a for the $3p(v'=0,1,2)$ excitation can be obtained from the values of the Auger electron asymmetry parameters β and the molecular alignment parameters taken from [14]. For the complete spectator group following the decay from the $3p$ resonance we obtain $c_a \approx 0.45$. This value is clearly larger than the value of $c_a \approx 0.15$ [1], determined for the Auger decay at the σ^* shape resonance, where the coupling between the photoelectron and the valence electrons should be negligible. In addition, for the shape resonance, the c_a parameter has been found to vary between 0.37 and -0.3 for individual Auger decay channels [2]. Such a large variation is not observed in the present study of the $3p$ resonance, for which the c_a parameters vary roughly between 0.3 and 0.7. However, after corrections for the differences in alignment parameter, this angular anisotropy of the Auger decay resembles more closely the Auger decay of the $2\pi^*$ resonance. For the latter resonance, the c_a parameters have been found to vary between 0.3 and 0.6 [2]. This indicates that a spectator electron in the $3p$ Rydberg orbital couples in a similar way to the valence electrons as a spectator electron in the $2\pi^*$ orbital, as expected from symmetry considerations. However, from coupling strength considerations one would expect the intrinsic anisotropy of the Auger decay to be similar to the values observed in shape resonance studies. This suggests that even a weak coupling between the $3p$ Rydberg orbital and the valence orbitals could have a considerable effect on the angular anisotropy of the Auger decay.

The Auger decay from the $3p(v'=0,1,2)$ resonances shows some notable features in the angular anisotropy of the transitions to the $X+3p$ final state. We have consistently observed that the transitions that take place at the outermost part of the potential curves for the intermediate state have β parameters that are lower than the transitions occurring at the inner part of the potential curve. This is clearly seen in the $3p(v'=1)$ and $3p(v'=2)$ decay spectra, where transitions from the inner and outer parts of the intermediate state potential curve are split into two different subgroups in the spectra. The trend towards decreasing β with decreasing vibrational quantum number for the $3p(v'=0)$ to $X+3p$ Auger decay is also a consequence of this effect. This novel angular effect is only observed for transitions to the $X+3p$ final state; the group of lines [peak 2 Fig. 3(b)] corresponding to the transitions to the $A+3p$ final state do not exhibit this angular effect even though the group is split into two subgroups.

One explanation could be interference between a direct photoionization channel populating the $X+3p$ singly ionized state and the corresponding resonant channel. The direct channel should have both an angular dependence similar to the 5σ valence photoelectron line and a similar vibrational progression. The 5σ valence line is known to be populated mainly by the lowest vibrational level with a β parameter slightly below 2 [22]. Interference with the direct channel would then influence mainly transitions to the lowest vibra-

tional level of the Auger $X+3p$ final state. This is in accordance with the angular dependence in the $3p(v'=1)$ decay. However, for the decay of the $3p(v'=0)$ intermediate state a trend towards decreasing β parameters for lower vibrational levels is observed. In addition, for the decay spectra from the $3p(v'=2)$ intermediate state an angular dependence similar to the $3p(v'=1)$ decay was observed. But for the $3p(v'=2)$ decay, transitions occurring at the outer part of the potential curve of the intermediate state populate additional vibrational levels of the $X+3p$ final state. The value of the β parameter is similar in both the $3p(v'=1)$ and the $3p(v'=2)$ decays for transitions from the outer part of the potential curve. This observation is also in contradiction with the interference explanation, since the C $1s \rightarrow 3p(v'=2)$ photon excitation probability is lower than for the C $1s \rightarrow 3p(v'=1)$ excitation. A larger effect is thus expected in the angular dependence for the decay from the $3p(v'=2)$ intermediate state.

Another explanation is that this vibration-dependent angular anisotropy could be an effect of valence electron correlations. In the configuration interaction (CI) picture the electron correlation is taken into account by inclusion of several electron configurations of higher multiply excited states. For CO it is well known from theoretical studies on the double-hole states, particularly for the X, A, and B states, that large errors are introduced in the calculated binding energies if CI is not properly taken into account [6,7,24]. For the X state the 0.661(5σ) 0.150$(5\sigma 4\sigma)$ 0.014(4σ) 0.005$(3\sigma 5\sigma)$ 0.004(1π) composition was used in Ref. [7]. The angular distribution of the Auger electrons depends upon the symmetry of the intermediate as well as the final state. If the valence electron configuration (and hence the symmetry of either the intermediate or final state) varies over the potential curve, this directly influences the β parameter of the Auger decay. Such an explanation, which goes beyond the Born-Oppenheimer approximation, seems to be the most reasonable one for the angular dependence of the Auger decay observed in the present study. From earlier studies on resonant Auger decay in atoms, it is generally known that the angular dependence parameter is a very sensitive probe of electron correlation effects. Only by inclusion of CI in both the intermediate and final states could the angular dependence be reasonably reproduced [30]. Therefore, additional theoretical studies seem necessary in order to describe the angular anisotropy of resonant Auger decay in small molecules.

IV. CONCLUSIONS

Vibrationally selective resonant Auger decay of the $3p$ Rydberg level in CO has been studied with angular resolution. It is found that the participator contribution to the resonant Auger decay for an excitation to the $3p$ Rydberg level is negligible. The spectator decay has been analyzed within the framework of the strict spectator model and comparison to former studies of the normal Auger decay. Features belonging to a $3p \rightarrow 4p$ shakeup have been observed in the decay spectra. Depending on the vibrational level of the intermediate core excited state, distinct differences in the decay spectra are observed; this is particularly striking when comparing deexcitation spectra of the C $1s \rightarrow 3p(v'=0)$ excitation with C $1s \rightarrow 3p(v'=1,2)$ excitations. This is a consequence of the

differences in decay paths, where the wave function of the $3p(v'=0)$ intermediate state is located mainly at the equilibrium internuclear distance of the potential curve, whereas the $3p(v'=1,2)$ intermediate states are located at the turning points of the potential curves. The angular anisotropy of the resonant Auger decay has been found to show a weak dependence upon the final electronic states. Together with the values of the intrinsic Auger anisotropy parameters, this resembles the angular anisotropy found earlier for the Auger decay at the $2\pi^*$ resonance [2]. We interpret this as evidence that the $3p$ Rydberg orbital has a weak but non-negligible valence character. For transitions to the $X+3p$ state, an angular anisotropy of the Auger decay dependent upon the vibrational level of the $X+3p$ final state is observed. This behavior has been interpreted as being due to electron correlation effects.

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