Effects of nuclear dynamics in the low-kinetic-energy Auger spectra of CO and CO₂

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The CO and CO₂ carbon and oxygen Auger spectra have been measured by electron impact and compared with accurate theoretical calculations accounting for the effects of the dynamics of the nuclei on the energy and linewidth of the Auger bands. The calculations for CO were previously published [L. S. Cederbaum et al., J. Chem. Phys. 95, 6634 (1991)], while for CO₂ they are new and presented here for the first time. For both molecules, particular attention has been paid to the low-kinetic-energy region of the spectra, which corresponds to doubly charged ion states with the two holes mainly localized in the inner valence region. New bands have been observed. It is shown that a proper consideration of the vibrational broadening and shift of the bands due to the dynamics of the nuclei is needed to assign these features. For CO, very large energy shifts between corresponding features in the C 1s and O 1s spectra have been observed, confirming the theoretical predictions of 1991. The new computed spectra of CO₂ allow a very accurate analysis of the experiments over the whole energy range. © 2005 American Institute of Physics.

I. INTRODUCTION

The production of a core hole by electron impact or photoabsorption leaves a molecule in a highly excited state, which may decay either via nonradiative Auger electron emission or by fluorescence. In the case of Auger decay (by far the more likely decay channel for light elements) the final product is a doubly charged ion. Auger electron spectroscopy is a very powerful tool to investigate the properties of the neutral and final doubly charged states of a molecule, to unravel the dynamics of the molecular ion dissociation, and to provide analytical information for elemental analysis.¹ A detailed interpretation of Auger spectra is complicated for several reasons. First, the initial state of the system is not the neutral molecular ground state, but that of a high-energy singly charged ion with the molecular orbitals relaxed due to the presence of the core hole. Second, the Auger decay involves the simultaneous filling of the core hole by an outer electron and ejection of a second electron leaving a final state with two holes which may interact.² Third, the exact determination of the Auger transition rates requires a knowledge of the wave function of the secondary ejected electron. A further

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difficulty is due to the combined effect of the nuclear motion in both the core ionized and the final doubly charged ion states that is reflected in the vibrational band structure of the Auger spectra. The vibrational distribution affects both the width of the bands as well as the energy position of their maxima. Moreover, the effect will be different in spectra of the same molecule for core ionization of different atoms. Thus the analysis of the molecular Auger spectra in terms of vertical electronic transition energies may be even qualitatively inadequate. This becomes more and more important in the region of the inner valence double ionization, due to the high density of doubly charged ion states.

On the experimental side the fine details of the vibrational structure of the Auger spectra can be resolved only using electron-electron coincidence experiments. This technique allows one to select a particular initial state and to follow the possible pathways of its decay. It is then possible to disentangle the many overlapping contributions of all the possible initial states that hide any fine structure in a simple noncoincidence spectrum. However, the main effects on the widths and positions of the bands generated by an initial hole in different sites of the same molecule can also be observed in the usual noncoincidence spectra. Here we have measured the C 1s and O 1s Auger spectra of CO and CO2 over the double-ionization energy (DIE) region 40–100 eV, and compared them with an accurate ab initio theoretical approach which permits the efficient direct calculation of the whole spectrum of double-ionization energies, as well as a qualitative estimate of the Auger intensities and of the main effects of nuclear dynamics on the Auger band widths and energy centroids. Particular attention has been paid to the region of the high DIE, where new spectral features have been observed. This region, due to the high density of electronic states involved, is particularly difficult to explore theoretically and only our methodology, so far, was proved capable to produce results with any meaningful accuracy. The theoretical calculations of the CO spectra were previously published and are compared here with the new experiments. The CO2 spectra have been theoretically computed anew using the same methods.

II. EXPERIMENT

The CO C 1s and O 1s Auger spectra were studied by electron impact at electron energies ranging from 0.5 to 3 keV, while the CO2 spectra have been measured at 1.5 and 2.5 keV. The measurements were performed with the multicoincidence electron end station of the Gas Phase beamline at Eletra, that for these experiments was equipped with an electron gun (EKF 300, Omicon GmdH). The design and operating principles of the experimental apparatus are described in detail in Ref. 9. In the present experiments we have taken advantage of the high luminosity of the spectrometer by measuring simultaneously the Auger spectra with seven analyzers, all placed in a plane perpendicular to the direction of the incident beam. The spectrum produced by each analyzer was first calibrated in energy and then corrected by the transmission function of the analyzer, and then the seven spectra, all measured at an ejection angle of 90°, were added to improve statistics. The energy of the Auger spectra was calibrated using the value of 201.1 eV for the kinetic energy of the $L_{3s}M_{2,3}^2(3d_N)$ Auger line of Ar (Ref. 10) and 520.0 eV of the $L_{2}S_{2}N_{4.5}(3d_G)$ Auger line of Xe. For the sake of comparison the CO C 1s Auger spectrum at 1 keV was also measured with the electron spectrometer at CNR-IMIP in Rome. The two sets of spectra were found to be consistent, therefore in the following sections only the spectra obtained with multicoincidence spectrometer will be presented and discussed.

III. THEORY

To compute the double-ionization spectrum of CO2 we used the second-order algebraic diagrammatic construction method [ADC(2)], in analogy with what was done for the CO molecule. The method gives rise to a symmetric eigenvalue problem in the space of the $\left(N-2\right)$-electron configurations, which on the basis of the Hartree-Fock (HF) $N$-electron closed-shell ground state are classified as $2h$ (two holes, i.e., two electrons removed from the occupied orbitals) and $3h1p$ (two holes plus one particle-hole excitation). The eigenvalues are the vertical double-ionization energies of the system, while the eigenvectors are related to the spectroscopic factors. In the ADC(2) scheme, the double-ionization energies are accurate to second-order perturbation theory with respect to the main $2h$ configurations. To estimate the Auger intensities and, more generally, to perform an analysis of the two-vacancy density in the doubly ionized states, we carried out an atomic two-hole population analysis. To obtain useful estimates of the effects of the nuclear dynamics on the energy position and broadening of the Auger lines, we used the method proposed in the previous study of the Auger spectra of CO (Ref. 8) and discussed in great detail in Ref. 7. This method, based on the time-dependent formalism, provides a simple scheme within the harmonic approximation for computing the broadening (variance of the nuclear level distribution) of the Auger lines and their energy position (first moment) relative to the vertical Auger decay. The final working equations in atomic units for a molecule possessing a single totally symmetric normal mode of nuclear motion, such as the carbon oxides, read

$$\langle E \rangle = \Delta - 2\frac{\kappa\beta}{\omega} \left[ 1 - \frac{\Gamma^2}{\Gamma^2 + \omega^2} \right]$$

(1)

for the energy centroid of an Auger line, and

$$\langle E^2 \rangle - \langle E \rangle^2 = \beta^2 + 2\left(\frac{\kappa\beta}{\omega}\right)^2 \left[ 1 + \frac{\Gamma^2}{\Gamma^2 + 4\omega^2} \right]$$

$$- 2\left(\frac{\Gamma^2}{\Gamma^2 + \omega^2}\right)^2 + \frac{\Gamma^2}{8\ln 2}$$

(2)

for its broadening. In these equations, $\Delta$ is the vertical energy (at the neutral ground-state geometry), $\omega$ is the neutral molecule harmonic frequency of the normal mode, and $\Gamma$ is the energy width (inverse lifetime) of the decaying core-hole state. $\kappa$ and $\beta$ are the slopes of the electronic energy of the core-hole state and of the decay energy (Auger kinetic energy), respectively, with respect to the dimensionless normal
mode. They too are computed at the neutral ground-state geometry.

The calculation of the CO$_2$ spectrum was carried out using an aug-cc-pVTZ basis set and the experimental bond length. We have computed the harmonic totally symmetric normal coordinate using the corresponding vibrational frequency. The core-hole state lifetimes used for CO$_2$ are consistent with those used for CO. The principal dicationic states lying above 90 eV were all predicted to shift by roughly 3 eV to higher energy with respect to the vertical DIE in the C 1s Auger spectrum, but by about 0.5 eV toward lower energy in the O 1s spectrum (see Table III of Ref. 8). The resulting difference of about 3.5 eV matches well the value we observed.

FIG. 1. The C 1s and O 1s Auger spectra excited by electron impact at 1.5 keV. The labeling of the features follows Moddeman et al. (Ref. 16). In the inset, the region of DIE between 85 and 110 eV is shown in greater detail. The question mark indicates the new observed feature.

Before we analyze in greater detail these effects, we discuss and rule out another possible origin for the high-energy peak in the C 1s spectrum, namely, the occurrence of an interatomic Auger process. This process implies an intermediate state with a core hole in the O 1s and a final doubly ionized state with one hole in the C 1s and the other in the valence. Preliminary evidence of such a process has been given in Ref. 20 and its probability with respect to the normal C 1s Auger decay was estimated to be 0.3% of the main features (lines B1–B3) in the C 1s Auger spectrum. A calculation with hydrodynamic wave functions predicted a value of 0.5%, consistent with the experimental observation. That the decay of inner holes may be accompanied by the creation of a secondary electron vacancy in regions even very distant from the primary hole—the so-called interatomic coulombic decay (ICD) process—is now well established. More recently evidence of the transfer of the inner hole between nearby atoms in a molecule has been obtained in nondipolar photoionization experiments. The energy, nature, and spectroscopy of core-valence doubly ionized states were theoretically studied by Schulte et al. By using the O 1s ionization potential and the energy of the core-valence doubly ionized states given in Table III of Ref. 28, we have calculated that the bands due to the interatomic Auger process should appear in the C 1s Auger spectra at kinetic energies between 184 and 217 eV. This means that on the DIE scale of Fig. 1 they should contribute in the binding-energy region 79–112 eV, which is indeed the region of the novel peak observed in the C 1s spectrum. In order to discriminate between the two processes, i.e., the “normal” and interatomic Auger decay that may lead to the newly observed feature in the C 1s Auger spectra, several measurements were performed at various incident energies between 0.5 and 3 eV. In Fig. 2 the ratio between the areas of the feature at 98.6 eV and the main Auger lines (peaks B1–B3 in Fig. 1) is reported versus the incident energy. This ratio is almost constant within the experimental uncertainty at a value of about 2.4%.

IV. RESULTS AND DISCUSSION

A. CO

The C 1s and O 1s Auger spectra of CO obtained by electron impact at 1.5 keV are presented in Fig. 1. The two spectra are reported on the DIE scale of CO. This scale has been obtained by subtracting the measured kinetic energy of the Auger electrons from the known C and O 1s ionization potentials of 296.2 and 542.5 eV, respectively. In the figure, the labeling of the different features follows Moddeman et al. A number of CO Auger electron spectra have been reported in the literature and the spectra shown in Fig.
Most importantly, it does not vanish when the incident energy is below the O 1s ionization potential, as should happen for the interatomic process. This result has been further confirmed by two photoionization measurements at the Gas Phase beamline of Elettra storage ring above and below the O 1s ionization potential, respectively. Thus the observed feature has to be attributed to an Auger band with the two final holes in the inner valence states and confirms fully the theoretical predictions of Ref. 8.

We show in Fig. 3 a more detailed comparison between experiment and theory in the high double-ionization energy region of the C 1s and O 1s Auger spectra. The theoretical data are those of Ref. 8 but the theoretical profiles have been shifted up in energy by 2 eV in order to achieve alignment with the experimental bands. A rigid shift of the whole double-ionization spectrum is often necessary due to the implicit error in the balance of correlation energy between the ground state and dicaticonic states. The theoretical profile is obtained by convoluting the discrete lines with Gaussians whose position and width results from the nuclear-dynamics analysis. For the sake of a better comparison with the theory, the background contribution of the secondary electrons to the experimental spectra has been removed by fitting it with a polynomial function. As the figure shows, the match between the experimental and computed profiles is very good up to about 100 eV and, in particular, the agreement is unambiguous for the features of interest here. Only at higher energy does the agreement between theory and experiment deteriorate, especially because of a band appearing in both theoretical spectra where none seems to be detected experimentally. The good theoretical representation of the experiment is remarkable considering the numerous and significant difficulties in simulating theoretically such high-energy, extremely dense electron spectra. It is only through the use of direct, Green’s-function-based approaches that the vast number of excited electronic states involved (visible as vertical bars in the figure) can be accessed computationally. The theoretical models used to estimate the Auger line intensities, broadenings, and energy shifts are sufficiently accurate in this case to reproduce quite well the line shapes of the features of main interest seen in the figure, namely, the peak at about 94 eV in the oxygen spectrum and the broader band at about 98 eV in the carbon spectrum. Both peaks have a visibly composite structure, due to the many transitions producing them, which is also satisfactorily accounted for. The calculations show that the dicaticonic states responsible for these peaks involve mainly double ionization of the inner valence orbitals. In the figure we have also marked the position of the hypothetical peak maxima computed using the vertical ionization energies, i.e., in the absence of shifts due to nuclear dynamics.
the bond length in the C 1\text{s} hole state is shorter than in the CO ground state, while it is longer in the O 1\text{s} hole state.

B. CO\textsubscript{2}

The C 1\text{s} and O 1\text{s} Auger spectra of CO\textsubscript{2} measured by electron impact at 1.5 keV incident energy are presented in Fig. 4. The two spectra are reported on the DIE scale obtained by the measured kinetic energy of the Auger electrons and the known C and O 1\text{s} ionization potential of 297.7 and 541.3 eV,\textsuperscript{30} respectively. The labeling of the different features in the figure follows Moddeman et al.\textsuperscript{16} Two CO\textsubscript{2} Auger electron spectra over the full extent of the binding-energy range have previously been reported in the literature.\textsuperscript{16,31} The positions and relative intensities of the features observed in both the C 1\text{s} and O 1\text{s} Auger spectra are in very good agreement with the ones recently measured by proton impact.\textsuperscript{31} In Fig. 5 the experimental spectra are compared with the theoretical calculations, which provide the first complete \textit{ab initio} simulations of the full Auger spectra of this molecule. As for CO, the spectra were obtained by convoluting with Gaussian functions the discrete lines of the double-ionization spectrum, of intensity estimated by the two-hole population analysis.\textsuperscript{6} The lines were shifted in energy and broadened according to the results of the nuclear-dynamics calculations detailed in Sec. III. Here, no further shift has been applied to the data. Although CO\textsubscript{2} is a small molecule, it is again evident that producing reliable theoretical Auger spectra is a complicated task. The number of computed dicationic states found to give significant contributions and used to generate the spectra between 20 and 110 eV is of the order of 2000, the most important of which are visible in the bar spectra of the figure. This indicates the extent of correlation effects in the system. The agreement between the computed and experimental spectra is generally good, especially for the C 1\text{s} spectrum, and, in spite of some evident shortcomings in the estimated relative intensities of the bands, leaves no doubt as to the interpretation and assignments which the calculations provide with great detail. A first cursory inspection of the spectra shows that the effects of nuclear dynamics on the position and shape of the various bands is much less pronounced in CO\textsubscript{2} than in CO. While in the monoxide the computed vibrational shifts were positive for the C bands and negative for all but three bands in O, in CO\textsubscript{2} all the shifts are positive and of comparable magnitude. The widths calculated for the O 1\text{s} spectrum are generally slightly larger than those in the C 1\text{s} spectrum, which makes the O 1\text{s} spectrum appear simpler.

The precise way in which the nuclear-dynamics effects were estimated in the CO\textsubscript{2} case is interesting and we briefly comment on it. As we have detailed in Sec. III and elsewhere,\textsuperscript{3} the principal nuclear-dynamics effects on the Auger lines are the results of state-specific factors essentially determined by the slopes of the double-ionization energies with respect to the totally symmetric normal modes, and of spectrum-specific factors due to the slopes of the intermediate decaying core-hole states. We calculate the DIE slopes numerically by repeating the ADC calculations along the various normal modes of the molecule under study, and the core-hole state slopes by \textit{ab initio} calculations, which at the simplest, and often sufficient, level are HF \textit{\&} SCF. However,
it may, of course, happen that the final computed Auger line shapes and positions are very sensitive to the accuracy of the core-hole state slopes, or that the ΔSCF results are simply too crude to permit even a qualitatively correct reproduction of the Auger profile. In this case, one should, of course, resort to higher-level calculations of the core-hole states, including electron correlation to a sufficient degree. But when an experimental Auger spectrum is available, and in the simplest case of a system with a unique totally symmetric normal mode such as CO₂, it is also conceivable to adopt a reverse approach and treat the relevant core-hole state slope as an adjustable parameter. If a suitable and narrow choice of this parameter exists (within properly estimated bounds) that yields a marked improvement in the detail of reproduction of the spectral profile, it is reasonable to adopt it as an effective way of estimating the core-hole state slope by comparison between experiment and theory. The C 1 s Auger spectrum of CO₂ provides a good example. Using the ΔSCF C 1 s hole state slope of 0.48 eV yields a theoretical Auger spectrum in unacceptably severe disagreement with experiment. In particular, the computed widths of the Auger lines are much too large, so that essentially only three very broad bands appear, one between 35 and 55 eV, the second between 60 and 80 eV, and the third between 90 and 100 eV. The rich structure of the experimental profile, which hints at much smaller linewidths, is entirely lost. The theoretical C 1 s Auger spectrum shown in Fig. 5 has instead been obtained by adjusting the C 1 s slope so that the experimental profile is best reproduced. This results in a slope of 0.19 eV and, as is evident, it provides an excellent account of the low-energy part of the spectrum, where other sources of theoretical error (such as higher-order electron correlation effects and nonadiabatic nuclear motion effects) are less pronounced. Note, in particular, the reproduction of the very sharp B4 feature appearing on the low-energy side of the most intense B5 structure. We shall discuss shortly in some detail the interpretation of the spectra.

Although the quality of the C 1 s spectrum obtained leaves little doubt about our procedure, it is nevertheless somewhat disturbing that the fitted slope is so much smaller than the ΔSCF one. Therefore, we performed some additional calculations to verify that inclusion of electron correlation supports our result as expected. Indeed we found that a simple inclusion of configuration interaction with single and double excitations with the C 1 s hole state already reduces the computed slope to about 2/3 of the ΔSCF value. For the O 1 s spectrum, the results obtained using the ΔSCF computed slope of 0.25 eV were already satisfactory, at least qualitatively (see Fig. 5), and we decided to accept them without further refinements. This apparent discrepancy between the quality of the ΔSCF results for the C 1 s and O 1 s core-hole states of CO₂ calls for further study.

We turn now to a discussion of the principal features of the CO₂ spectra resulting from our calculations. Given the large number of contributing dicatomic states, we limit our analysis to a description of the main features of the Auger spectra in terms of the much fewer two-hole (2h) configurations. At lowest DIE, below 40 eV, both the C 1 s and the O 1 s spectra show a peak (B1) which is due essentially to the 1 π₂⁻ configuration, with a small 1 π_u⁻ component. The peak appears much sharper and more intense in the experimental oxygen spectrum than in the calculations. The next intense peak in the carbon spectrum (B2) already has several 2h contributions, the dominant ones being 1 π_u⁻3σ_g⁻ at low energy and 1 π_u⁻4σ_g⁻ at high energy, accompanied by small 1 π_u⁻4σ_e⁻ and 1 π_u⁻3σ_u⁻ admixtures, respectively. This peak corresponds to the weak second band in the theoretical O 1 s spectrum at 42.1 eV (i.e., about 0.5 eV lower than B2), which appears as a shoulder of the intense B3 peak in the experimental spectrum. This B3 peak has mainly 1 π_u⁻1 π_u⁻ character (broad) accompanied by narrow 3σ_u⁻ and 4σ_g⁻ components. It is quite interesting that relatively intense 1 π_u⁻1 π_u⁻ states are also present in the carbon spectrum but they are very broad and are responsible for the low-energy broadening of the B5 peak from which the less intense but very sharp B4 feature emerges. The latter is due to a 1 σ_u⁻ state with 3σ_u⁻ and 1 π_u⁻ components. Note that Hiltunen et al.31 indeed observed a feature located between the B2 and B4 bands and attributed it to a shakeup satellite. Peak B5 is computed to have many contributions, the principal ones being, in order of increasing DIE, 1 π_u⁻, 1 π_u⁻13σ_u⁻ (with smaller 1 π_u⁻4σ_g⁻ contribution), and 1 π_u⁻14σ_e⁻ (with smaller 1 π_u⁻3σ_u⁻ contribution). The next B6 peak has a 3σ_u⁻4σ_g⁻ component at low energy and a 4σ_g⁻ admixture at higher energy, with smaller 3σ_u⁻ and 1 π_u⁻ contributions. The position of this peak is computed to differ by only 0.1 eV between the C and O 1 s spectra. At higher DIE, the C 1 s spectrum has a more complex and structured appearance than the oxygen one. Above about 55 eV, in the region of inner valence double ionization, the density of contributing states increases very rapidly and there are some more evident difficulties in the exact theoretical simulation of the experimental profile. Electron correlation causes an almost complete breakdown of the 2h configurations over a vast number of states, and excited dicatomic configurations (satellite states) play the dominant role. In the region of peaks B8 and C2 in the C 1 s spectrum, the composition of the dicatomic states involves primarily, in order of importance, the 2h configurations: 1 π_u⁻2σ_u⁻, 1 π_u⁻5σ_u⁻, 1 π_u⁻2σ_u⁻, 1 π_u⁻3σ_u⁻, 3σ_u⁻3σ_u⁻, and 4σ_g⁻2σ_u⁻. For peak C3, the configuration 3σ_u⁻2σ_u⁻ and 4σ_g⁻3σ_u⁻ also contribute significantly. A large number of states are responsible for the broad features B7 and C1 in the O 1 s spectrum, although with generally much smaller intensity. Peaks C4 in the oxygen spectrum and C5 in the carbon spectrum are also due to a very large cluster of states showing a similar 2h composition, at DIE values around and above 70 eV. At lower energy the components of the type (1 π_u⁻1 π_u⁻)⁻/(2σ_u⁻3σ_u⁻), that is with one hole in the π orbitals and one in the 2σ_u⁻ or 3σ_u⁻ orbitals, are most significant, while in the high-energy tail (C6 in the oxygen spectrum) the principal contributions are (3σ_u⁻4σ_g⁻)⁻/(2σ_u⁻3σ_u⁻). Again the same configurations appear in the satellite states which are responsible for the weak features C7 and C8 of the O 1 s spectrum. The theoretical carbon spectrum also shows similar broad and weak structures between 75 and 80 eV, which are barely detectable from the background in the experimental profile. Between 85 and 88 eV in the C 1 s spectrum the theoretical analysis shows tails of the double inner valence...
states \((2\sigma_g,3\pi_g)^{-2}\). This broad structure is much more evident in the experiment than in the calculated spectrum.

Finally, as for the CO case, we show in Fig. 6 a detailed comparison between experiment and theory for the high DIE bands of the Auger spectra, around and above 90 eV. The figure demonstrates clearly the very large number of dicationic states present in the area. They arise mostly as total breakdown of the inner valence \((2\sigma_g,3\pi_g)^{-2}\) configurations but, in the high-energy tail, barely visible in the region around and above 95 eV, many outer valence satellites of \((1\pi_g,1\pi_u)^{-1}(3\sigma_g,4\sigma_g)^{-1}\) nature play the dominant role. This again testifies of the complexity of high-energy Auger spectra. The band at higher energy in the C 1s spectrum, at about 92 eV, was not present in the first spectrum measured by Moddeman et al.,\(^1\) while it was observed in the recent work by Hiltunen et al.\(^3\) However, the latter authors followed the assignment of Moddeman et al. and considered the features in the O 1s and C 1s spectrum as different bands. The present calculations, despite the fact that they do not reproduce correctly the relative intensity of the two bands at about 85 and 92 eV in the C 1s spectrum, clearly show that the bands at highest energy in the O 1s and C 1s spectra have the same final state configuration. As mentioned, the impact of nuclear dynamics on the relative shift of the bands is smaller than in CO (about 2 eV in the experimental spectra) and it is clearly underestimated in our calculations (note that the theoretical O 1s spectrum has been shifted down in energy by 1.7 eV in order to align it with the experimental data).

V. SUMMARY AND CONCLUSIONS

The carbon and oxygen Auger spectra of CO and CO\(_2\) have been studied by electron impact between 0.5–3.0 keV. The spectra of CO\(_2\) were studied theoretically with good accuracy by Green’s-function calculations of the double-ionization spectra and theoretical models to estimate Auger intensities and nuclear-dynamics effects. The theoretically simulated spectra reproduce the experimental measurements remarkably well and permit a complete assignment. For CO, we based our analysis on previously published similar calculations.\(^5\) We devoted particular attention to the study of the high double-ionization energy region of the spectra, where some previously unobserved features were found, and to the impact of nuclear-dynamics effects of the energy positions and broadenings of the bands. In CO, for the same final states, we observed significant energy shifts between the bands of the C and O 1s Auger, matching very precisely the theoretical predictions.\(^5\) Shifts as large as 4 eV between bands originating from the same final states in the C and O 1s spectra were experimentally observed for the first time, especially in the high double-ionization energy region. In the case of CO\(_2\), the observed shifts due to the nuclear dynamics are smaller, but again consistent with the theoretical calculations.

These findings confirm that the usual interpretation of the Auger spectra, based on vertical electronic transition energies and the neglect of vibrational effects, can lead to qualitatively incorrect identification and assignments of corresponding peaks in the different spectra of the same system. This becomes more and more important as dicaticonic states of higher binding energies are considered.

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