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Carbon 1*s* core-hole lifetime in CO_2

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The carbon 1*s* photoelectron spectrum has been measured for CO_2 at photon energies of 308, 320, and 330 eV with an instrumental resolution about half the natural linewidth. These spectra have been analyzed to obtain vibrational spacings, vibrational intensities, and the lifetime, τ, of the carbon 1*s* core-hole state. Theoretical calculation of the lifetime width, $\hbar/\tau$, using a one-center model, which assumes that only the valence electrons localized on the atom with the core hole can participate in Auger deexcitation of the core hole, predicts a value of 66 meV, considerably smaller than that predicted for CH_4 (96 meV). Experimental measurements indicate, however, that the CO_2 carbon 1*s* width is, in fact, much larger than expected—99 ± 2 meV—and is approximately the same as that found experimentally for CH_4 (95 ± 2 meV). This result indicates that valence electrons on the oxygen atoms may play a role in the Auger decay the carbon 1*s* core hole in CO_2, and, hence, that a multicenter model may be necessary to describe the Auger process.

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I. INTRODUCTION

Recent progress in the development of high-brightness, high-resolution x-ray sources at synchrotrons has made it possible to study features of x-ray photoelectron spectra that were not clear at lower resolution. Among these are the effects of atoms that have only slightly different ionization energies even though they are chemically inequivalent [1], vibrational structure [2–10], molecular-field splitting [3,11,12], the intrinsic lineshape [9], and effects arising because of equivalent atoms of the same element in a molecule, such as the splitting of the $^2\Sigma_g$ and $^2\Sigma_u$ carbon 1*s* core-hole states in ethyne [13,14] or vibronic coupling in the oxygen 1*s* photoelectron spectrum of CO_2 [15].

Our immediate concern is with the intrinsic lineshape, which reflects the lifetime of the core hole and the interaction of the photoelectrons and the Auger electrons emitted when the core hole deexcites (post-collision interaction, or PCI). The lifetime τ is related to the intrinsic linewidth, Γ, as $\tau\Gamma=\hbar$; for a carbon 1*s* hole τ is typically about 6 fs, corresponding to a linewidth of about 100 meV. PCI distorts the photoelectron spectrum, producing a tail to lower kinetic energies. The degree of distortion depends on the lifetime of the core hole and is especially sensitive to lifetime at photon energies close to the threshold for core ionization. The interest in lifetime originates in theoretical predictions that the lifetime depends on the electronegativity of the ligands attached to the atom with the core hole [16,17]. According to the calculations of Coville and Thomas [16], the widths range from 96 meV for CH_4 and other hydrocarbons to 73 meV for CO, 66 meV for CO_2, and 63 meV for CF_4. Similar, but slightly higher, values have been calculated by Larkins [18].

In addition to the possible chemical effects on lifetime, the lifetimes are also of interest in terms of their relationship to the theory of Auger decay. Core-ionized molecules can deexcite via two pathways, radiative or nonradiative. For first-row elements the nonradiative mechanism (Auger decay) dominates strongly, and the Auger transition rate largely determines the core-hole lifetime and hence the natural linewidth. Calculations of Auger transition rates and Auger spectra are usually based on the one-center approximation, which assumes that only valence electrons localized on the atom with the core hole contribute significantly to the Auger decay rate. The predictions of lifetimes by Coville and Thomas mentioned above were calculated with this approximation. There are, however, calculations that do not involve this simplifying approximation. Using a multicenter approach, which

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allows for contributions from electrons on the other atoms, Hartmann [17] obtained results for CX_4 ($X = \mathrm{H, F, Cl}$) that are considerably at odds with those of Coville and Thomas. For instance, his calculations give a linewidth for CH_4 of 75 meV, in contrast with that calculated by Coville and Thomas [16] of 96 meV and that found experimentally by Carroll et al. [9] of 95 meV. In addition, the trend with molecular composition predicted by Hartmann is quite different from that predicted by Coville and Thomas. Going from CH_4 to CF_4, Hartmann predicts an *increase* in linewidth from 75 to 88 meV, whereas Coville and Thomas predict a *decrease* from 96 to 63 meV. This result can be interpreted to mean that it is the total number of valence electrons that is important, rather than just the electrons localized on the atom with the core vacancy.

Investigation of the effect of molecular composition on linewidth is, therefore, important as a test of these theoretical predictions and, especially, as a test of the one-center model, which has played an important role in the theory of molecular core-valence-valence Auger spectroscopy. A number of experimental linewidths have been reported, but, for the most part, both the uncertainties associated with the measurements and the spread in reported values are large. For instance, for methane the reported values of the lifetime are 107± 10 meV [19], 120± 10 meV [20], 83± 10 meV [21], and 95± 2 meV [9]. The last value, 95 meV, from recent high-resolution measurements of the photoelectron spectra of CH_4 and CD_4, compares well with that calculated using the one-center model, 96 meV. As noted above, the multicenter prediction is significantly smaller, 75 meV.

Carbon dioxide, CO_2, provides a useful target for further investigation. The carbon 1*s* photoelectron spectrum is simple, consisting of only one progression, due to excitation of the symmetric carbon-oxygen stretching mode [15,22,23]. Calculations based on the one-center model predict a large difference between the linewidth for CO_2 and that for CH_4. The CNDO calculations of Coville and Thomas [16] give 66 meV for CO_2 compared with 96 meV for CH_4, and the INDO calculations of Larkins [18] give 72 and 102 meV, respectively. Previously reported experimental estimates of the carbon 1*s* linewidth in CO_2 are 78± 15 meV, from photoelectron spectroscopy [15,23], and 70± 20 meV from x-ray emission spectroscopy [24]. These are close to the predicted value, but the reported uncertainties are large. Moreover, in the case of the x-ray emission spectrum, the lifetime was not determined from a least-squares fit to the data and lifetime-vibrational interference effects were not considered.

Here, we investigate high-resolution carbon 1*s* photoelectron spectra of CO_2 measured at three photon energies close to threshold. The measurements were made under the same conditions as for CH_4 and CD_4 [9] and with better resolution than previously attainable for CO_2—less than half the natural linewidth. They have been analyzed with careful attention paid to vibrational excitation and, especially, to determination of the intrinsic linewidth for the core-ionized molecule.

II. EXPERIMENTAL PROCEDURE AND DATA ANALYSIS

Carbon 1*s* photoelectron spectra of CO_2 were measured on Beamline 9.0.1 of the Advanced Light Source of the Lawrence Berkeley National Laboratory at photon energies of 308, 320, and 330 eV, approximately 10, 22, and 32 eV above the carbon 1*s* threshold (297.65 eV, given by Nordgren *et al.* for the adiabatic ionization energy [24]). Beam line 9.0.1 receives its radiation from an undulator (U10) with a 10-cm period. It is equipped with a spherical-grating monochromator that is capable of a resolving power of greater than 10^4. Photon-absorption measurements to determine energy calibration and photon resolution were made in a parallel-plate ion-yield analyzer. Photoelectron spectra were measured in a spherical-sector electrostatic analyzer at the two lower photon energies, and with a Scienta SES-200 spectrometer [25] at 330 eV.

The resolution of the monochromator was determined by measuring the photon absorption spectrum for CO near the carbon ($1s \rightarrow \pi^*$) resonance at 287.4 eV. A Voigt function fits this spectrum well, while fitting with a function in which the asymmetry is an adjustable parameter, showed negligible asymmetry. The Lorentzian components derived from the fits are in satisfactory agreement with the value of 85 meV reported by others [26]. From these analyses, we conclude that the photon-energy distribution is approximately Gaussian. A Gaussian width of 39 meV was measured at the two lower photon energies and 32 meV at 330 eV. At the higher energy, we made measurements over a range of gas pressures; the Gaussian widths derived from these fits have a root-mean-square deviation of 7 meV, which we assign to the uncertainty in this component of the resolution.

Electron-analyzer resolutions were determined by measuring the photoelectron spectra of argon 3*p* electrons (spherical sector analyzer) and xenon 5*s* electrons (Scienta analyzer) at several photon energies. The resolution function of the spherical sector analyzer was not purely Gaussian, and a Voigt function was used to provide better fits. At 10-eV kinetic energy the full widths at half maximum Γ were $\Gamma_G = 27\,\mathrm{meV}$, $\Gamma_L = 11\,\mathrm{meV}$; at 22 eV kinetic energy they were $\Gamma_G = 32\,\mathrm{meV}$, $\Gamma_L = 11\,\mathrm{meV}$. The resolution function of the Scienta analyzer was slightly skewed and slightly flat-topped compared to a Gaussian. It was accurately described by a function of the form $\exp[-Q(x-x_0)]$, where $Q(x)$ is a fourth-order polynomial. However, the difference between this shape and a Gaussian of the same width (28 meV) does not significantly affect the results of our analysis. The resolution due to the monochromator combines with that due to the electron spectrometer to give a resulting instrumental resolution of about 55 meV for the low-energy data and about 42 meV for the measurements at 330 eV. In addition, we must include a contribution from Doppler broadening, which is 12 meV at a photon energy of 330 eV. The combined Gaussian width for the 330 eV data is 44± 5 meV, where the uncertainty is derived from the uncertainty in the resolution of the monochromator.

The transmission of the Scienta analyzer as a function of electron kinetic energy was determined using the procedure developed by Jauhiainen *et al.* [27]. This involves measurements of the xenon $N_{45}OO$. Auger and xenon 4*d* photoelectron spectra. From these results we conclude that under the conditions of our experiment the transmission varies nearly as the reciprocal of the kinetic energy that the electron has before it enters the analyzer. Since this is the expected behavior, we have assumed that the transmission of the spherical sector analyzer follows the same function. The spectra were corrected using this assumption, but the correction is small and makes little difference in the final results.

The xenon measurements also provided a calibration of the energy scale of the Scienta analyzer. Comparing our measurements of the positions of the Auger lines with those given by Jauhiainen *et al.* gives agreement within 0.2%. Measurements of the position of the xenon $4d$ and $5s$ photoelectron lines as a function of photon energy show that the shift of position with change in photon energy is within 0.1% of the expected amount. The $4d$ spin-orbit splitting was found to be 1979(3) meV, in excellent agreement with the value of 1982(2) meV given by Ausmees *et al.* [28]. Measurement of the actual retarding voltage applied to the Scienta analyzer as a function of nominal voltage for kinetic energies from 5–60 eV show that these correlate with one another with a slope of 1.00000(4) and that the root-mean-square deviation between actual and nominal voltage is ± 2 meV. Over a wide scanning range, the analyzer uses three different high-voltage supplies to establish the retarding voltage. However, over the ranges 5–20 and 25–35 eV, only one of these is varied. The correlation between measured voltage and nominal voltage over these ranges has a slope of 1.0004 and a root-mean-square deviation of about 0.5 meV. Thus, we can expect the uncertainty in relative energies measured with the Scienta analyzer over a narrow range to be the convolution of 0.5 meV with the statistical uncertainty in the peak positions. In addition, measured energy differences should be increased by 0.04% over the nominal value indicated by the Scienta system. For present purposes this is negligible. For the spherical sector analyzer, we conclude that the uncertainty in the calibration is about 0.6% on the basis of measurements of the argon $3p$ photoelectron spectrum and its shift with photon energy.

Data were taken in series of short runs. Each spectrum was inspected and adjustments were made for drifts from one run to another of the order of 10 meV in the energy. After these adjustments, the data were combined to give a summed spectrum for each of the three experiments. The experimental results are shown in Fig. 1 as the circles. The solid lines represent least-squares fits to the data (discussed in the following paragraph).

In the fits, the basic line shape is the PCI function of van der Straten, Morgenstern, and Niehaus [29], convoluted with the experimental resolution function and an additional Gaussian function to account for Doppler broadening. Fits using the function given by Kuchiev and Sheinerman [30] are indistinguishable from those obtained using the function of van der Straten *et al.* For each fit, a value of the Lorentzian linewidth was chosen. Then a least-squares fitting procedure was used to fit four peaks to each spectrum. In these fits, the seven adjustable parameters were a constant background, the position and intensity of the $v=0$ peak, the separation between the $v=0$ and $v=1$ peaks, and intensities of the $v=1$, 2, and 3 peaks relative to the main peak [31]. The separation between successive peaks was taken to be the same as that between the first two; thus, the vibrational frequencies were treated as if they were harmonic. The points were weighted according to the reciprocal of the standard deviation of each point. This procedure was repeated for different choices of the Lorentzian width to determine the value that gives the lowest value of χ^2. The fits obtained in this way are compared with the experimental data in Fig. 1, where it can be seen that, for the most part, the agreement between fit and data is quite good. The spectra were also fit using the linear-coupling model [32], which requires only 5 parameters. No significant difference between the two methods was observed. The results obtained from these fitting procedures are summarized in Table I and are discussed in detail in the next section.

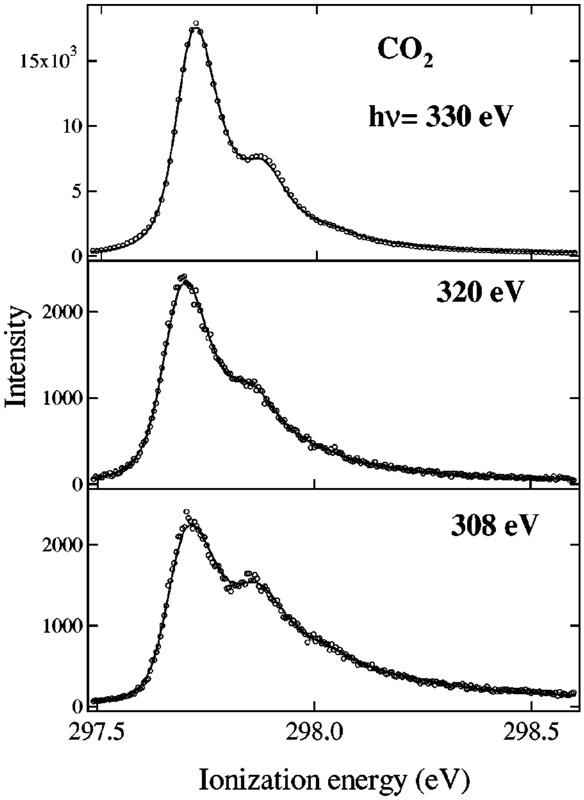

FIG. 1. Carbon 1s photoelectron spectra of CO_2 measured at three different photon energies. Points show the data and the lines show the results of a least-squares fit described in the text.

III. RESULTS

Vibrational structure

The fundamental vibrational frequency, determined at a photon energy of 330 eV, is 165.6 ± 0.7 meV; the uncertainty includes both the statistical uncertainty from the fit and the uncertainty in the energy calibration. This frequency is in agreement with previously reported values of 161 ± 7 meV [15,23] and 167 ± 4 meV [22], and falls between the value of 164 and 168 meV from the data at 320 and 308 eV. These values are approximately the same as that suggested by Shimanouchi [33] for the ground state of CO_2 165.3 meV [34], and significantly lower than has been reported for the ground state of the equivalent-cores ion, $NO_2{}^+$, 173.1 meV [35].

TABLE I. Results from fitting the carbon 1s photoelectron spectra of CO_2.

	308 eV	320 eV	330 eV
ν, meV	168(1)[a]	164(1)	165.6±0.7
Intensity, $v=0$	1	1	1
$v=1$	0.321(4)	0.235(4)	0.241(2)
$v=2$	0.060(3)/[0.051][b]	0.027(2)/[0.027]	0.016(1)/[0.029]
$v=3$	0.016(2)/[0.004]	0.006(1)/[0.002]	0[d]/[0.002]
$\|\Delta R_{CC}\|, pm$[c]	2.25(1)	1.93(2)	1.95(1)
Γ, meV	103(1)	100(1)	99±2

[a] Statistical uncertainty given by the least-squares fits for the last digit is shown in parentheses. Where ± is shown the quantity represents an estimate of the total uncertainty.

[b] Quantities given in brackets are relative intensities, assuming a harmonic oscillator model and a change in CO bond length that reproduces the relative intensity of the $v=1$ transition.

[c] Change in CO bond length that reproduces the relative intensity of the $v=1$ transition. Only the absolute value can be determined from this analysis.

[d] Constrained.

This result is surprising in that, in general, vibrational frequencies for core-ionized molecules are higher than those of the ground state.

The vibrational intensities show that there is a higher degree of vibrational excitation at a photon energy of 308 eV than at the higher photon energies, in accord with the observations of Köppe *et al.* [22] and of Neeb *et al.* [23]. The ratio of intensities for $v=1$ relative to $v=0$ can be used together with the harmonic-oscillator model and the vibrational frequencies to determine the bond-length change, ΔR, that accompanies core ionization of CO_2; this ratio is a very sensitive measure of this quantity. The values derived in this way are listed in Table I and are all close to 2 pm, with the sign unknown, because the harmonic Franck-Condon intensities depend only on the square of ΔR. The vibrational profile changes with photon energy, and the value of ΔR changes accordingly. The value determined at 330 eV, 1.95 pm, is in excellent agreement with the value of -2.0 pm found by Nordgren *et al.* from x-ray emission spectroscopy [24]. From the $v=1/v=0$ intensity ratio and the harmonic oscillator model, we can also calculate Franck-Condon factors for the other transitions. These are shown in brackets in Table I, where it can be seen that this model predicts more intensity to $v=2$ and 3 than is observed at 330 eV and less intensity than is observed at 308 eV. A prediction of higher than observed intensity can be a consequence of neglect of anharmonicity.

Lifetime widths

At photon energies of 308, 320, and 330 eV Lorentzian (lifetime) widths were determined to be 103, 100, and 99 meV, respectively, as can be seen from Table I. Statistical uncertainties are estimated to be 1 meV. We note the trend toward larger Lorentzian widths as the photon energy decreases, a trend that has been previously seen in the CH_4 data [9]. It is possible that the PCI function does not accurately describe the spectrum at energies very close to threshold. To investigate this possibility, we have measured the Ar $2p_{3/2}$ spectrum at photon energies ranging from 5 to 80 eV above threshold. At the lower energies the best fits to these spectra were achieved with natural linewidth values appreciably greater than the accepted value of 120 meV [36]. At 40 eV above threshold, the spectrum is well described by the theoretical function with a lifetime width of 120 meV. It is likely, then, that the best value for the carbon 1s lifetime width is that derived from the 330 eV spectrum: 99 meV, with an estimated uncertainty of about 2 meV, which reflects the effect of the 7 meV uncertainty in the resolution of the photons as well as the statistical uncertainty of the fit.

The value of 99 meV is significantly larger than that of 78±15 meV, obtained from the photoelectron spectrum by Kivimäki *et al.* [15], and 70±20 meV, derived from the x-ray emission spectrum by Nordgren *et al.* [24]. It is significantly lower than the value of 120 meV reported by Ma *et al.* [37] for the 3s and 3p Rydberg states of carbon 1s core-excited CO_2. With regard to the last of these three comparisons, it is not known what uncertainty to assign to the reported linewidth, nor is it certain that core-hole lifetimes for low-lying core-excited Rydberg states *should* be the same as for the core-ionized state. The first two results have uncertainties much larger than that associated with the lifetime width reported in this paper, but we have tried to determine the possible sources of the discrepancies. We have reexamined both of these spectra, and the results of this reexamination are discussed in the following paragraphs.

In the case of the x-ray photoemission spectrum of Kivimäki *et al.*, we were provided with a set of their data. Their reported instrumental resolution was 80 meV (photon) and 60 meV (analyzer) for a total (assuming Gaussian character) of 100 meV. Using the same procedure as that used to analyze our data, we performed least-squares fits of PCI line shapes to their data at a number of values of the Lorentzian width. The best fit occurs with $\Gamma=88$ meV, higher than they have reported. Increasing the resolution to 110 meV leads to a value of Γ of 78 meV, which is the value they have reported. Discussion with one of the authors [38] of Neeb *et al.* [23] indicates that they used a resolution function that was not Gaussian in obtaining their result. It is apparent that the

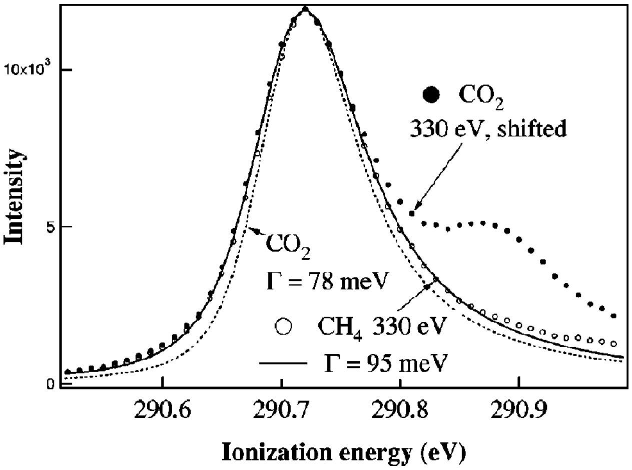

FIG. 2. Comparison of the $v=0$ peaks from the carbon 1*s* photoelectron spectra of CH_4 and CO_2 taken at a photon energy of 330 eV. The CO_2 spectrum has been shifted in position and normalized in height for a best match with the CH_4 spectrum. Circles show the data. The solid line shows a fit to the CH_4 data assuming a lifetime width of 95 meV. The dotted line is calculated for CO_2 assuming a lifetime width of 78 meV (as reported by Neeb *et al.* [23]).

derived value of lifetime depends on both the assumed value of the resolution and on the assumed shape of the resolution function. This dependence becomes less critical as the resolution improves.

Our measurements for CO_2 were obtained under exactly the same conditions as those for our measurements for CH_4, for which we found an intrinsic linewidth of 95 meV. If the linewidth for CO_2 is appreciably different from this, it should be apparent in a comparison of the two spectra. In Fig. 2, the $v=0$ peaks for the two molecules are compared. In this case, the CO_2 spectrum (closed circles) has been adjusted in position and height to match as closely as possible the CH_4 spectrum (open circles). The two spectra diverge on the high-ionization-energy side because of the appearance of the $v=1$ peak in the CO_2 spectrum at an excitation energy of 166 meV. However, at ionization energies below this point of divergence, the two sets of data match very closely, indicating similar contributions from the lifetime. The solid line represents the theoretical spectrum for methane, assuming a linewidth of 95 meV; it matches both curves well, especially on the low-ionization-energy side, where neither set of data is distorted by the onset of vibrational excitation. The dotted curve in Fig. 2 shows the prediction for CO_2 if the linewidth were 78 meV, as indicated by Kivimäki *et al.* [15]; this is noticeably narrower than the experimental peak. We have also tried fitting the data with the Lorentzian width constrained to 78 meV and the Gaussian width as an adjustable parameter. This produces an inferior fit and a total Gaussian width of more than 70 meV, which cannot be reconciled with our measured width of 44 meV. It is apparent that our data are not consistent with an intrinsic linewidth as narrow as 78 meV. At this time, the disagreement between our results and those of Kivimäki *et al.* remains unresolved.

For the carbon x-ray emission spectrum of Nordgren *et al.* [24], we have digitized the densitometer trace given in their paper of the photographic plate on which the x-ray spectrum was recorded. In analyzing their results it is necessary to take into account a number of factors: vibrational excitation and lifetime of the core-ionized state, deexcitation to final states of ${CO_2}^+$, lifetime-vibrational interference [39], anharmonicity of the vibrational motion, resolution, and saturation effects arising because the data were recorded photographically. Our analysis of the x-ray emission spectrum involved a least-squares fitting procedure that included all of these; it yields a Lorentzian width of 97 meV, in good agreement with the value of 99 meV we have determined from the photoelectron spectrum. Thus, there appears to be no discrepancy between the data of Nordgren *et al.* [24] and the value of 99 meV that we have found. We conclude, therefore, that the lifetime for the Auger deexcitation of a carbon 1*s* hole in CO_2 is about the same as it is in CH_4.

IV. DISCUSSION

As was mentioned in the introduction, theoretical Auger rate calculations indicate that there should be observable molecular effects on inner-shell lifetimes. Calculations based on a one-center model [16,18] indicate a clear trend towards lower decay rates as electronegative ligands remove valence electron density from the atom with the core hole. Opposed to this are the multicenter calculations of Hartmann [17], which appear to indicate the reverse; that is, faster decay rates for CF_4 and CCl_4 than for CH_4. This could arise if the one-center approximation is not valid, and if the valence electrons localized on the ligands are, in fact, able to participate in the Auger process. Evidence that this might be the case in some systems has recently been presented by Kay *et al.* [40]. In view of these results, it is worthwhile to review the arguments for the validity of the one-center approximation.

For core-valence-valence Auger decay the rate is determined by the matrix element

$$\langle \Psi_{\mathrm{core}} \chi | 1/r_{12} | \Psi_{\mathrm{val}} \Psi'_{\mathrm{val}} \rangle, \tag{1}$$

where Ψ_{core} is the molecular orbital for the core hole, localized on atom A, χ is the continuum wave function for the emitted electron, and Ψ_{val} and Ψ'_{val} are the molecular orbitals for the final holes in the valence shell. To simplify the illustration, we assume a diatomic molecule AB and approximate the molecular orbitals Ψ as linear combinations of atomic orbitals. Thus, $\Psi_{\mathrm{core}} = \psi_A$, where ψ_A is a core atomic orbital on A, and $\Psi_{\mathrm{val}} = c_A \phi_A + c_B \phi_B$ and $\Psi'_{\mathrm{val}} = c'_A \phi_A + c'_B \phi_B$, where ϕ_A and ϕ_B are valence atomic orbitals on A and B, respectively.

In this picture, the Auger transition rate, τ^{-1}, is proportional to

$$|\langle \psi_A \chi | 1/r_{12} | (c_A \phi_A + c_B \phi_B)(c'_A \phi_A + c'_B \phi_B) \rangle|^2. \tag{2}$$

In the one-center approximation, only those terms are kept for which all indices are the same as that of the atom with the core hole, that is, atom A. Then

$$\tau^{-1} \propto |c_A c'_A|^2 |\langle \psi_A \chi | 1/r_{12} | \phi_A \phi_A \rangle|^2, \tag{3}$$

and it is apparent that the Auger rate depends on the density of valence electrons on atom *A*, that is, on $|c_A c_A'|^2$.

A more careful look at expression (3) shows that the expansion leads to four kinds of terms. The first is an intra-atomic term, $|\langle \psi_A \chi | 1/r_{12} | \phi_A \phi_A \rangle|^2$, which is the same as found in expression (4). Next are two intra-inter-atomic terms, $|\langle \psi_A \chi | 1/r_{12} | \phi_A \phi_B \rangle|^2$ and $|\langle \psi_A \chi | 1/r_{12} | \phi_B \phi_A \rangle|^2$. The second of these is expected to be negligible, since the core wave function on *A*, ψ_A, and the valence wave function on *B*, ϕ_B, have only very small overlap. The first term is considered in more detail below. Inter-inter-atomic terms, $|\langle \psi_A \chi | 1/r_{12} | \phi_B \phi_B \rangle|^2$, are expected to be small for the same reason that the second intra-inter-atomic term is small. Finally, there are interference terms, of which the most important type is $\langle \psi_A \chi | 1/r_{12} | \phi_A \phi_A \rangle \langle \psi_A \chi | 1/r_{12} | \phi_B \phi_B \rangle + \mathrm{c.c.}$ This contains the same factors as do the intra-atomic and intra-inter-atomic terms.

As has been recently noted by Kay *et al.* [41], there is no *a priori* reason to expect the first intra-inter-atomic term, $|\langle \psi_A \chi | 1/r_{12} | \phi_A \phi_B \rangle|^2$, to be small, and one might therefore expect contributions to the transition rate from intra-inter-atomic transitions. As evidence for such, Ågren [41] has noted that the two highest energy transitions observed in the CO_2 carbon Auger spectrum involve the $1\pi_g$ molecular orbital. In simplest approximation, this orbital has no density on the carbon atom and, in the one-center approximation, should not contribute to the Auger spectrum. It has been noted by Millié *et al.* [42] that the states of ${CO_2}^{2+}$ that have primarily π_g^{-2} character also have a significant admixture of π_u^{-2}. Since the *u* orbital does have density on the carbon atom, this admixture can lead to Auger transitions to the π_g^{-2} state without breakdown of the one-center approximation. However, it is difficult to find a similar configuration that could lead to population of the state that is predominantly $\pi_g^{-1}\pi_u^{-1}$. That population of this state is observed in the Auger spectrum indicates either a breakdown of the one-center approximation (as noted by Ågren [42]) or carbon *d*-orbital participation in the π_g state [43].

Quantitative arguments for the validity of the one-center approximation were given by Matthew and Komninos [44], who showed (approximately) that the contribution from intra-inter-atomic Auger transitions falls off as the sixth power of the interatomic distance and as the fourth power of the Auger transition energy. Specifically, they have concluded for CH_4 and CF_4 that the intra-inter-atomic transition rate is less than 10^{-4} of the intra-atomic rate, and hence is negligible. For CO_2, with a CO distance that is intermediate between the CH distance in CH_4 and the CF distance in CF_4 and comparable Auger transition energies, we might expect a similar result. Their conclusions have, however, been criticized by Wormeester *et al.* [45], who concluded that Matthew and Komninos had neglected significant terms and that, in certain circumstances, the role of intra-inter-atomic transitions can be much more important than one would conclude from the estimates made by Matthew and Komninos.

From the previous discussion, we see that there is evidence in the CO_2 carbon Auger spectrum for breakdown of the one-center approximation and that the quantitative theoretical argument for the lack of multicenter terms is not strong. We now consider the quality of theory that was used by Coville and Thomas [16] in their prediction of Auger transition rates. As noted, these were based on the one-center approximation. Beyond this, they used the approximate CNDO theory to obtain molecular orbital coefficients. In this procedure, there is no consideration of either *d*-orbital participation or of the effects of electron correlation. Recent calculations by Larkins and McColl [46] at a considerably higher level (but still with a one-center model) give 116 meV for the carbon 1*s* linewidth of CH_4—considerably higher than the value of 96 meV calculated by Coville and Thomas with simpler theory. The disagreement between these two calculations indicates that there is a need for further work in this area.

V. CONCLUSION

The value of the lifetime linewidth for CO_2 found from high-resolution carbon 1*s* photoelectron spectroscopy is 99 ± 2 meV. Although this is higher than others have reported, comparison of CO_2 and CH_4 photoelectron spectra taken under identical conditions indicates no apparent difference between the linewidths for the two molecules. Both the magnitude of the CO_2 linewidth and the lack of difference between the CH_4 and CO_2 linewidths are not consistent with predictions based on the one-center model of molecular core-valence-valence Auger decay. The Auger spectrum itself shows features that cannot be accounted for in the one-center approximation. It is noted also that the semiquantitative underpinning of the one-center model has been questioned. These observations point to the need for a more critical look at this model, which has played an important role in the theory of molecular Auger spectroscopy.

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