

AUTOIONIZATION OF CO AFTER C $1s \rightarrow 2\pi^*$ EXCITATION: A COMPARISON WITH PHOTOEMISSION AND AUGER DECAY

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We have calculated the entire autoionization spectrum of CO following core-to-bound, i.e. C $1s \rightarrow 2\pi^*$ excitation, within a Green's function formalism. Approximate autoionization transition intensities can be related to the Hamiltonian matrix elements. Initial-state screening is important for obtaining realistic autoionization probabilities. For the low-lying ion states there is a one-to-one correspondence between the photoelectron and the autoionization spectrum. The connection between autoionization and Auger decay is discussed.

1. Introduction

The core excitation spectra of diatomic molecules exhibit strong resonances above and below the $1s$ ionization thresholds of their atomic constituents [1–8]. These resonances are due to the particular shape of the molecular potentials [1]. Resonances of both π and σ symmetry are known, and have been successfully utilized to determine the geometric and electronic structure of adsorbed diatomics [5,6,9–16]. A sensitive probe for the nature of such resonances are electrons emitted through radiationless decay, i.e. autoionization of the resonance [17–21]. As has already been suggested by Moddeman et al. [21] the decay of the $2\pi^*$ resonance of CO can either take place with (direct recombination) or without (spectator decay) participation of the excited electron in the decay process. Very recently, detailed experimental information has become available through the use of synchrotron radiation [4–7,12–14] which allows one to tune the photon energy into the resonance and watch the decay without interference from other decay processes, e.g. direct Auger decay [21]. It was shown for the C $1s \rightarrow 2\pi^*$ resonance of CO that both spectator decay and direct recombination are active [4–6,13,14] but

a detailed assignment of the autoionization spectrum has so far not been given. In principle, autoionization leads to final states that may also be populated via photoemission, namely normal hole states, and so-called shake-up states. This suggests a comparison of the autoionization spectrum with the photoelectron spectrum may help to assign the former. However, it is not obvious that photoemission – which is governed by the dipole matrix element [22] – populates the same ion states as autoionization, which is governed by the Coulomb matrix element [23,24]. Plummer et al. [5] have suggested that the spectator decay part of the autoionization spectrum should be compared with the corresponding Auger spectrum, and the latter shifted by a constant energy relative to the autoionization spectrum. This is meant to take into account the extra hole-hole correlation in the Auger spectrum, which is assumed to be basically the same for all spectator lines since the spectator electron always “sits” in the same orbital.

The present Letter aims at a simultaneous semi-quantitative description of three types of spectroscopy – photoelectron, autoionization and Auger spectroscopy – in order to analyze the questions raised above, and to comparatively assign the spectra.

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2. Theoretical consideration

The results of a Green's function calculation by Schirmer and Walter [25], which describes the valence ion states of CO up to 50 eV binding energy within the limit of the sudden approximation [22], has been used as the basis for the calculated photoelectron spectrum shown in fig. 1 (bottom) which is in fact a Lorentzian convolution of the results obtained by Schirmer and Walter [25]. Their calculation is based on the extended two-particle-hole (2ph) Tamm-Dancoff approximation which corresponds to a 2ph configuration interaction (CI) calculation on the ion states. The ionization probability within the sudden approximation corresponds to the pole strength obtained from the Tamm-Dancoff calculation [26,27]. Liegener [28] has previously compared a Green's function calculation of the KVV Auger spectrum of CO [29] with the same results [25]. A Lorentzian convolution of the calculated Auger spectrum is shown in fig. 1 (top). We have used the ion state CI eigenvectors from ref. [25] to calculate the radiationless transition probabilities for autoionization [23,24],

$$I_{ab} \propto \sum_{l,m} |\langle \psi_{\text{ion}}^{b(lm)} | e | \hat{H} | \psi_{\text{neutr}}^a \rangle|^2, \quad (1)$$

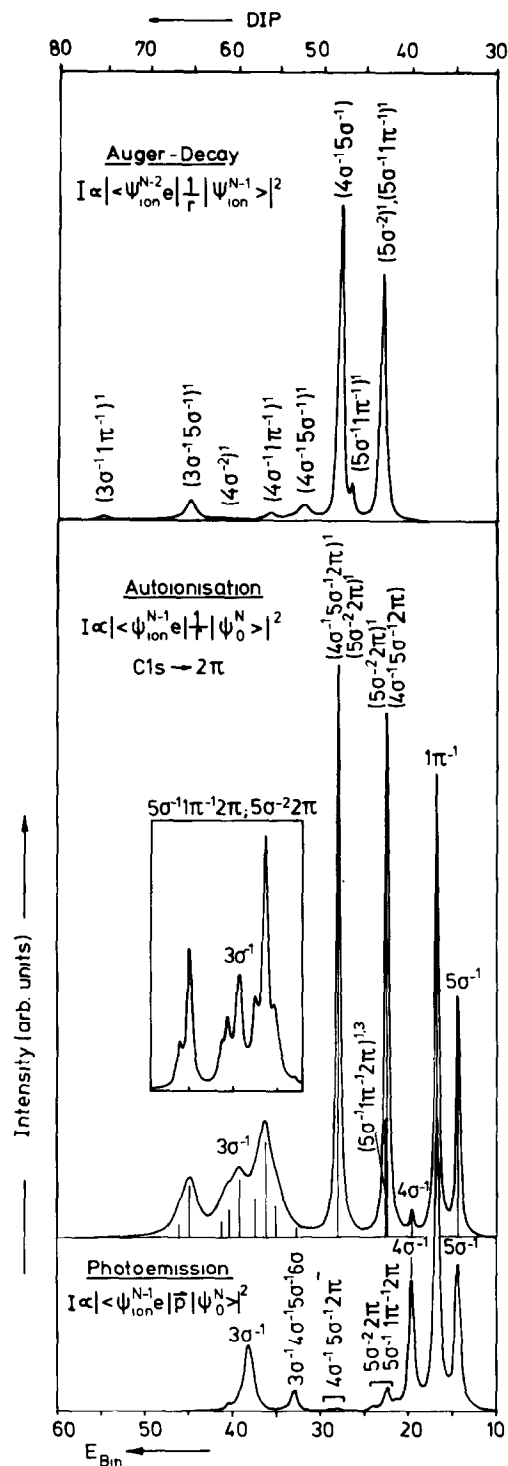
where ψ_{ion}^b is the final ion state in question, ψ_{neutr}^a is the excited initial autoionizing state of the molecule and \hat{H} is the Hamiltonian. We make the following approximations for the wavefunctions involved:

$$|\psi_{\text{neutr}}^a \rangle \approx |\Phi_{1s \rightarrow 2\pi} \rangle, \quad (2a)$$

$$|\psi_{\text{ion}}^b \rangle \approx A \sum_{\mu} c_{\mu b} |\Phi_{\mu} \rangle \psi_{lm}, \quad (2b)$$

where $|\Phi \rangle$ are the SCF Hartree-Fock eigenstates, $c_{\mu b}$ are the configuration interaction coefficients necessary to give an appropriate description of the ion states, ψ_{lm} are spherical continuum orbitals for the outgoing electron centered at the site of the core hole characterized by a set (ml) of angular momentum

Fig. 1. (a) Lorentzian convolutions of calculated photoelectron [25] (bottom), autoionization (middle), and Auger [28] (top) spectra. Dominant hole and 2ph configurations are indicated whenever possible. The binding energy scale at the bottom refers to the photoelectron and the autoionization spectra. The double-ionization potential (DIP) energy scale refers to the Auger spectrum. Energies are in eV. Intensities are in arbitrary units.



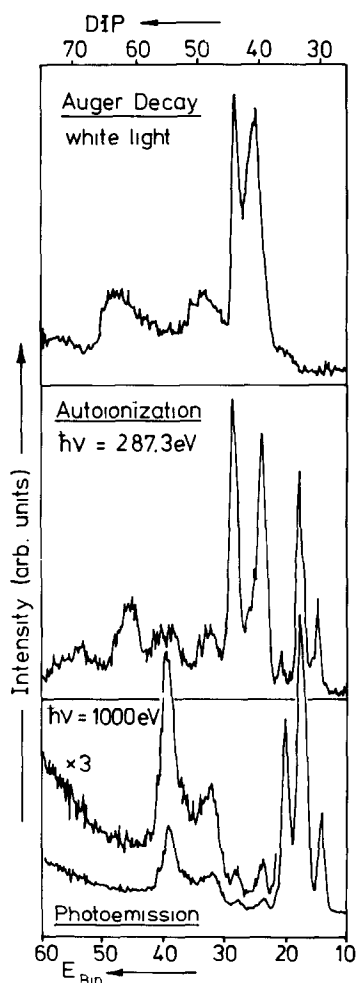


Fig. 1. (b) Experimental photoelectron [6] (bottom), autoionization [5,6] (middle), and Auger [5] spectra. The bottom binding energy scale refers to the photoelectron and the autoionization spectra, while the top double-ionization potential scale (DIOP) refers to the Auger spectrum ($DIP = C\ 1s - E_{bin}^C$). All energies are in eV.

quantum numbers [30] and A is the antisymmetrizer. With these approximations the intensity becomes

$$I_{ab} \propto \sum_{l,m} \sum_{\mu,\nu} c_{\mu b} c_{\nu b}^+ M_{\mu}^{lm} M_{\nu}^{+lm}, \quad (3)$$

with

$$M_{\mu}^{lm} = |\langle \Phi_i | \hat{H} | A \Phi_{\mu} \psi_{lm} \rangle|^2. \quad (4)$$

For normal hole states (the hole situated at orbital i) we obtain

$$M_{\mu}^{lm} = 2V_{1s\nu 2\pi i} - V_{1s\nu i 2\pi}, \quad (5)$$

where

$$V_{1s\nu 2\pi i} = \langle 1s(1) \psi_{lm}(1) | 1/r_{12} | 2\pi(2) i(2) \rangle. \quad (6)$$

For the 2ph states we have to differentiate between two cases:

(a) the two holes reside in the same spatial orbital ($i=j$),

$$M_{\mu}^{lm} = V_{1s\nu ii}, \quad (7a)$$

(b) the two holes reside in different orbitals ($i < j$),

$$M_{\mu}^{lm} = 2^{-1/2} (V_{1s\nu ij} + V_{1s\nu ji})$$

singlet coupled,

$$M_{\mu}^{lm} = 2^{-1/2} (V_{1s\nu ij} - V_{1s\nu ji})$$

triplet coupled. (7)

In addition we neglect vibrational coupling which, in certain cases, has been shown to be of importance [20]. The integrals $V_{1s\nu ij}$ are evaluated according to the one-center approximation [31,32] employing the atomic radial integrals of McGuire [30]. We have used two approximations for the orbitals of the initial state, namely unscreened – where we have used the one-electron states of the neutral CO molecule to approximate the C $1s \rightarrow 2\pi^*$ excited state of the neutral molecule, which is known to be a poor approximation – and screened, where the equivalent core states of NO are used instead. This yields good results, for example, as far as core-to-bound excitation energies are concerned [15,16]. In the present study we have tested both cases in order to evaluate the influence of screening on the intensity distribution in the autoionization spectra. This is an important issue in view of a possible application of autoionization spectroscopy to adsorbate studies [5,12–14].

3. Results and discussion

Fig. 1a shows our calculated autoionization spectrum in comparison with the calculated photoelectron and Auger spectra. The main configurations of the various ion states are indicated in those cases where such an assignment is reasonable. In cases where many configurations of a similar weight contribute, i.e. below 30 eV binding energy, no assign-

Table 1
Intensity contributions due to pure configurations ^{a)}

Type	NO	CO
($3\sigma^{-2}2\pi$)	0.0084	0.0027
($3\sigma^{-1}4\sigma^{-1}2\pi$)	0.0666/0.0003	0.0189/0.000
($3\sigma^{-1}1\pi^{-1}2\pi$)	0.0246/0.0004	0.0089/0.000
($3\sigma^{-1}5\sigma^{-1}2\pi$)	0.1075/0.0018	0.0729/0.0012
($4\sigma^{-2}2\pi$)	0.1503	0.043
($4\sigma^{-1}1\pi^{-1}2\pi$)	0.0758/0.0023	0.0242/0.0007
($4\sigma^{-1}5\sigma^{-1}2\pi$)	0.3958/0.0034	0.2614/0.0018
($1\pi^{-2}2\pi$)	0.0574/0.0712	0.0215/0.0267
($5\sigma^{-1}1\pi^{-1}2\pi$)	0.1689/0.0023	0.1153/0.0019
($5\sigma^{-2}2\pi$)	0.3424	0.4847
($3\sigma^{-1}$)	0.0167	0.0127
($4\sigma^{-1}$)	0.0013	0.0016
($1\pi^{-1}$)	0.1771	0.1512
($5\sigma^{-1}$)	0.1079	0.1484

^{a)} For configurations (doublets) with possible singlet and triplet parentage two numbers are given: singlet/triplet.

ment to specific configurations is indicated. Table 1 collects the intensities calculated assuming that one given configuration describes the ion state. The results for both screened and unscreened initial states are given. Only a few configurations lead to large matrix elements, the relative magnitudes of which, however, strongly depend on the chosen initial state. Clearly, the largest matrix elements originate from 2ph states, rather than single hole states, with the ($5\sigma^{-2}2\pi$) configuration the most important. Considering the rules of thumb known from Auger spectroscopy [21] (which is governed by matrix elements similar to eq. (1) [23,24]), one basically probes the overlap between initial and final states. The calculated autoionization spectrum in fig. 1 reflects this: (i) the 2ph state induced lines are more intense than the single hole states below 20 eV binding energy; (ii) there are two sharp peaks between 20 and 30 eV binding energy due to only three ion states; (iii) there are three broad features above 35–40 eV binding energy which are due to a superposition of many components. Note that in this energy region we have chosen a linewidth four times larger than that used in the energy region below 30 eV as the ion states in this energy region are energetically close to the double ionization continuum [6]. Part of the second peak in the region above 20 eV originates from a state with a $3\sigma^{-1}$ single hole as the dominating configuration.

With the above results in mind we can proceed to a comparative assignment of photoemission, autoionization, and Auger spectra. The dominant peaks in the photoelectron spectrum (bottom fig. 1a) are due to normal hole states. Their relative intensities are governed in the sudden approximation by the product of the one-electron dipole matrix element between the ionized electron and the continuum orbital, with the projection of the hypothetical frozen orbital ion state onto the relaxed ion-state wavefunction. For the 4σ , 5σ and 1π hole states the projection leads to a dominant ($\approx 90\%$) term, while the 3σ projection is distributed over several terms ("breakdown of the single-particle picture [26,27]"). As was previously discussed in detail by Cederbaum and co-workers [26,27] the rather complex spectrum between 30 and 40 eV is basically due to ionization of the 3σ electron. The weak multipeak structure between 20 and 30 eV is caused by the other valence 4σ , 5σ , and 1π ionizations. The leading configurations in the ion states that borrow most of the intensity are indicated in the spectrum. The autoionization spectrum (fig. 1a middle) shows below 20 eV binding energy the normal hole states. The intensity distribution is quite different from the photoemission spectrum since the intensity in this case is governed by the Coulomb matrix element (see table 1). In the presence of an extra (spectator $2\pi^*$) electron in the π space the 1π electrons experience the strongest Coulomb interaction and thus dominate the single hole-state decay channels. The σ -hole states are less pronounced. The 5σ channel dominates due to the larger interaction between the $1s$ hole localized on the carbon atom, and the 5σ electron also localized at the carbon. For the same reasons the 2ph states exhibit large intensities, in particular those which have configurations with 5σ character admixed (see table 1). As stated above, only a few configurations contribute to the Coulomb matrix elements. The $5\sigma^{-2}2\pi$ configuration is so dominant in this respect that 2ph states which only have a small admixture of this configuration exhibit an appreciable autoionization probability. The largest CI coefficients of the dominating configurations are found for the ion states between 20 and 30 eV binding energy. The ion states that exhibit very small intensity in photoemission therefore dominate the autoionization decay. Consequently, in this energy regime there is a one-to-one

correspondence between photoionization and autoionization, and one might expect this to be the case over the entire spectrum. However, as is evident from the comparison, above a binding energy of 30 eV the one-to-one correspondence is lost. For example, the rather intense 3σ satellite at 34 eV binding energy has only a very weak corresponding autoionization peak. The reason is that – according to the photoionization calculation – the corresponding ion state is dominated by the $4\sigma^{-1}5\sigma^{-1}6\sigma$ configuration, which in turn does not contribute to the autoionization decay. Generally speaking the 2ph states in this energy region cannot be assigned to dominating configurations. They do, however, contain smaller contributions from those configurations which lead to the calculated autoionization probability (see insert in fig. 1a for a plot of this region with smaller linewidth). Clearly, the ion states in this energy range interact with the double ionization continuum, so that a description using a finite basis set, as is attempted in most calculations, leads to less reliable wavefunctions. A comparison of the intensity differences in photoemission and autoionization calculated in the present work with experiment [5,7] shows excellent agreement in the 10–30 eV energy region. Our calculations basically reproduce the experimental spectra, and this result puts our conclusions on a firm basis. The spectral functions in the binding energy range above 30 eV are less reliable, as expected, but qualitatively a three-peak structure is predicted and also observed. The spectrum shown in fig. 1a has been calculated using intensities based on a screened initial core-to-bound excited state. Had we used the unscreened initial state, we would have found strong variations in the relative intensities as can be estimated from an inspection of table 1. We therefore suggest that the autoionization intensities will strongly depend on the chemistry within a system since this may significantly alter the wavefunctions.

Finally, we compare the calculated autoionization spectrum with the calculated Auger spectrum (top fig. 1a). The Auger spectrum of CO has been discussed elsewhere [28,29] and we refer to the literature for details. The double-hole state configurations are indicated. The energy scale shown at the top refers to the calculated double-ionization potentials. Clearly, the dominating peaks in the spectrum (note

the assumed broader linewidths above 45 eV) are due to the $5\sigma^{-2}$, the $5\sigma^{-1}1\pi^{-1}$, and the $4\sigma^{-1}5\sigma^{-1}$ double-hole configurations. If we add a $2\pi^*$ electron to these double-hole state configurations we get exactly the same 2ph configurations that dominate the autoionization spectrum. This correspondence also expresses itself in the energy separation of the two dominant peaks, which is 5 eV in the Auger and 5.7 eV in the autoionization spectrum. In other words, within 15% error the energy to ionize a $2\pi^*$ electron out of the 2ph states is the same. This result lends some support to the procedure proposed by Plummer et al. [5] of shifting the Auger spectrum by a fixed amount in order to estimate the peak energies in the autoionization spectrum.

The experimental spectra corresponding to those calculated and presented in fig. 1a are shown in fig. 1b. The spectrum at the bottom shows a photoelectron spectrum taken at $\hbar\omega = 100$ eV [6]. The spectrum in the middle has been taken from the work of Plummer et al. [5], and shows the autoionization spectrum after C $1s \rightarrow 2\pi$ excitation, and at the top a photon-excited Auger spectrum is shown [6]. The comparison between experimental and theoretical spectra is very good in the lower energy region of the spectra (i.e. below 30 eV binding energy and 60 eV double-ionization energy). In the high energy region the agreement is less convincing but this is not unexpected if one takes into account that in this region the degeneracy with the continuum needs to be considered.

Summarizing, we have been able to discuss – on the basis of explicit numerical calculations – the connection between the photoelectron, the autoionization and the Auger spectrum of CO, and to demonstrate the influence of screening in the initial state of the autoionization spectrum. It is of considerable interest to extend such an analysis to adsorbed molecules, and a similar study for such a system is currently under way on the basis of calculations of the photoelectron spectra of model clusters [33].

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