Band shape and vibrational structure in Auger spectra: Theory and application to carbon monoxide

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A time-dependent approach to Auger spectra is presented and used to derive simple working equations for computing the vibrational broadening and the vibrationally induced shift of the peaks in the spectrum. The formulas give the explicit dependence of the vibrational envelope on the local details of the electronic potential energy surfaces of the intermediate and final states, providing interesting general insights which we discuss in detail. It is shown that, in polyatomic molecules, relevant interaction terms among different nuclear modes arise. The theory applies as well to other processes which involve a core ionized or core excited intermediate state like, for instance, x-ray emission or resonant Auger decay. As a test application, the double ionization spectrum of CO is computed by the Green's function method, and the new equations, together with a two-hole population analysis of the pole strengths, are used to obtain theoretical Auger spectra. The experimental spectral profiles, characteristically shaped by the varying vibrational broadening and substantial energy shifts, are accurately reproduced, giving most peak positions to within a few tenths of eV. The results present very different vibrational effects for the carbon and oxygen spectra, showing the general inadequacy of interpretations based on vertical transition energies only. Hole localization in the dicaticionic states is discussed in the light of the population analysis results and used to estimate the electronic Auger transition rates.

I. INTRODUCTION

The complexity of the rigorous theoretical calculation of Auger spectra of polyatomic molecules is evidenced already by considering the very large number of observable electronic states of the final dicaticonic species populated upon the decay of a core hole. In principle, all these states contribute to the spectrum and the calculation of their cross sections involves the computation of the scattering wave function for the escaping Auger electron. Apart from the necessity to compute many energies and cross sections, a further considerable difficulty arises from the consideration of the effects of nuclear motion. In comparison to most spectroscopies, the vibrational structure of an Auger band is much complicated by the fact that it reflects the combined effect of nuclear motion in both the short-lived intermediate (core ionized) state and in the final state. The relevant general theory has been developed in detail but, because of this complication and of the large number of electronic potential energy surfaces involved, the calculation of the vibrational fine structure of the Auger spectra of polyatomic molecules is a very impractical task. As a result, very few detailed theoretical studies, limited to small molecules and selected vibrationally resolved Auger bands, have been carried out.

The high-resolution spectra, the available calculations, and, in general, the simple consideration that the final states following Auger decay have two valence electron vacancies show that the vibrational effects on Auger bands may be quite pronounced and vary appreciably from state to state. In addition, the typically small spacing among dicaticonic states can give rise to substantial overlap of vibrational progressions. The vibrational cross-section distribution influences the width of the bands as well as the energy position of their maximum and, due to the contribution of nuclear vibrations in the intermediate state, these effects are different for the spectra of a given system arising from core ionization of different atoms. It is thus clear that, especially in the outer valence and intermediate regions of the spectra where the Auger intensity is not too smeared out by the very high density of states and strong vibronic coupling, one can expect vibrational effects to influence the band-shape appearance of Auger spectra significantly. In such cases the analysis in terms of vertical electronic transition energies may become even qualitatively inadequate.

In view of the aforementioned considerations, it would be very useful, especially in the study of larger molecules, to have some simple but reliable method to estimate the major vibrational effects on the Auger profiles. It is clear that already a moderate density of states can prevent the fine structure of the Auger spectra to be resolved. Nevertheless, the vibrational broadening and overlap of the bands may still confer fingerprinting appearance characteristics to the spectra. The present work focuses on this aspect and, abandoning the idea of computing individual vibrational progressions, concentrates instead on the effects of nuclear motion on the essential relevant features of an Auger electronic band, namely its vibrationally corrected position and width. In the assumption that the band shape is approximately symmetric, and if nonadiabatic couplings do not complicate the pic-
ture exceedingly, these parameters provide sufficient information, together with the electronic transition rate and the core-hole lifetime, to reconstruct the vibrational envelope theoretically. The center of gravity and width of a band are determined by the lowest-order moments of the vibrational cross-section distribution. We start from a time-dependent formulation and, by integrating the relevant equations, we derive simple approximations to the first and second moments. The formulas give the explicit dependence of the Auger band shape on the characteristics of the intermediate and final-state potential-energy surfaces and provide interesting insights, which we discuss in some detail.

As a first meaningful and interesting test, we apply our method to the calculation of the vibrational structure of the carbon and oxygen KLL Auger spectra of CO,6-8 for which detailed calculations on a few vibrational progressions are available.9 For the calculation of the double-ionization spectrum of this molecule we use the Green's function algebraic diagrammatic construction (ADC) method10 to second order of perturbation theory, ADC(2), which is designed explicitly to permit the efficient calculation of many vertical double-ionization energies and pole strengths.9b,10c. Of particular interest in the present work is the application of a recently proposed method for the analysis of double hole atomic localization in dicaticonic states.11 This two-hole population analysis also enables us to project the one-center localized components of the Green's function pole strengths which we use to estimate relative Auger transition rates. This simple approach has proved very useful for the interpretation of Auger spectra both in cases of strong localization11 and full delocalization10c,12 of the valence electron vacancies. CO is in this respect an intermediate case which affords a further assessment of the efficacy of this approach.

II. THEORY

We discuss here the vibrational structure of an electronic band in the Auger spectrum. Let the band correspond to the final dicaticonic state |Ψ_f⟩, with vibrational levels |n⟩ and energies E_{n}. The corresponding Auger spectrum, as a function of the Auger electron energy E, is given by

\[ \sigma_f(E) \sim \frac{\Gamma}{4\pi} \sum \left| \sum \frac{\langle n_f | n_n \rangle \langle n_n | 0 \rangle}{E - (E_{n} - E_{n'}) + i\Gamma/2} \right|^2, \]  

(1)

where |0⟩ is the ground vibrational state of the target molecule, |n_n⟩ denote the vibrational states of the intermediate, core ionized, molecule, and E_{n} the corresponding energies. 2π/\Gamma is the lifetime of the core hole. The dependence of \( \Gamma \) on the internuclear dynamics is neglected.3 Expressions similar to Eq. (1) hold also for other decay processes involving core ionized or excited molecules.2-5 Therefore, the following considerations apply to a whole class of processes, which includes, e.g., x-ray emission, resonant Auger, and other autoionization processes. The term "Auger" is used symbolically for all of them.

Introducing the Hamiltonians \( H_f \) and \( H_c \) for the nuclear dynamics in the final dicaticonic and core-hole states, respectively, we may rewrite Eq. (1) to obtain

\[ \sigma_f(E) \sim \frac{\Gamma}{4\pi} \int_0^\infty e^{-\frac{\Gamma t^2}{2}} \left( \int_{-\infty}^\infty e^{iH_c (T-\frac{t}{2})} \langle 0 | e^{iH_f (T-\frac{t}{2})} | 0 \rangle dt \right) dt'. \]  

(2)

In deriving Eq. (2) we have made use of the fact that |n_n⟩ and |n_f⟩ are eigenstates of \( H_c \) and \( H_f \), respectively. Expression (2) is useful for discussing and evaluating the Auger spectrum in a time-dependent picture. It is amenable to techniques for wave-packet propagation and, hence, is particularly suited for computations in cases where dissociation processes in the intermediate or final electronic states are of relevance.

In the limit of infinite lifetime of the core hole, i.e., \( \Gamma \to 0 \), the Lorentzians in Eq. (1) become δ functions and Eq. (2) simplifies somewhat into

\[ \sigma_f(E) \sim \frac{\Gamma}{4\pi} \int_0^\infty e^{-\frac{\Gamma t^2}{2}} \left( \int_{-\infty}^\infty e^{iH_c (T+\frac{t}{2})} \langle 0 | e^{iH_f (T-\frac{t}{2})} | 0 \rangle dt \right) dt', \]  

(3)

where \( \Gamma \to 0 \) must be performed after the integration. It should be noted that a finite lifetime leads to interesting interference effects2-5 if the vibrational levels in the intermediate electronic state overlap owing to their lifetime broadening. The gross features of the bands in the spectrum are, however, hardly affected at all by these interference effects, which influence only the fine structure.

The energy moments of Eq. (3) provide relevant information on the spectrum. The center of gravity of the band in the spectrum is given by the first moment

\[ \langle E \rangle = \int \sigma_f(E) dE \]  

(4a)

and the width of the band is related to \( \langle E^2 \rangle - \langle E \rangle^2 \), where \( \langle E^2 \rangle \) is the second moment of \( \sigma_f(E) \),

\[ \langle E^2 \rangle = \int E^2 \sigma_f(E) dE. \]  

(4b)

After some algebra, these moments can be expressed by

\[ \langle E \rangle = \Gamma \int_0^\infty e^{-\frac{\Gamma t^2}{2}} \langle 0 | e^{iH_c (\Delta H_{cf})} e^{-iH_c T} | 0 \rangle dT, \]  

(5a)

\[ \langle E^2 \rangle = \Gamma \int_0^\infty e^{-\frac{\Gamma t^2}{2}} \langle 0 | e^{iH_c (\Delta H_{cf})^2} e^{-iH_c T} | 0 \rangle dT, \]  

(5b)

where \( \Delta H_{cf} \) is the difference between the core-hole and final-state Hamiltonians,

\[ \Delta H_{cf} = H_c - H_f. \]  

(5c)

It can be seen from the above equations that the moments of the spectrum depend explicitly on the core-hole state dynamics, but their dependence on final-state dynamics is only via \( \Delta H_{cf} \).

Equations (5) are exact in the limit of infinite lifetime of the core vacancy, and their evaluation requires the knowledge of \( H_c \) and \( \Delta H_{cf} \). We are now interested in deriving simple and useful formulas for the positions and widths of the bands in the Auger spectrum due to vibrational motion. To proceed, we initially concentrate on a diatomic system and assume that the potential curves involved in the process are harmonic oscillators of frequency \( \omega \), shifted with respect
to each other in energy and coordinates. Then

$$\Delta H_{cf} = \Delta + \beta (b + b^\dagger),$$

where $\Delta$ is the vertical electronic energy difference between the core-hole and final dicaticonic states evaluated at the equilibrium geometry of the target molecule and $\beta$ is the analogous difference between the slopes of the corresponding curves with respect to the normal coordinate. $b$ and $b^\dagger$ are destruction and creation operators, respectively, for vibrational quanta.

Using the expansion

$$e^{-A}e^B = B + [B, A] + \frac{1}{2!} [[B, A], A] + \cdots$$

for two generic operators $A$ and $B$, where $[A, B] = AB - BA$, and also the relations

$$[b, b^\dagger] = 1,$$

$$[b b^\dagger, b b^\dagger] = 2 (bb^\dagger b^\dagger bb^\dagger),$$

$$[b + b^\dagger, H] = \omega (b - b^\dagger),$$

one can evaluate Eqs. (5). After some lengthy but straightforward algebra, we obtain (for $\Gamma = 0$) the final expression of the first moment,

$$\langle E \rangle = \Delta - 2\beta \omega / \omega,$$

where $\kappa$ is the slope of the core-hole state, again evaluated at the equilibrium geometry of the target system. Notice that we use everywhere atomic units ($\hbar = 1$). For a diatomic molecule, the quantities appearing in Eq. (9) read explicitly

$$\Delta = E_c(R_0) - E_f(R_0),$$

$$\kappa = \left( \frac{1}{2\mu \omega} \right)^{1/2} \left( \frac{\delta E_c(R)}{\delta R} \right) R_0,$$

$$\beta = \left( \frac{1}{2\mu \omega} \right)^{1/2} \left( \frac{\delta [E_c(R) - E_f(R)]}{\delta R} \right) R_0,$$

where $\mu$ is the reduced mass of the molecule, $E_c(R)$ and $E_f(R)$ are the electronic potential-energy curves for the core-hole and final state, respectively, and $R_0$ is the equilibrium geometry of the target system. For the second moment we similarly obtain

$$\langle E^2 \rangle - \langle E \rangle^2 = \beta^2 (1 + 2\kappa^2 / \omega^2).$$

Let us now briefly discuss the relevant equations (9)--(11). The first important consideration is that these equations are also useful when the potential curves are nonharmonic, and even when the final dicaticonic states are repulsive and do not support bound states: $\omega$ is then the frequency of the target molecule. The gross features of the spectrum like the center of gravity and the width are determined by the short-time behavior of the wave packet of the vibrational ground state transferred to the excited states. This behavior is, in turn, determined by the local changes of the potential-energy surfaces around $R_0$, since there is only little time for the wave packet to move. The details of the band, of course, depend on the details of the surfaces. Only when a potential-energy curve is strongly varying with $R$ in the Franck–Condon zone, as, e.g., in the presence of a narrow avoided crossing, we might be forced to discard the present explicit equations. In the ideal case of truly harmonic energy curves, we may write

$$\kappa = \left( \frac{\mu \omega^3}{2} \right)^{1/2} (R_o - R_e),$$

$$\beta = \left( \frac{\mu \omega^3}{2} \right)^{1/2} (R_f - R_e),$$

i.e., $\kappa$ is related to the change in bond length upon core ionization and $\beta$ is related to the difference between the equilibrium distances $R_f$ and $R_e$ of the final dicaticonic and core-hole states. Then, the first moment can be rewritten to give

$$\langle E \rangle = E_c(R_e) - E_f(R_f) - \beta^2 / \omega.$$

This equation resembles the first moment of the vibrational motion of an effective potential-energy curve: only the difference between the slopes of $E_c(R)$ and $E_f(R)$ at $R = R_0$ enters.

The expression for the width of a band in the Auger spectrum is somewhat more involved and requires some clarification. Equations (9) and (11) have been derived in the limit of infinite lifetime for the core hole. While the position $\langle E \rangle$ of a band does not change if we assume a finite lifetime, i.e., if the $\delta$ functions are replaced by Lorentzians or Gaussians, the width does change slightly. Choosing for simplicity a Gaussian instead of a Lorentzian with the same full width at half maximum (FWHM) $\Gamma$, the variance, Eq. (11), becomes

$$\langle E^2 \rangle - \langle E \rangle^2 = \beta^2 (1 + 2\kappa^2 / \omega^2) + (\Gamma^2 / 8 \ln 2).$$

Assuming now that the whole electronic band in the spectrum takes on the appearance of a Gaussian, then the position of this Gaussian is given by $\langle E \rangle$ in Eq. (9) and its FWHM $W$ reads

$$W = [8 \ln 2 (\langle E^2 \rangle - \langle E \rangle^2)]^{1/2}.$$

$\Gamma$ in Eq. (14) may be chosen to include also the experimental resolution of the apparatus. If the spectral band has a highly asymmetric shape, Eq. (15) can still be used to estimate its width. It should be remembered, however, that in this case $\langle E \rangle$ does not correspond to the maximum of the band, but rather to its center of gravity. The asymmetry of the band can of course also be determined by computing the third moment of the spectrum.

In case the potential-energy curve of the core ionized state is parallel to that of the target system (i.e., $\kappa = 0$), then the position of the band is just given by the vertical energy difference $\Delta$. Hence, it can be computed at a fixed geometry, and even when the final dicaticonic states are parallel to each other, the band position is just given by $\beta^2 / \omega$. In another limiting case, when the energy curves of the final dicaticonic and core ionized states are parallel to each other, one finds $\beta = 0$. In this situation the position of the band is again given by $\Delta$, but its width reduces to $W = \Gamma$ [see Eqs. (14) and (15)]. In other words, the band consists of a single vibrational component, whose width is solely determined by the lifetime broadening of the core hole. This very interesting result is independent from the form of the potential-energy curve of the target system and follows from the basic Eq. (1) also for any nonharmonic curve.

To each Auger spectrum of a given system, e.g., the car-
energy derivatives with respect to the dimensionless normal
coordinates $Q_1$ (see, e.g., Ref. 14),

$$\Delta H_d = \Delta + \sum_{j=1}^{M} \beta_j (b_j + b_j^\dagger)$$

(16)

and a derivation analogous to the one previously described
leads to

$$\langle E \rangle = \Delta - 2 \sum_{j=1}^{M} \beta_j \kappa_j/\omega_j$$

(17)

for the center of gravity of the band under investigation.
Here, $\Delta$ is the same as in Eq. (10) and the $\alpha_j$ and $\kappa_j$
are energy derivatives with respect to the dimensionless normal
coordinates $Q_j$ (see, e.g., Ref. 14),

$$\kappa_j = (1/\sqrt{2}) \left( \frac{\delta E_c(Q)}{\delta Q_j} \right)_{Q=\alpha_0},$$

$$\beta_j = (1/\sqrt{2}) \left( \frac{\delta [E_c(Q) - E_f(Q)]}{\delta Q_j} \right)_{Q=\alpha_0}.$$  

(18)

The equation for the bandwidth is slightly more involved. We obtain

$$\langle E^2 \rangle - \langle E \rangle^2 = \sum_{j=1}^{M} \beta_j^2 + 2 \left( \sum_{j=1}^{M} \beta_j \kappa_j/\omega_j \right)^2.$$  

(19)

This relation holds if the frequencies $\omega_j$ are all different and
the lifetime of the core hole is long. For those modes which are
degenerate, the second summation over the modes in Eq. (19)
must be shifted into the brackets in the last term on the
r.h.s. in order to arrive at the exact expression. We thus see
that the various degenerate degrees of freedom couple in the
expression for the width, although no coupling terms are
present in the Hamiltonians. It is quite surprising and inter-
resting to note that such mode-mixing effects are always pres-
cent in the case of intermediate and short lifetime as long as
quasidegeneracy (in the sense that $\langle \omega_j - \omega_i \rangle < \Gamma$) holds. These
relevant cases will be discussed elsewhere.

In polyatomic molecules one may encounter conical inter-
sections of potential-energy surfaces, and the correspond-
ing strong nonadiabatic effects may greatly influence the ap-
pearance of the spectra. In such situations, one can also easily
derive a basic equation similar to Eq. (1) and then use
simple, but powerful, Hamiltonians to evaluate the mo-
mments, along similar lines as done here. Such Hamiltonians
are well known for the Jahn–Teller case and general coni-
cal intersection situations.

III. APPLICATION TO THE AUGER SPECTRA
OF CARBON MONOXIDE

The Auger spectra of CO (Refs. 4 and 6–8) have been
theoretically investigated by several authors using different
methods (Refs. 4, 16, and 17). Related information on the
doubly-ionized states of this system is also available from
other experiments of photolization, fragmentation, double charge transfer and electron capture, as well as from
calculations of dicaticionic potential-energy curves
The analysis of these works suggests that the two Auger
spectra of carbon monoxide constitute a simple but extremely
interestig global test for all the phases of our theoretical
approach, for several reasons. The main focus of attention is,
of course, on the vibrational analysis of the Auger bands.
Previous ab initio calculations have shown, by computing
the Auger vibrational progressions for the lowest lying states
and fitting the energy shifts and total intensities to the high-
resolution spectra, that some very distinctive features of the
spectra can only be explained by considering vibrational ef-
fects. The most striking example of this is the extreme nar-
rowness of the second ($B^1 \Sigma^+ \rightarrow$) band in the carbon
spectrum. In the context of our theoretical framework, we should
expect for this state a very small $\beta$ value, i.e., a slope very
close to that of the $C 1s$ core-hole state. Similarly, the high-
resolution spectra and the calculations have evidenced that
the shape of the first carbon KLL band originates from a
superposition of the vibrational progressions in the close ly-
ing $X^1 \Sigma^+$ and $A^1 \Pi$ dicaticionic states, the latter having a
rather broader vibrational envelope than the former.

The aforementioned examples implicitly point out a sec-
ond crucial testing ground which the CO case presents to a
theoretical method, namely the ability to treat with suffi-
cient accuracy the substantial final-state electron correlation
effects. The lowest three $CO^2+$ singlet electronic states lie
very close to each other; at a bond distance of about 3.0 bohr
the two $1 \Sigma^+$ states have an avoided crossing and in the
vicinity of the neutral ground-state distance, the lowest $1 \Sigma^+$
and $1 \Pi$ states cross. In fact, at the Hartree–Fock and limited
configuration interaction levels of theory, the $1 \Pi$ has been
computed to be the lowest singlet dicaticionic state by about 1
and 0.5 eV, respectively. It is evident that only if the correct
ordering of states and sufficiently accurate potential-
energy curves in the relevant region are computed, meaning-
ful slopes and Auger vibrational parameters can be obtained.
Substantial correlation effects visibly influence other fea-
tures of the Auger spectra of CO. For example, the two peaks
in the oxygen spectrum denoted as $B 9$ and $B 11$ in Ref. 7 have
been interpreted as mainly due to a splitting of the $4 \sigma \rightarrow$
configuration, and the broad band $C 2$ should contain several
states arising from the breakdown of the $3 \sigma \rightarrow 1 \sigma$ and
$3 \sigma \rightarrow 1 \pi$ configurations. Finally, we anticipate a further
key issue for a successful calculations of the theoretical Auger
spectra of CO. The oxygen and carbon KLL spectra appear
very different in the energy position of the peaks, indicating
that, though CO is a strongly covalent bonded molecule, the
space localization of the holes in several final states is pro-
ounced and affects both the oxygen and carbon spectra in
essentially equal measure. This situation is radically differ-
ent from the ionic BF$_3$ case, where most of the electron den-
sity is located on the widely spaced fluorine atoms, inducing a clear cut characterization of the dicaticonic states as having the two holes either located on the same fluorine atom or on two different ones. In this respect, the CO case represents a further serious test for our population analysis-based approach to estimating Auger intensities.

The calculations of the Auger spectra of carbon monoxide in the present work have been carried out using two contracted Gaussian basis sets: a \([4s,2p]\) set augmented with one (Cartesian) \(d\) function on each atom, and a \([5s,3p]\) set plus two \(d\) functions on each atom (with exponents 1.3, 0.5 for carbon and 1.9, 0.9 for oxygen). The double ionization spectrum has been computed using the Green's function \(\text{ADC(2)}\) method. In order to obtain the dicaticonic state slopes needed in the Auger vibrational analysis, three sets of calculations have been performed: at the equilibrium bond distance of \(\text{CO} (\Sigma^+ \Sigma^+), R_0 = 1.128 \, \text{Å}\) and at \(R_0 \pm 0.01 \, \text{Å}\). Equations (9), (11), (14), and (15) have been used to evaluate the relevant vibrational parameters. The two-hole \((2h)\) population analysis of the Green's function pole strengths has been carried out as described in detail in Ref. 11.

By the Green's function \(\text{ADC(2)}\) method, using either basis set, we have computed, and used for generating the spectra, over 140 doubly ionized states of \(\text{CO}\) having a double-ionization energy of up to 100 eV. The results obtained with the two basis sets differ essentially only in the absolute double-ionization potentials (DIP's), the larger basis giving a better agreement with all the available experimental data. In the rest of the paper we shall thus always refer, except where explicitly discussed, to the results of the larger calculations. The fifty states with largest \(2h\) weight are listed in Table I, with their total \(2h\) pole strength and composition. Such a number of states should be compared with the mere 18 independent-particle valence dicaticonic states available for \(\text{CO}\), evidencing the general extent of correlation effects in the system. More specifically, one notices immediately in Table I that, except for the very outermost states, no other "main" state (and corresponding "satellites") can be identified; rather, a substantial breakdown of the two-hole configurations takes place into two or more relevant states. This is true, in particular, for all the states involving ionization of the inner valence 3\(s\) orbital and, to a lesser extent, for the 4\(\sigma\) \(-2\) configuration. Further, we find that the ordering of the lowest states of \(\text{CO}^{2+}\) computed by our calculations at the vertical geometry is in agreement with the interpretation of the Auger spectra and with other accurate calculations.

In the next step of our calculation, we have performed the two-hole atomic population analysis of the pole strengths, in order to obtain for each state a measure of the spatial distribution of the holes over the carbon and oxygen atoms. As previously described, this allows the separation of the \(2h\) character of a state into contributions describing two holes localized at the same atomic site (which we shall refer to as \(\text{C}^{-2}\) and \(\text{O}^{-2}\) for carbon and oxygen, respectively) and contributions of the two-site type \((\text{C}^{-1}\text{O}^{-1})\), where one hole is localized at each atom. Each state can thus be characterized according to its composition: the predominance of one contribution in a given state indicates that the two vacancies are strongly localized in space (either at the same or each at a different atomic center, according to the dominating component); states for which more than one component is significantly present are characterized instead as having correspondingly delocalized holes. Practically ideal examples of both cases have been found in first row fluorides and some hydrocarbon dications, respectively. In the former case, most states are dominated either by \(\text{F}^{-1}\text{F}^{-1}\) or by \(\text{F}^{-2}\) contributions. In the latter, the relevant one-site and two-site contributions for many states have been found to be identical to working accuracy.

The results of the two-hole population analysis for \(\text{CO}\) are reported in Table II, for the same subset of states as in Table I. We see that in this case many states have a mixed composition, characterized by the fact that both the two-site \(\text{C}^{-1}\text{O}^{-1}\) component and one of the one-site contributions are of comparable magnitude. This is indicative of a partial, but far from complete, delocalization of the two holes which is consistent with the covalent polar character of the electronic structure in \(\text{CO}\). More in particular, we find that large \(\text{C}^{-2}\) terms (mostly in the very upper valence region) are invariably accompanied by a similar, when not larger, \(\text{C}^{-1}\text{O}^{-1}\) character. For some states, however, a predominance of interatomic double-hole localization is observed (i.e., with one hole localized on the oxygen and one on the carbon), while in other states, particularly those involving \(3\sigma\) ionization, the two holes appear markedly localized on oxygen alone. The relevance of such analysis in our approach to the calculation of Auger spectra lies in the reasonable assumption (see Ref. 11 for a more detailed discussion) that the only significant contribution to the Auger transition rates upon core ionization of a given atom comes from the corresponding localized one-site component of the pole strengths, so that the transition rates are approximately proportional to these components. In this connection, as we have already observed (see Table II), we find that all the states of \(\text{CO}^{2+}\) characterized by significant relative values of the one-site population on one atom have a very small relative intra-atomic component on the other atom. This is in satisfactory qualitative agreement with the very different appearance of the two Auger spectra.

In the last stage of our calculations, we have computed the derivatives of the double-ionization energies of \(\text{CO}\) at the ground-state equilibrium bond distance \(R_0\) (which involved repeating the ADC calculations at two other values of the bond length) and the first and second moments of the Auger spectra for each state, according to the expressions derived in Sec. II. In the latter, we have used the experimental ground-state frequency, \(\omega_0\), of \(\text{CO}\) and the chemical shifts, \(\kappa\), of the core-hole states computed in Ref. 4. The slopes of the most important dicaticonic states and their resulting vibrational center of gravity and Gaussian width for both the carbon and oxygen Auger spectra are listed in Table III. The centers of gravity are reported as energy shifts with respect to the double-ionization energies computed by ADC at \(R_0\). The widths in the table have been computed with the \(\Gamma\) parameter of Eq. (14) (accounting for the core-hole lifetimes and the experimental resolution) set equal to zero, to
show the purely vibrational broadening. Table III exhibits some remarkable features, which are worthwhile to discuss in some detail and are amenable to generalization. Firstly, we notice that all the dicatonic state slopes, except for the lowest $^2\Sigma^-$ and the $B^1\Sigma^+$ states, are negative, in obvious agreement with the general expectation of bond lengthening upon removal of two valence electrons. But it is indeed the unusual positive value found for the $A^1\Sigma^+$ state, in agreement with previous calculations, which is particularly relevant in view of its consequences on the carbon Auger spectrum. As is well known, C 1s ionization in CO also leads to a shortening of the bond distance, with a computed slope at $R_o$ of 3.973 eV/bohr. This means that the difference in slope between the C 1s hole state and the $B^1\Sigma^+$ final state, and thus the vibrational width of the latter in the carbon Auger, will be particularly small. Notice that, as previously found and consistent with its large C $^2$ population (see Table II), the $B^1\Sigma^+$ state contributes significantly to the carbon spectrum. As observed, the lowest $^2\Sigma^+$ state also has a positive, though smaller, slope. However, since the latter state is a triplet and, in addition, has a computed much smaller C $^2$ population, its expected contribution to the Auger spectrum is marginal.

As Table III shows, the computed vibrational widths of the Auger peaks vary substantially from state to state from a fraction of eV to several eV, depending on the relative values...
of the final-state slopes. One can see that, in general, the widths tend to increase in the inner valence part of the spectrum, both as a consequence of the ionization of the more strongly bonding electrons and of the increased density of states. This occurrence should be of general relevance in molecular Auger spectroscopy and, together with the increase in density of states itself and vibronic coupling effects, is the major cause of the substantial broadening of the spectra and lack of sharp peaks as normally observed experimentally in this region.

Inspection of the computed center of gravity shifts in Table III leads immediately to some interesting conclusions. The positive \( \kappa \) value of the \( 1s \) hole state, in combination with the negative slope computed for the dicaticionic states (with the two mentioned exceptions), has the consequence that all the computed bond distance slopes (eV/bohr) at the neutral ground-state equilibrium distance (see the text for details).

### Table III: Computed center of gravity shift (eV) and Gaussian FWHM (eV) for the Auger bands of the states of \( CO^2+ \) reported in Tables I and II. The centers of gravity are obtained by adding the shifts to the shown vertical DIPs (eV). Also shown are the computed bond distance slopes (eV/bohr) of the dicationic states of CO reported in Table I. (see the text for details).

<table>
<thead>
<tr>
<th>State</th>
<th>Vertical DIP</th>
<th>C(^{-2})</th>
<th>O(^{-2})</th>
<th>C(^{-2})O(^{-2})</th>
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*With the \( 4\Sigma_2p_1 \) basis the computed O\(^{-2}\) populations are 0.013 (\( ^{1}\Sigma^+ \)) and 0.028 (\( ^{3}\Pi \)). See discussion in text.

*This state has a computed slightly negative (\(-0.113\)) or positive (0.002) O\(^{-2}\) population depending on the basis set used. See discussion in text.
Auger bands are positive. By contrast, O 1s ionization causes a slight bond length increase and the computed derivative of the O 1s hole state at \( R_0 \) is \( -1.380 \) eV/bohr.\(^4\) This value is smaller in magnitude than all the negative final-state slopes (except for the \( X^1\Sigma^+ \)); consequently, all but three of the computerized center of gravity shifts for the oxygen spectrum are negative. Because of the small \( \kappa \) value for oxygen, we also observe that both the shifts and the widths are smaller in size than for carbon. As a general rule, if we can reasonably expect many of the valence dicationic state slopes to be negative and large compared to the core-hole state slopes, the vibrational center of gravity shifts for those states will have the same sign as \( \kappa \) [see Eqs. (9) and (10)]. Therefore, the effect of the shifts on the different appearance of the Auger spectra of a system will tend to be particularly enhanced in those cases, such as carbon monoxide, where different intermediate core-hole states have opposite slopes. Even more relevant is the magnitude of the shifts for the various final states in a given spectrum, which affects the absolute energy position of the peaks and, more important, their separation. One can indeed notice in Table III that the shifts can vary substantially over the spectrum and, for large \( \kappa \) values such as that for the carbon core-hole, can reach values of several eV. These quantitative findings have obvious general implications and should suggest great caution in the usual interpretations of Auger spectra based on vertical electronic transition energies only. Neglect of vibrational effects can lead to qualitatively incorrect conclusions, for example, in the identification of corresponding peaks in different spectra of the same system (once the appropriate core binding energy is subtracted) as due to the same final states.

To assess more quantitatively the results of our approach, we have finally drawn the theoretical carbon and oxygen Auger spectra of CO, using for each state a Gaussian function of area proportional to its degeneracy and to its respective \( C^-\) and \( O^-\) pole strength population. The origin and FWHM of the Gaussians have been taken according to the computed vibrational parameters, but in the widths we have now included, according to Eq. (14), a resolution parameter \( \Gamma \) fixed at 0.2 eV. This quantity accounts for the finite lifetime of the core-hole (0.1 eV) (Ref. 28) and for the experimental resolution. We have verified that a reasonably wide variation of this parameter (from 0.1 to 0.5 eV) does not alter appreciably the results to be discussed. As usual in our procedure,\(^{10,11}\) the low transition rate of the triplet states has been simply accounted for by reducing their computed intensity by \( \frac{1}{3} \). Having again noted that our results are essentially insensitive to fine tuning this ratio. The resulting spectra are displayed in Fig. 1(b), and 2(b) for carbon and oxygen, respectively, together with the experimental spectral profiles taken from Ref. 7 and reported on the double-ionization energy scale. The striking general agreement between the theoretical and experimental band shapes in the figures does not need to be emphasized. For comparison purposes, we have also illustrated in Figs. 1(a) and 2(a) the corresponding distributions of the one-site pole strengths computed without consideration of vibrational effects, i.e., using Gaussians centered at the vertical ADC DIPs and of width fixed at an average value of 2 eV. The comparison makes visually evident the effects of the varying vibrational broadening and shift of the bands, especially remarkable, as expected, in the carbon spectrum.

The qualitative assignment of the spectra derivable from our calculations coincides essentially with that of previous studies\(^4,16\) and, therefore, we shall not discuss it at length. Rather, we would like to illustrate a few more quantitative considerations afforded by our spectra. The accuracy achieved in the carbon spectrum is eye-catching, particularly for the first two bands (at low DIP). The first theoretical band peaks at 41.5 eV, to be compared with the experimentally deduced value of 41.7 eV.\(^4\) In agreement with the vibrational calculations of Correia et al.,\(^4\) the band is mainly attributed to a narrow \( X^1\Sigma^+ \) component which is broadened on the left by the \( A^1\Pi \) state. We notice from Table III and Fig. 1(a) that, besides the difference in FWHM between the two components, it is only by accounting for their different vibrational shift, which increases their separation with respect to the vertical DIPs by more than 0.5 eV, that the exact band shape is reproduced. The shift is also responsible for the accuracy of the computed absolute peak position, as can be seen by comparing with the ADC DIP for \( X^1\Sigma^+ \) of 40.86 eV. Incidentally, we note that this latter value confirms the observed photoionization appearance threshold for CO\(^2+\) of 40.75 eV.\(^18\) Similar accuracy is obtained for the second band, attributed to the \( B^1\Sigma^+ \) state. The fingerprinting sharpness of this band, due to the discussed narrow vibronic envelope, is exactly reproduced, although its absolute energy position is somewhat underestimated. The agreement in the computed width indicates that this latter discrepancy is not due to a too small computed vibrational shift and we should, therefore, attribute it to an underestimation of the vertical DIP which is found in the ADC(2) as well as in other \textit{ab initio} calculations.\(^4,16\)

As anticipated, the inner part of the spectrum is much more complex, with many states contributing and intensities generally smearing out. In this situation it is obviously expected that the exact Auger band shapes not only depend on their vibrational structure, but also on electron correlation terms not fully accounted for in the present calculation (correlation effects are very strong in this energy range and difficult to assess properly) and vibronic coupling effects.\(^29\) Moreover, the expressions we have derived in Sec. II may become inadequate on a detailed scale, due to avoided crossings among the final states. Very interestingly, however, our calculations show that the straightforward estimation of the major vibrational effects we propose can already be sufficient to improve some theoretical results considerably. Notice, in particular, the prominent feature at 62.5 eV exhibited by the spectrum computed without vibrational effects [Fig. 1(a)]. This is clearly to be associated with the broad experimental band with a maximum at about 65 eV but, apart from the evident inadequacy of the fixed width, it appears unsatisfactorily low in energy. As Fig. 1(b) shows, this discrepancy is almost entirely recovered by accounting for the very large vibrational shift of the band maximum, which is now computed at 64.3 eV.

The main features of the oxygen spectrum are also very well described by our calculations and in this case, as antici-
FIG. 1. (a) Gaussian convolution of the vertical dicationic states of CO. The FWHM is fixed at 2 eV and the area of each Gaussian, shown as a vertical bar of proportional height, is proportional to the C−2 population and degeneracy of the corresponding state, reduced by 1 for triplets. (b) Experimental (upper) and theoretical (lower) carbon KLL Auger spectra of CO. The theoretical spectrum is obtained by drawing the theoretical Auger Gaussian envelopes of the dicationic states, using the computed vibrational widths and vibrationally corrected positions (see Table III and the text). An inherent broadening is included ($\Gamma = 0.2$ eV) accounting for the finite lifetime of the core-hole and the experimental resolution. The relative area of each Gaussian, shown by a vertical bar of proportional height, is computed as in Fig. 1(a).

The effects of the vibrational broadening and shift are generally far less dramatic than in the carbon spectrum. In the following we compare the computed DIP appearance of the bands with experimental values obtained by subtracting the O 1s ionization energy of 542.1 eV (Ref. 6) from the Auger kinetic energies extracted from the high-resolution spectrum in Fig. 2 of Ref. 4. As for the carbon spectrum, the first peak is computed at 41.5 eV, to be compared with the observed value of 41.0 eV. Its intensity, mainly due to the $A'\Pi$ state, appears lower than in the recorded spectrum because of a too small computed O−2 weight, especially for the very narrow $X'\Sigma^+$ component. This may also be the cause of the slight discrepancy in the peak position. In this respect, we mention that in the calculations we have carried out using the smaller [4s,2p,1d] basis set, we have obtained a somewhat different two-hole population distribution for the lowest four dicationic states, finding higher O−2 and correspondingly lower C−1O−1 components. In particular, the smaller basis gives an oxygen intensity ratio between $A'\Pi$ and $X'\Sigma^+$ of 100:23, in agreement with the value of 100:20 found in Ref. 4, and a total intensity for the first peak 3 times larger than in Fig. 2(a), yielding an overall better band shape. This finding reflects apparently the occasional instability of Mulliken-like analyses to the inclusion of more diffuse functions in the basis set. Notice that the correct composition of the first
peak, using either basis sets, is again obtained through consideration of the vibrational shift which, contrary to the carbon case, brings the $X'\Sigma^+$ and $A'\Pi$ components closer to each other relative to the vertical energies (see Table III). The two close lying most intense bands of the spectrum contain many significant electronic contributions. Despite this complexity, their profile is very satisfactorily reproduced. In particular, the energy position of the two maxima, computed at 46.8 and 49.7 eV, respectively, matches nearly exactly the values of 46.7 and 49.6 eV extracted from the experiment.\textsuperscript{6,6}

Except for the $3\Sigma^+$ state, whose center of gravity is computed to lie at 43.0 eV, we do not find evidence of Auger transitions in correspondence of the very weak feature at about 43.2 eV, which has instead been attributed to $B'\Sigma^+$ in Ref. 4. The $3\Sigma^+$ state is computed to have a negligible O$^{-2}$ component and thus has little intensity in the Auger spectrum (see Table III). However, since this state is well isolated from others and has low transition rate, the inaccuracies of our statistically based\textsuperscript{10,11} intensity estimation and chosen triplet reduction factor are of course fully felt here. Notice that the value of the O$^{-2}$ population of this state appears to be particularly basis set dependent (see above), being slightly negative with the [5s,3p,2d] basis and positive with the [4s,2p,1d] basis. Concerning the assignment of Ref. 4, where the exact energy position of the theoretical peaks was adjusted to experiment rather than computed, we recall that the $B'\Sigma^+$ state unquestionably corresponds to the narrow peak at 45.4 eV in the carbon spectrum, and thus note that the proposed assignment would imply a double-ionization energy difference of about 2 eV between the appearance of $B'\Sigma^+$ in the carbon and oxygen spectra. It is clear that such a large value cannot be explained within our picture without destroying the sharpness of the carbon peak. Furthermore, according to our calculations, a difference larger than 0.38 eV between the centers of gravity of $B'\Sigma^+$ in carbon and oxygen would imply a negative slope at $R_0$, in contradiction with the known theoretical results.\textsuperscript{4,18} One should note that the potential-energy curve of $B'\Sigma^+$ has been computed to be predissociative and have avoided crossings with both the upper and lower lying $1\Sigma^+$ states,\textsuperscript{4,18,23} which give rise to a maximum at about 1.3 Å and a second shallow minimum at about 1.6 Å. Although the evidently strong configuration interaction imposes some caution in stating the accuracy of these computed features, they appear to occur well outside the Franck–Condon zone\textsuperscript{18} and, in the short-time scale of Auger decay, should not substantially affect the vibrational envelopes that we compute.

The two experimental peaks at 53.5 and 56.2 eV are attributed, as in previous studies,\textsuperscript{4,16,17} to two states mainly originating from 4s$^{-2}$ ionization. It appears clearly, however, that the split of this configuration is unsatisfactorily described at this level of theory, the lowest DIP state having a too large $2k$ weight than the other. The need for an account of correlation effects involving higher-final state excitations is evidenced also by the unusual inaccuracy in the energy position of the two peaks, computed at 54.7 and 57.5 eV, respectively.

Our results indicate a very pronounced breakdown of Auger intensity over many states occurring in the energy region above 60 eV, with double ionizations involving one inner valence and one outer valence electrons, or two inner valence electrons. The accuracy of the spectral profile we obtain in this region, as Fig. 2(b) shows, is probably very close to the limit one can achieve without inclusion of vibronic coupling effects, and indicates the usefulness of the Green's function statistical approach. The most prominent broad feature of the spectrum, is centered at about 72.7 eV in the experimental spectrum and is computed at 72.9 eV. Comparison with Fig. 2(a) shows again that the good accuracy obtained even in this region is due to consideration of the substantial vibrational shifts and widths. We emphasize again that this finding should be seen in the context of a statistical approach: the high density of states produces effects that may invalidate the approximations used for some individual components; nevertheless, the overall appearance of the composite bands is expected to be of good accuracy since the spectral parameters are averaged over many states. Furthermore, a comparison between the computed and experimental broadening of the bands indicates that the intensity breakdown is more pronounced than computed. This is particularly evident above 80 eV, where our calculations still produce some distinct bands, whereas an essentially featureless spectrum is observed. In the higher energy range, higher excited configurations, as well as more complete basis sets, are needed for a more accurate description.

\section{IV. SUMMARY AND CONCLUSIONS}

In this work we have discussed the vibrational structure of Auger spectra and proposed some useful \textit{ab initio} equations to compute the broadening and center of gravity of the electronic bands due to nuclear motion. These equations have been obtained by deriving the leading terms in the expressions for the first and second moments of the cross section using a time-dependent approach. The formulas provide new and interesting insights into the theory of Auger band-shape formation, showing explicitly the dependence upon the local characteristics of the potential-energy surfaces of the intermediate and final states. Of particular interest is the finding that nondiagonal contributions to the bandwidths arise in which different normal modes of a polyatomic system couple. The equations are of general relevance for the spectroscopy of other processes of decay of an intermediate core ionized or core excited state, as x-ray emission or autoionization.

The scope of the present work was of mainly methodological character and, as a first test application of our approach, we have computed the carbon and oxygen Auger spectra of carbon monoxide. Although many theoretical studies have already been carried out on the spectra of this molecule by computing vertical electronic transition energies, it has been shown that correct Auger band shapes and positions can only be obtained by accounting for vibrational effects, which are particularly remarkable in the carbon KLL spectrum. The theoretical spectra we have obtained reproduce these features with striking accuracy. We have
found that the vibrational effects influence in a substantial way both the widths and the energy positions of the Auger bands. In the case of CO, a quantitative agreement within 0.2 eV has been obtained in the absolute energy positions of many peaks, whereas vertical transition energies differ by up to a few eV from experiment. Note, in addition, that very different shifts and widths may affect the different spectra of the same system, reflecting the different normal coordinate slopes of the corresponding core-hole states. Similarly, a "state-dependent" factor of the vibrational parameters, related to the slope of the final dicaticonic states, alters the width and energy separation of the bands in the same spectrum. In the case of carbon monoxide, the core-ionized states were already available from accurate ab initio calculations.

A further point of interest of the present work was the first application of our two-hole population analysis to a strongly covalent polar molecule. In general, this analysis is designed to give quantitative information on the extent of atomic localization of the electron vacancies in the final dicaticonic states. In particular, we also use it to project the one-center localized components of the Green's function 2h pole strengths, which we assume to be approximately proportional to the Auger intensities. This approach, which has a justification of statistical nature, is well suited in situations of high density of states but has been found to work satisfactorily also for relatively small systems, both in cases of strong localization and of full delocalization of the holes. As our theoretical spectra show, the statistical approach gives good results also for intermediate cases, both in the outer valence and in the inner valence regimes. It is instructive to observe, particularly upon comparison of the theoretical carbon spectra in Figs. 1(a) and 1(b), that it may be very difficult to evaluate the accuracy of theoretical Auger intensity ratios without consideration of vibrational effects on the band shapes and positions.

The Green's function ADC method is particularly suited for the computation of Auger spectra of large polyatomic molecules, where the very many dicaticionic states that contribute can be computed much more efficiently than with other accurate ab initio methods. For such systems the detailed calculation of vibrational progressions of the Auger bands becomes equally impractical and the much simpler approximations we have proposed should be particularly useful. Of course, Auger spectra can be more complicated yet: both core-hole localization in the intermediate state and the high density of dicaticionic states in polyatomic systems give rise to multimode vibronic coupling effects which are neglected in the present picture. Analogous working equations accounting for such effects can be derived and we are currently working in this direction.

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