Vibrational structure of the O 1s ionization spectrum of CO_2

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The dynamical localization of the O 1s core holes in the CO_2 molecule is studied *ab initio* beyond the linear vibronic coupling model. The vibrational structure of the O 1s x-ray photoelectron spectrum (XPS) has been calculated employing accurate potential energy surfaces of the ground and ionized diabatic electronic states obtained at the self-consistent field and singles and doubles configuration-interaction (SDCI) methods. A very good agreement of the SDCI computed vibrational structure of the O 1s XPS with the respective experimental high-resolution spectrum has been obtained. The anharmonicity of the ionic state potential-energy surface induced mostly by the ground-state surface anharmonicity plays a crucial role in the proper description of the vibrational line intensities. The linear model is discussed in detail. The linear model based on the vibronic coupling constants obtained from the geometry change in the ionized state relative to the ground-state reference configuration has been shown to contain a hidden renormalization of the coupling constants. This improves the agreement of the calculated intensities of the vibrational lines in the spectrum with the experiment, compared to the case of the strict linear model. The limitations of this renormalized linear model are discussed. Electron relaxation and correlation considerably affect the vibrational line intensities. The popular equivalent core approximation is tested for CO_2. The calculation of the O 1s XPS performed at the SDCI level with and without this approximation is shown to provide almost identical results on the vibrational intensities. [S1050-2947(99)00309-1]

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I. INTRODUCTION

Core ionization of molecules is usually accompanied by vibrational excitations that form an inherent fine structure of the electronic spectral lines. In most cases the intensity distribution within the vibrational progression can be described by the well-known Born-Oppenheimer (BO) adiabatic and Franck-Condon approximations. The feasibility of the adiabatic approximation is based on the fact that the energy gaps between electronic states are usually large compared to typical vibrational spacings. When the electronic states are closely placed they can be coupled via the nuclear motion and one should go beyond the adiabatic approximation to describe the spectral band shape. Nonadiabatic effects can significantly change the spectral band shape compared to the intensity distribution, which describes the case of noncoupled electronic states [1].

Molecules with several equivalent atoms are ideal objects for studying nonadiabatic effects. Indeed, the ionization (excitation) of core electrons of equivalent atoms in the molecule gives rise to a manifold of nearly degenerate electronic states that can interact vibronically via nontotally symmetric vibrational modes. Depending on the strength of the vibronic interaction and energy separation between the electronic states a symmetry breaking can occur that results in localized core holes. In this case intense structures appear in the spectrum due to the strong excitation of the nontotally symmetric modes. This phenomenon, dynamical localization of core holes in symmetrical molecules, has been predicted about 20 years ago [2]. As an example the authors of Ref. [2] calculated the vibrational structure of the O 1s line in the x-ray

photoelectron spectrum (XPS) of the CO_2 molecule. The calculation predicted a strong excitation of the nontotally symmetric stretching mode and a relatively weak excitation of the symmetric stretching mode. The linear coupling model [3] was used in this calculation. The vibronic coupling constants were obtained from self-consistent field (SCF) calculations on the neutral CO_2 molecule with the use of the frozen orbital approximation (FOA). Thus, this calculation did not include reorganization effects due to the relaxation of the electronic subsystem in the presence of a hole in the O 1s level of the molecule. The results of *ab initio* calculations of the vibrational structure of the O 1s XPS of CO_2 were reported also in Ref. [4]. The authors of this work used SCF direct core-hole calculations to obtain the equilibrium geometry and second-order force constants for the core-ionized states and, therefore, their consideration included some fraction of the reorganization effects. The results for the excitation of the nontotally symmetric stretching mode presented in this paper and those reported in Ref. [2] are very similar to each other. The excitation of the symmetric stretching mode, which was found weak in Ref. [2], has been completely neglected in Ref. [4].

In the last decade great progress in the field of high-resolution core-level spectroscopy has been made that allowed us to experimentally detect the phenomenon of dynamical core-hole localization in symmetrical molecules. Excitations of nontotally symmetric stretching modes have been observed in the core absorption spectra of C_6H_6 [5], C_2H_4 [5–7], and in the core ionization spectrum of CO_2 [8]. Although the experiments unambiguously strengthen the theoretical prediction of the phenomenon of dynamical core-

hole localization, the quantitative agreement between the computed vibrational structure of the O $1s$ line in the XPS of the molecule and that of the high-resolution experimental spectrum [8] is not good. Recently, results of *ab initio* calculations of the vibrational structure of the O $1s$ XPS of CO_2 have been reported [9]. A reasonable agreement with the experimental spectrum has been obtained. To incorporate the effects of electron reorganization in the calculations the authors of Ref. [9] used the equivalent core (or the $Z+1$ model) approximation (ECA). Specifically, the O $1s$ ionized state of the CO_2 molecule was approximated by the ground state (GS) of the FCO^+ cation. Another approximation used in this paper was a linear-coupling model similar, but not fully equivalent to that used in Ref. [2]. The linear-coupling constants used in Ref. [2] were essentially the first derivatives of the total energy of the core-ionized molecule taken at the equilibrium geometry of the reference GS of the neutral molecule with respect to the normal coordinates. The authors of Ref. [9], on the other hand, extracted the coupling constants from the changes of the C-O interatomic distances in the core-ionized state relative to those of the neutral ground state *assuming* that the changes are well described by the linear-coupling model. Interestingly, although the authors of Ref. [4] calculated the coupling constants also from the geometry changes, their results on the excitation of the nontotally symmetric stretching mode are not similar to those reported in Ref. [9] but instead are close to the results of Ref. [2]. The equilibrium geometry of the ionized state has, however, been obtained in Refs. [4,9] with the use of different procedures. An unconstrained geometry optimization procedure was used in Ref. [9], whereas in Ref. [4] the equilibrium geometry for the ionized state was estimated from a quadratic fit to the potential-energy surface along the nontotally symmetric stretching mode. We thus conclude that the difference between the results obtained in Refs. [4,9] is due to a considerable *anharmonicity* of the potential-energy surface of the core-ionized state.

There is another factor not accounted for in the linear-coupling model that can affect results computed on the excitation of vibrational modes in ionized (excited) states. The normal coordinates can be different in the ground and ionized (excited) states. This implies that the vibrational problem for the ionized (excited) state cannot be considered separately for each vibrational mode. For a nondissociative ionized state the normal coordinates can be expressed in terms of linear combinations of the GS ones. In the Hamiltonian for the nuclear motion in the ionized state this change of normal coordinates is entirely described by the presence of bilinear and quadratic terms in the GS normal coordinates. Furthermore, as indicated above, higher-order terms must be included due to anharmonicity in cases where the ground and ionized (excited) state potential-energy surfaces cannot be approximated by second-order polynomials.

Except for the possible relevance of second- or even higher-order coupling terms mentioned above, the question of the coupling constants used deserves attention. Important factors are the relaxation and the change of electron correlation in the electronic subsystem of the molecule due to the presence of a core-hole. Relaxation is taken into account in SCF calculations of core-hole states, but to make the treatment highly accurate one should certainly use a many-body

approach to incorporate in the calculation also electron correlation. Many-body calculations of the ground and ionized states of the CO_2 molecule have been performed in Ref. [9] at the level of the second-order Møller-Plesset perturbation theory (MP2). Comparing the SCF, MP2, and the experimental results reported in Ref. [9] one can see that the agreement between the spectrum calculated at the MP2 level and the experimental one is noticeably worse than in case of the SCF spectrum. It is unclear whether this fact should be related solely to the use of the equivalent core approximation, or whether the MP2 calculations are not good enough in this particular case.

Summarizing, there are several important questions to be answered: (i) Is the linear vibronic coupling model a proper approximation for the description of the vibrational structure of the O $1s$ XPS of CO_2?, (ii) Is the equivalent core approximation very accurate for the calculation of the spectrum?, and (iii) How does electron correlation affect the intensity distribution in the vibrational progressions of the spectrum? The answers to these questions concerning the particular case of the O $1s$ ionization of CO_2 are expected to be of general importance for the problem of the vibrational structure of core-level spectra.

In the present paper we report on the results of *ab-initio* calculations of the vibrational structure of the O $1s$ XPS of the CO_2 molecule. The main emphasis is put on a detailed analysis of all relevant factors potentially important for a proper description of the vibronic coupling effects in the O $1s$ core-hole spectrum of the CO_2 molecule. Another reason, which stimulated us to write this paper, was a necessity to bring some additional clarity into the problem of dynamical localization of core holes in highly symmetrical molecules, which is sometimes misunderstood. Our calculations are not restricted by the use of the linear vibronic coupling model. We solve the two-state two-mode vibronic coupling problem for the O $1s$ ionization of CO_2 using accurate potential-energy surfaces for the ground and ionized states of the CO_2 molecule calculated at the SCF and configuration-interaction (CI) levels. The use of the equivalent core approximation is discussed, too.

II. THEORETICAL APPROACH

A. Multimode multistate nuclear dynamics

In the vicinity of avoided crossings of potential-energy surfaces the adiabatic electronic states, which are the eigenvectors of the Schrödinger equation with fixed nucleis, undergo very fast changes with the nuclear coordinates. Therefore, in the basis of the adiabatic electronic states, the nonadiabatic operators which, are essentially the matrix elements of the nuclear kinetic-energy operator, also undergo fast changes. This complicates considerably the solution of the Schrödinger equation for the electron-nuclear problem. To overcome these complications the adiabatic electronic states are replaced by smooth and slowly varying functions of the nuclear coordinates that correspond to potential-energy surfaces, which may cross at the avoided crossings of the adiabatic ones. These new electronic states that can be introduced by an orthogonal transformation of the adiabatic states are called *diabatic* states [1,10]. Thus, in the diabatic basis the vibronic coupling is introduced via the potential

energy rather than via the nuclear kinetic energy. In the basis of vibronically interacting diabatic states the matrix Hamiltonian is given by

$$\mathcal{H}=T_N\mathbf{I}+\mathbf{W}(\vec{Q}), \tag{1}$$

where T_N is the nuclear kinetic-energy operator, $\mathbf{I}$ is the unity matrix, and $\mathbf{W}(\vec{Q})$ is the potential matrix with matrix elements defined as follows:

$$W_{nm}(\vec{Q})=\int dr\Phi_n^*(\vec{r},\vec{Q})H_{el}\Phi_m(\vec{r},\vec{Q}), \tag{2}$$

where $\vec{Q}$ is the vector of nuclear coordinates, $\Phi_n(\vec{r},\vec{Q})$ are the diabatic electronic states, and H_{el} is the electronic Hamiltonian.

Assuming that the matrix elements W_{nm} are slowly varying functions of nuclear coordinates we can expand $\mathbf{W}-V_0\mathbf{I}$ in Taylor series about a reference nuclear configuration Q_0. In the case of ionization (excitation) it is natural to choose the reference configuration to be the GS equilibrium geometry and $V_0(\vec{Q})$ to be the potential-energy surface of the ground state. Expanding about Q_0 we obtain for the matrix elements of Hamiltonian (1),

$$\mathcal{H}_{nn}=T_N+V_0(\vec{Q})+E_n+\sum_s k_s^{(n)}Q_s+\sum_{ss'} k_{ss'}^{(n)}Q_sQ_{s'}+\cdots,$$

$$\mathcal{H}_{nn'}=\sum_s \lambda_s^{(nn')}Q_s+\sum_{ss'} \lambda_{ss'}^{(nn')}Q_sQ_{s'}+\cdots, \tag{3}$$

where we assumed for simplicity the diabatic electronic states ϕ_n and $\phi_{n'}$ to be of different spatial symmetry. E_n are the vertical ionization (excitation) energies for the electronic states. The following symmetry-selection rules hold for the active vibrational modes entering the terms in Eq. (3) [1]:

$$k_s^{(n)}\neq 0; \quad \lambda_s^{(nn')}\neq 0: \quad \Gamma_n\times\Gamma_s\times\Gamma_{n'}\supset\Gamma_A,$$

$$k_{ss'}^{(n)}\neq 0; \quad \lambda_{ss'}^{(nn')}\neq 0: \quad \Gamma_n\times\Gamma_s\times\Gamma_{s'}\times\Gamma_{n'}\supset\Gamma_A, \tag{4}$$

$$\vdots$$

Γ_A is the totally symmetric representation of the symmetry point group of the molecule and Γ_n and Γ_s are irreducible representations associated with the electronic states and normal vibrational modes, respectively. To apply Eq. (4) to the $k_s^{(n)}$, $k_{ss'}^{(n)}$, ..., one must set $n=n'$.

The quantities k and λ are defined as follows:

$$k_s^{(n)}=\left\langle n\left|\frac{\partial H_{el}}{\partial Q_s}\right|n\right\rangle_{Q_0},$$

$$k_{ss'}^{(n)}=\frac{1}{2!}\left\langle n\left|\frac{\partial^2 H_{el}}{\partial Q_s\partial Q_{s'}}\right|n\right\rangle_{Q_0},$$

$$\vdots$$

$$\tag{5}$$

$$\lambda_s^{nn'}=\left\langle n'\left|\frac{\partial H_{el}}{\partial Q_s}\right|n\right\rangle_{Q_0},$$

$$\lambda_{ss'}^{nn'}=\frac{1}{2!}\left\langle n'\left|\frac{\partial^2 H_{el}}{\partial Q_s\partial Q_{s'}}\right|n\right\rangle_{Q_0},$$

$$\vdots$$

Usually, only the first-order Taylor expansion is used (the linear vibronic coupling model) and the linear coupling constants $k_s^{(n)}$ and $\lambda_s^{(nn')}$ are called intrastate and interstate electron-vibrational coupling constants, respectively. Obviously, the general meaning of the coupling constants is kept also in the case of higher-order Taylor expansions. From the definition of the coupling constants it is clear that the intrastate coupling constants are just the derivatives of the diabatic potential-energy surfaces associated with the electronic states taken at Q_0 with respect to the normal vibrational modes allowed by the symmetry-selection rules. If the vibronically coupled electronic states are of different symmetry, different modes appear in the linear-coupling model in the diagonal and nondiagonal elements of $\mathcal{H}$. In this case the derivatives of the diabatic and adiabatic potential surfaces with respect to totally symmetric coordinates are identical. The determination of the interstate coupling constants is more tedious. The interstate coupling constants determine the repulsion of the adiabatic potential-energy surfaces $V_n(Q)$ and $V_{n'}(Q)$ in the vicinity of Q_0. In the linear-coupling approach the $\lambda_s^{(nn')}$ constants are deduced from a comparison of the repulsion of the *ab initio* computed adiabatic surfaces along the coordinate Q_s with the repulsion of the surfaces obtained from the approximate Hamiltonian (3) (keeping only linear-coupling terms) [1].

When studying core ionization (excitation) of molecules with several equivalent atoms it is very useful to pass over to localized diabatic electronic states. In the case of the O $1s$ ionization of CO_2 we arrive at the localized representation of the Hamiltonian (3) using the following unitary transformation:

$$\mathcal{H}^{(L)}=U^\dagger\mathcal{H}U, \quad U=\frac{1}{\sqrt{2}}\begin{pmatrix}1 & 1 \\ 1 & -1\end{pmatrix}. \tag{6}$$

The matrix elements of the transformed Hamiltonian $\mathcal{H}^{(L)}$ are defined as follows:

$$\mathcal{H}_{11}^{(L)} = T_N + V_0(\vec{Q}) + E_0 + \sum_s k_s Q_s + \sum_{ss'} k_{ss'} Q_s Q_{s'} + \cdots$$
$$+ \sum_s \lambda_s Q_s + \sum_{ss'} \lambda_{ss'} Q_s Q_{s'} + \cdots,$$

$$\mathcal{H}_{22}^{(L)} = T_N + V_0(\vec{Q}) + E_0 + \sum_s k_s Q_s + \sum_{ss'} k_{ss'} Q_s Q_{s'} + \cdots$$
$$- \sum_s \lambda_s Q_s - \sum_{ss'} \lambda_{ss'} Q_s Q_{s'} + \cdots, \quad (7)$$

$$\mathcal{H}_{12}^{(L)} = \mathcal{H}_{21}^{(L)} = \Delta_0 + \sum_s \delta k_s Q_s + \sum_{ss'} \delta k_{ss'} Q_s Q_{s'} + \cdots,$$

where we use the following notation:

$$E_0 = \frac{(E_g + E_u)}{2},$$

$$\Delta_0 = \frac{(E_g - E_u)}{2},$$

$$k_s = \frac{(k_s^{(g)} + k_s^{(u)})}{2},$$

$$k_{ss'} = \frac{(k_{ss'}^{(g)} + k_{ss'}^{(u)})}{2},$$

$$\vdots \quad\quad (8)$$

$$\delta k_s = \frac{(k_s^{(g)} - k_s^{(u)})}{2},$$

$$\delta k_{ss'} = \frac{(k_{ss'}^{(g)} - k_{ss'}^{(u)})}{2},$$

$$\vdots$$

Here the indices g and u are related to the Σ_g and Σ_u O $1s$ ionized states of the CO_2 molecule, which has $D_{\infty h}$ symmetry in its ground state. To a very good approximation the off-diagonal elements of Hamiltonian (7) can be neglected in our case. Indeed, at the SCF level $\Delta_0 = 0.0012$ eV and the δk constants are also very small. Thus, Hamiltonian (7) becomes diagonal and the vibrational motion can be considered on the potential-energy surfaces of the *localized* core-hole states *separately*. This finding is nothing but the dynamical core-hole localization predicted in Ref. [2].

It should be mentioned that if the two atoms equivalent by symmetry are adjacent and strongly bonded, the energy split Δ_0 is non-negligible and the interaction $\mathcal{H}_{12}^{(L)}$ between the two localized states cannot be neglected. Prominent examples are C_2H_2 [11] and N_2 [12] where the atoms in question are triply bonded. In such cases the picture of localized core states does not hold. The energy split can be observed in experiment [11].

Using the concept of dynamical core-hole localization, we can also calculate the vibrational structure of the O $1s$ XPS of CO_2 taking into account anharmonicity both in the ground and ionized states. This just amounts to retaining also higher-order terms in Hamiltonian (7). Indeed, as far as our task now is the computation of the vibrational motion along the potential surface of the localized core-hole states, we can force the core hole to be localized in the *ab initio* calculations and, therefore, obtain the needed diabatic potential-energy surfaces. Solving the anharmonic oscillators problem for the ground and ionized states we obtain the vibrational frequencies and overlaps between the vibrational wave functions and thus the vibrational structure of the spectrum.

B. The linear vibronic coupling model: spectrum and coupling constants

In the linear vibronic coupling model it is assumed that terms other than linear in Hamiltonian (3) are negligible and the GS potential-energy surface is harmonic. In the case of CO_2 this approximation allows for an analytical solution of the vibronic coupling problem [2]. Indeed, in this approximation Hamiltonian (7) is just the Hamiltonian of a set of shifted harmonic oscillators and, consequently, the spectral intensity is given by the product of the Poisson distributions associated with each vibrational mode [2]

$$P_i(E) = 2|\tau|^2 \sum_{n=0}^{\infty} \frac{f_i^n}{n!} e^{-f_i} \delta(E - E_0 + f_i \omega_i - n\omega_i), \quad (9)$$

where τ is the photoionization amplitude of the O $1s$ core state, $f_i = k^2/2\omega_i^2$ for the totally symmetric stretching mode, and $f_i = \lambda^2/2\omega_i^2$ for the nontotally symmetric stretching mode, respectively, and ω_i are the frequencies of the vibrational modes for the ground electronic state. Then, the position of the minimum of the potential-energy surface of the ionized state relative to that of the GS is given by the following evident equations:

$$\Delta Q_g = -\frac{k}{\omega_g}, \quad \Delta Q_u = \pm\frac{\lambda}{\omega_u}. \quad (10)$$

Q_i are the dimensionless normal coordinates, $Q_i = \sqrt{\omega_i \mu_i} R_i$, where μ_i are the respective reduced masses, $R_i = (\Delta r_1 \pm \Delta r_2)/\sqrt{2}$, and $\Delta r_{1,2}$ denote the displacements of the oxygen atoms relative to their equilibrium positions. It should be noted that the bending mode is not of relevance here, as far as in the first order the degenerate bending mode (π symmetry) does not contribute to the vibronic coupling of the Σ_g and Σ_u O $1s$ ionized electronic states due to the symmetry selection rules [Eq. (4)]. From Eq. (10) one can see that the parameters f_i of the Poisson distributions in Eq. (9) are directly related to the change of the equilibrium geometry of the ionized state relative to that of the ground state

$$f_i = \frac{1}{2}(\Delta Q_i)^2. \quad (11)$$

Thus, in the linear vibronic coupling approximation one can obtain the coupling constants for the calculation of the

vibrational structure of the spectrum in two ways. The first way is to use the definition of the coupling constants [Eq. (5)]. The second way is to find the equilibrium geometry of the ionized state and then to calculate the coupling constants with the use of Eq. (10). If the ground- and ionic-state potential-energy surfaces can be described to a good approximation by the harmonic potential around the GS equilibrium geometry, these two approaches are equivalent. Obviously, in cases of strongly anharmonic surfaces the two approaches are no longer equivalent and, moreover, do not lead to reliable results.

C. The anharmonic coupled oscillators' calculations

We now proceed to solve the Hamiltonian (7) including also higher-order terms in Q_s, which represents the problem of two coupled anharmonic oscillators. To this end we expand the eigenfunctions $|i\rangle$ of the Hamiltonian in the direct product harmonic oscillator basis $|n_g\rangle|n_u\rangle$,

$$|i\rangle = \sum_{n_g,n_u} C^i_{n_g n_u} |n_g\rangle|n_u\rangle, \qquad (12)$$

where n_g, n_u denote the vibrational quanta for the ''g'' and ''u'' modes, respectively, and $C^i_{n_g n_u}$ are the expansion coefficients to be found numerically. An efficient method to solve Hamiltonian (7) has been reported in Ref. [13]. The representation of the Hamiltonian used there is nothing but the well-known discrete variable representation discussed in detail in Refs. [14,15]. Diagonalizing the resulting secular matrix we get the vibrational energies and the coefficients of the expansion [Eq. (12)].

The vibrational line intensity in the XPS is given by the squared overlap between the initial vibrational wave function of the ground electronic state and the respective vibrational wave functions of the ionized state

$$I_{o\rightarrow i} = \sum_{n_g,n_u} |C^i_{n_g n_u} \widetilde{C}^0_{n_g n_u}|^2, \qquad (13)$$

where $\widetilde{C}^0_{n_g n_u}$ are the respective coefficients in the expansion of the initial vibrational wave function (usually GS) in the same set of product harmonic oscillators as in Eq (12). For the practical calculations the following sequence of steps is performed. At the first step the eigenvalue problem for the normal coordinate operator $\hat{Q}_k$ is solved separately for each vibrational mode. Then the matrix with the matrix elements H_{kl} defined on the grid $n \times m$ is diagonalized. The dimension of the matrix $n \times m$ is defined by the numbers n and m of the harmonic basis functions used for the totally symmetric and nontotally symmetric stretching modes ''g'' and ''u,'' respectively. The diagonalization of these matrices for the ground and ionized states yields the vibrational excitation energies and the respective eigenvectors defined by their expansion coefficients $\widetilde{C}^0_{n_g n_u}$ and $C^i_{n_g n_u}$, respectively. The intensities are calculated using Eq. (13) with the coefficients $\widetilde{C}^0_{n_g n_u}$ of the lowest energy vibrational level of the electronic ground state. In our calculations we restricted the size of the expansion Eq. (12) by taking up to 20 vibrational quanta for

each of the ''g'' and ''u'' modes. This allowed us to obtain results, which have converged with respect to the basis set size.

III. DETAILS OF THE ELECTRONIC STRUCTURE CALCULATIONS

To investigate the vibronic coupling of the O $1s$ ionized states of the linear CO_2 molecule we calculated the potential-energy surfaces for the ground and ionized states at the SCF and CI levels. Only the stretching modes were taken into account keeping the O-C-O angle equal to 180°. For the caclulations of the ground and O $1s$ core-hole states the correlation consistent valence triple zeta set with polarization functions (cc-pVTZ) basis set [16] was used. To map the potential-energy surfaces the calculations have been performed on a grid of 41 points in the space of linear displacements of the two oxygen atoms. The least-squares procedure was used to fit the potential-energy surfaces with 4th-order polynomials with respect to the oxygen atoms displacements. SCF and single-reference CI calculations have been performed using the GAMESS-UK code [17]. The configuration space for the CI calculations of the GS and O $1s$ ionized states comprised all single and double excitations (SDCI) with respect to the reference SCF GS, and O $1s$ core-hole configurations, respectively. This scheme *a priori* gives rise to localized O $1s$ core-holes and, consequently, allowed us to obtain the diabatic single-minimum surfaces for the localized electronic states instead of the known (one double-minimum and one single-minimum) adiabatic surfaces [1,2] we would get using a symmetry-adapted basis set. To account for the lacking size consistency of the SDCI method the Davidson correction was added to the SDCI total energies.

The calculations of the O $1s$ core-hole states using the equivalent core approximation have been performed on the OCF^+ cation at the SCF and SDCI levels. The cc-pVTZ basis set [16] for the O, C, and F atoms was used. The potential-energy surface obtained from these ECA calculations has been fitted similarly to that of the direct core-hole calculations on the CO_2 molecule.

IV. RESULTS

A. The GS potential-energy surface

As discussed in Sec. III the *ab initio* computed potential-energy surface of the GS of CO_2 is represented by a 4th-order polynomial expansion. The coefficients of this expansion in terms of the dimensionless normal coordinates for the two stretching modes are listed in Table I. The dimensionless normal coordinates were constructed using the vibrational frequencies obtained from the solution of the vibrational Hamiltonian with the respective potential energy. The vibrational frequencies used were the energies of the lowest excitations of the respective modes. The SCF values of the ω_g and ω_u frequencies are found to be within 11% and 7% of the experimental values, respectively. The agreement between the theoretical and experimental frequencies improves considerably when accounting for electron correlation in the calculation of the potential surface. The frequencies ω_g and ω_u obtained at the SDCI level are within only 4% and 2% of the experimental values. As seen from Table I the polynomial expansion coefficients at the level of SDCI are also

TABLE I. The coefficients of the 4th-order polynomial expansion of the ground electronic-state potential-energy surface of the CO_2 molecule and the frequencies ω_g and ω_u of the totally symmetric (g)4 and nontotally symmetric (u) vibrational stretching modes calculated at the SCF and SDCI levels. The expansion is in terms of the dimensionless normal coordinates constructed using the vibrational frequencies listed in the table (for details see text). All quantities are in eV.

	SCF	SDCI	Experiment[a]
ω_g	0.1850	0.1732	0.1658
ω_u	0.3132	0.3011	0.2937
a_{gg}	0.094706	0.088278	0.084967
a_{ggg}	−0.005514	−0.005679	−0.005779
a_{gggg}	0.000118	0.000244	0.000186
a_{uu}	0.161377	0.154553	0.150253
a_{guu}	−0.034265	−0.032557	−0.031431
a_{gguu}	0.002145	0.002659	0.002477
a_{uuuu}	0.000784	0.000864	0.001043

[a]Reference [18].

closer to those experimentally derived than the respective values obtained at the SCF level. The GS potential-energy surface calculated using the SDCI method is of acceptable quality to be used in the calculation of the vibrational structure of the O 1*s* XPS of CO_2. It should be noted, however, that the shapes of all the three surfaces are very similar to each other as seen from the contour plots depicted in Fig. 1. There is one feature of the GS surface that should be emphasized. This is the large value of the a_{guu} coefficient of the third-order $Q_g Q_u^2$ term implying that the surface is appreciably *anharmonic*. We shall see below that this anharmonicity reflects itself also in the final electronic states of the ionization process and thus makes questionable the use of the linear coupling model (Sec. II B) in the present case, at least if an accurate description of the XPS spectrum is needed.
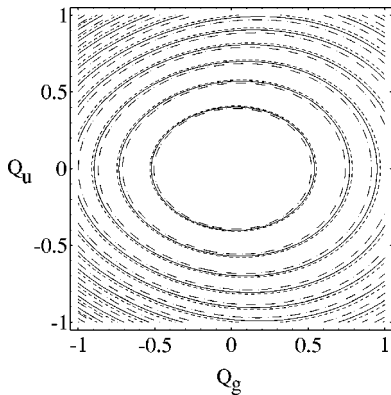

FIG. 1. Contour plots of the GS potential-energy surface of the CO_2 molecule computed by different methods. The solid line represents the contour plots of the GS obtained by the SDCI method. The dashed-dotted line represents the contour plots obtained by the SCF method. The dashed line represents the experimentally derived GS potential-energy surface [18]. The contours are taken at the same equally spaced values of the potential energy for all the surfaces. All the potential-energy surfaces are represented in their own dimensionless normal coordinates Q_g and Q_u.

TABLE II. The coefficients of the 4th-order polynomial expansion of the localized O 1*s* ionized electronic-state potential-energy surfaces of the CO_2 molecule and the frequencies ω_g and ω_u of the totally symmetric (g) and nontotally symmetric (u) vibrational stretching modes computed from this expansion. Shown are the SCF and SDCI results. The expansion is in terms of the dimensionless normal coordinates of the respective GS. The columns indicated by the "*" have been obtained by a reexpansion of GS data from Table I (see text). All quantities are in eV. Since one potential-energy surface of the ion can be obtained from the other one by $Q_u \rightarrow -Q_u$, we present here only one of them.

	SCF	SDCI	SCF*	SDCI*
ω_g	0.1772	0.1655	0.1850	0.1732
ω_u	0.3408	0.3187	0.3132	0.3011
a_g	0.060632	0.030602	−0.023578	−0.031746
a_u	0.425084	0.352282	0.379297	0.332180
a_{gg}	0.090651	0.084565	0.095619	0.090808
a_{gu}	−0.010846	−0.011607	−0.080313	−0.069184
a_{uu}	0.170282	0.161686	0.163650	0.159505
a_{ggg}	−0.005738	−0.005708	−0.005453	−0.005650
a_{ggu}	−0.000150	0.000020	0.005110	0.005677
a_{guu}	−0.034561	−0.033204	−0.033709	−0.032400
a_{uuu}	−0.001115	−0.000309	0.003735	0.003689
a_{gggg}	0.000178	0.000198	0.000118	0.000244
a_{gggu}	−0.000061	−0.000033	0.0	0.0
a_{gguu}	0.002226	0.002565	0.002145	0.002659
a_{guuu}	−0.000076	−0.000018	0.0	0.0
a_{uuuu}	0.000787	0.000868	0.000784	0.000864

B. The potential-energy surfaces of the localized ionic states

The coefficients of the 4th-order polynomial expansion for the potential-energy surfaces of the O 1*s* ionized states of CO_2, computed at the SCF and SDCI levels, are listed in Table II. The center of expansion is the GS reference nuclear geometry. From this table one can see that the coefficient a_u of the linear term Q_u is rather large for both the SCF and SDCI surfaces indicating a strong excitation of the "u" mode in the O 1*s* XPS. In contrast, the coefficient a_g of the Q_g term is quite small and, consequently, the excitation of the "g" mode is expected to be rather weak. It is worth noting that the coefficients a_{ggg}, a_{gggg}, a_{guu}, a_{gguu}, and a_{uuuu} of the respective anharmonic terms in the expansion of the ionic surface are very similar to those of the GS surface. This applies to the results obtained by both the SCF and SDCI calculations. The GS anharmonicity reflects itself in the ionic states underlying the relevance of the expansion used to describe Hamiltonians (3) and (7).

It is interesting to analyze how much of the shape of the ionic surface is determined from that of GS after shifting the reference geometry to coincide with the minimum of an ionic surface. To test this possibility we reexpanded this shifted GS surface about the position of the original minimum. Since one potential surface of the ion can be obtained from the other one by $Q_u \rightarrow -Q_u$ it generally suffices to discuss one of these surfaces only. The polynomial coefficients of the "ionic" surface simulated in this way are also listed in Table II. One can see that the coefficients of the linear terms of the simulated surfaces are considerably different from
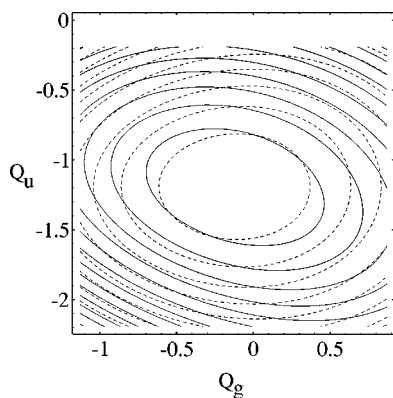
FIG. 2. Contour plots of the O 1s ionized state of the CO_2 molecule obtained by the SCF method (solid line). The simulated ionic-state potential-energy surface depicted by the dashed line has been obtained reexpanding the ground-state surface around the minimum position of the actual ionic surface. The contours are taken at equally spaced values of the potential energy starting from the value at the minimum of the surfaces.

those of the actual ionic surface. Moreover, the magnitude of the a_{gu} coefficient of the bilinear term in the expansion of the simulated surfaces is comparable with that of the quadratic terms and is about seven times larger than the corresponding term in the expansion of the actual surface. In spite of this large bilinear term the simulated ionic surface has the same shape and orientation in the space of the GS normal coordinates as the GS surface. This is a consequence of the underlying GS anharmonicity, particularly of the large contribution of the $Q_g Q_u^2$ term in the surface expansions (see Tables I and II). The contour plots of the actual ionic surfaces show that their orientation is rotated relative to that of the GS (Figs. 2 and 3). The analysis of the various contributions in the ionic surface expansion reveals that this rotation is almost entirely due to the presence of the rather large anharmonic $Q_g Q_u^2$ term (which is very similar in the GS and ionic surfaces; see Tables I and II). Obviously, any strict harmonic analysis can be very misleading in the present ex-
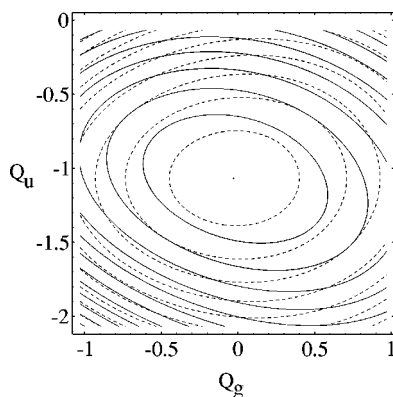

FIG. 3. Contour plots of the O 1s ionized state of the CO_2 molecule obtained by the SDCI method (solid line). The simulated ionic-state potential-energy surface depicted by the dashed line has been obtained re-expanding the ground-state surface around the minimum position of the actual ionic surface. The contours are taken at equally spaced values of the potential energy starting from the value at the minimum of the surfaces.

ample. The O 1s ionic surface of CO_2 can hardly be described within the linear model in terms of normal coordinates obtained from the GS ones by a linear transformation, as it has been done in Ref. [9].

Summarizing all the above findings we conclude that a reliable analysis of the vibrational structure of the O 1s XPS of CO_2 should necessarily be based on an approach, which goes beyond the simple harmonic approximation.

C. The energies and intensities of the vibrational lines in the O 1s XPS of CO_2

The Schrödinger equation for the coupled anharmonic oscillators determined in the preceeding subsections has been solved as described in Sec. II C. The results of our numerical calculations on the energies and intensities of the vibrational lines in the O 1s XPS of CO_2 are collected in Table III, and a comparison with the experimental data is shown in Fig. 4. The theoretical bandshapes in this figure have been obtained by convoluting the individual vibrational lines with the experimental line profile, which includes the lifetime broadening, the post collisional interaction effects, and the spectrometer specific profile [19].

The agreement between the experiment [19] and the theoretical spectrum computed using the SDCI GS and O 1s ionic surfaces is very good (Fig. 4). The intensity ratios $I_{(00)\to(10)}/I_{(00)\to(00)}$ and $(I_{(00)\to(01)}+I_{(00)\to(20)*})/I_{(00)\to(00)}$ hereafter denoted as f_g and f_u are 0.010 and 0.576, respectively. Here $(00)\to(00)$, $(00)\to(10)$, and $(00)\to(01)$ denote the vibrational transitions from the lowest vibrational level of the ground electronic state to the lowest and first excited vibrational levels of the ionic electronic state. The vibrational states are specified by the number of vibrational quanta associated with each vibrational mode $(g u)$. From Table III one can see that except for the $(1,0)$ state, higher excitations associated with the ''g'' mode appear in the spectrum energetically very close to the excitations of the ''u'' mode. This accidental near degeneracy (the Fermi resonance) leads to the fact that the components of such pairs share intensity due to mixed terms in the expansion of the potential surface. The components of the pairs are not resolved in the experimental spectrum. This is why in the above definition of f_u we used the sum of the intensities of the $(0,1)$ and $(2,0)*$ vibrational lines. The star indicates that excitations of the other symmetry (in terms of the product basis wave functions) are strongly admixed to the state.

The above intensity sharing is especially pronounced in the vibrational spectrum computed using the equivalent core approximation (Table III). The two nearly degenerate components $(0,1)*$ and $(2,0)*$ of the resonance pair in the spectra obtained at the ECA SCF and ECA SDCI levels have comparable intensities. This is due to anharmonic cross terms in the expansion of the potential surface of OCF^+, which are markedly larger than those of the O 1s ionic surface of CO_2. It is reasonable to define f_u in this case also using the sum of the intensities of these two vibrational components.

The experimentally estimated upper limit for f_g is 0.02 [8]. The theoretical energy of the $(00)\to(01)$ vibrational transition is 0.3187 eV and is in a good agreement with the respective experimental value of 0.307 (±0.003) eV [8].

TABLE III. The energies (E_i), intensities (I_i), and assignments of the vibrational lines in the O $1s$ XPS of CO_2. Listed are the results of the numerical calculations on the coupled quartic anharmonic oscillators, performed for the potential surfaces obtained by different methods. The star indicates that there is a considerable admixture of excitations of the other vibrational symmetry (in terms of the product basis states) in the state.

	SCF			SDCI			ECA SCF			ECA SDCI	
State	E_i	I_i	State	E_i	I_i	State	E_i	I_i	State	E_i	I_i
(0,0)	0.0	0.4636	(0,0)	0.0	0.5500	(0,0)	0.0	0.5099	(0,0)	0.0	0.5541
(1,0)	0.1772	0.0019	(1,0)	0.1656	0.0060	(1,0)	0.1835	0.0127	(1,0)	0.1624	0.0041
(0,1)	0.3408	0.3188	(0,1)	0.3187	0.2955	(0,1)*	0.3597	0.1760	(2,0)*	0.3216	0.0936
(2,0)*	0.3548	0.0315	(2,0)*	0.3315	0.0214	(2,0)*	0.3699	0.1365	(0,1)*	0.3301	0.2224
(1,1)	0.5147	0.0048	(1,1)	0.4819	0.0086	(1,1)	0.5380	0.0069	(3,0)*	0.4802	0.0031
(3,0)*	0.5325	0.0010	(3,0)*	0.4973	0.0013	(3,0)*	0.5549	0.0073	(1,1)	0.4937	0.0049
(0,2)	0.6784	0.1033	(0,2)	0.6346	0.0763	(2,1)	0.7131	0.0149	(4,0)*	0.6376	0.0042
(2,1)	0.6901	0.0263	(2,1)	0.6459	0.0127	(0,2)	0.7246	0.0785	(0,2)*	0.6506	0.0596
(4,0)*	0.7099	0.0014	(4,0)*	0.6628	0.0007	(4,0)*	0.7402	0.0133	(2,1)	0.6593	0.0267
(1,2)	0.8496	0.0032	(1,2)	0.7959	0.0043	(1,2)	0.8877	0.0014	(3,1)	0.8099	0.0029
(3,1)	0.8656	0.0014	(3,1)	0.8100	0.0013	(3,1)	0.9052	0.0050	(1,2)	0.8238	0.0014
(0,3)*	1.0131	0.0210	4(0,3)*	0.9480	0.0129	(0,3)*	1.0765	0.0133	(2,2)	0.9666	0.0035
(2,2)	1.0232	0.0101	(2,2)	0.9585	0.0034	(2,2)	1.0885	0.0108	(0,3)*	0.9764	0.0121

The spectrum computed using the SCF ground and ionic surfaces agrees considerably worse with the experiment than that obtained from the SDCI calculations (Fig. 4). The SCF values for f_g and f_u are 0.004 and 0.755, respectively. The energy of the first vibrational line associated with the excitation of the ''u'' mode in the case of the SCF calculation is 0.3408 eV which clearly deviates from the experimental value (0.307 ± 0.003 eV). Thus, the effect of electron correlation taken into account in the SDCI calculations of the potential-energy surfaces is to weaken the excitation of the ''u'' mode in the O $1s$ XPS of CO_2. Interestingly, the value of f_g is larger in the case of SDCI than in that of the SCF spectrum.

We are now in a position to analyze the influence of different terms in the expansion of the diabatic potential-energy surfaces on the intensities of the vibrational lines in the spectrum. The f_g and f_u values calculated numerically for various numbers of terms in the polynomial expansion of the GS and ionic surfaces are listed in Table IV. From this table one can see that the f_u values gradually increase when going from the complete 4th-order expansion to the harmonic case. An interesting feature is observed for the ''g'' mode: the bilinear term $Q_g Q_u$ taken into account significantly increases the f_g value (0.1053 for SCF and 0.0442 for SDCI) compared to the case where only quadratic terms Q_g^2 and Q_u^2 are included (0.0565 for SCF and 0.0165 for SDCI). Here we should note that the number of terms in the GS and ionic state surfaces' expansions were changed consistently.

From Table IV it is seen that the anharmonic $Q_g Q_u^2$ term essentially compensates for the strong enhancement of the ''g'' mode excitation induced by the bilinear term. In contrast to the ''g'' mode the f_u value does not change dramatically with the change of the number of terms in the expan-
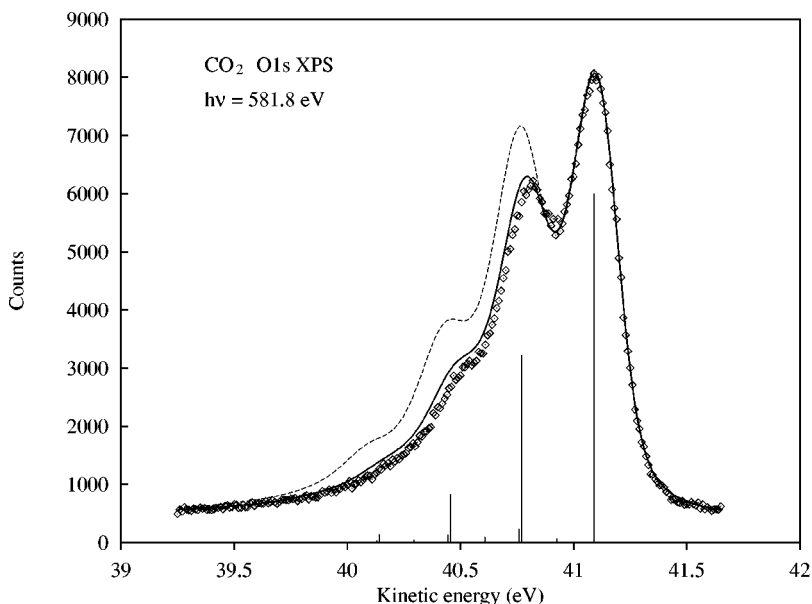

FIG. 4. Theoretical band shapes of the O $1s$ XPS of the CO_2 molecule obtained by different methods in comparison to the experimental spectrum [19]. The solid line represents the result of the SDCI calculation, the dashed line represents the result of the SCF calculation, and the experimental spectrum is depicted by the center-pointed squares. The theoretical spectral band shape has been obtained by broadening the discrete vibrational lines with the experimental line profiles [19]. The theoretical spectra have been normalized to the maximum of the intensity of the experimental spectrum and aligned with respect to the position of the maximum of the first (most intense) line in the experimental spectrum. No additional fitting has been used. The vertical lines represents the energies and intensities of the discrete vibrational lines obtained by the SDCI method.

TABLE IV. The f values and the vibrational frequencies for the GS and O $1s^{-1}$ states obtained from the numerical calculations on the coupled anharmonic oscillators for different numbers of terms in the polynomial expansion of the GS and ionic surfaces. Listed are the results of the SCF and SDCI calculations. The frequencies are in eV.

	4th order	3rd order	SCF 3rd order without $Q_gQ_u^2$	2nd order	2nd order without the bilinear term
ω_g^{GS}	0.1850	0.1833	0.1859	0.1872	0.1872
ω_u^{GS}	0.3132	0.3091	0.3179	0.3179	0.3179
ω_g^{ion}	0.1772	0.1679	0.1885	0.1829	0.1831
ω_u^{ion}	0.3408	0.3401	0.3306	0.3267	0.3266
f_g	0.0042	0.0129	0.0989	0.1053	0.0565
f_u	0.7556	0.7709	0.7680	0.7911	0.7916
			SDCI		
ω_g^{GS}	0.1732	0.1708	0.1735	0.1748	0.1748
ω_u^{GS}	0.3011	0.2963	0.3051	0.3051	0.3051
ω_g^{ion}	0.1656	0.1560	0.1737	0.1708	0.1711
ω_u^{ion}	0.3178	0.3164	0.3131	0.3122	0.3120
f_g	0.0109	0.0243	0.0426	0.0442	0.0165
f_u	0.5762	0.5869	0.5931	0.5994	0.6012

sions: the anharmonicity affects rather modestly the intensity of the ''u'' mode.

Because of the above one might expect the strict linear model to give intensities for the ''g'' and ''u'' modes similar to those obtained for the case of only quadratic expansion of the surfaces. Using the latter expansion the f_g and f_u values are 0.0565 and 0.7916 for SCF and 0.0165 and 0.6012 for SDCI, respectively. What actually happens is that the f_g and f_u values calculated using the strict linear model with the linear coupling constants taken from the 4th-order expansion of the ionic surface and the frequencies of the GS (Table I) are 0.0537 and 0.921 (SCF) and 0.0156 and 0.6841 (SDCI). The reason for this discrepancy is very simple. The strict linear model assumes that the vibrational frequencies of the ionic states are equal to those of the GS. Therefore, the co-

efficients a_{gg} and a_{uu} of the quadratic terms in the expansion of the ionic surface within the strict linear model are assumed to be equal to $\omega_g/2$ and $\omega_u/2$, respectively, where ω_g and ω_u are the GS vibrational frequencies used for the construction of the dimensionless normal coordinates. Obviously, these ''strict'' coefficients of the quadratic terms differ from the actual ones (see Table II). This immediately results in different positions of the minima of the ionic surface in these two cases.

The minimum positions and the f_g and f_u values computed using these positions [Eq. (11)] are presented in Table V for a sequence of expansions ranging from the complete 4th-order expansion to the linear one. It is worth noting that the values of $f_i(i=g,u)$ obtained from the quadratic expansion are related to the f_i^{strict} values of the strict linear model by the following evident equation:

$$f_i^{strict} = \left(\frac{2a_{ii}}{w_i}\right)^2 f_i, \quad i = g, u \qquad (14)$$

where a_{ii} are the coefficients of the quadratic terms in the polynomial expansion of the ionic surface (Table II) and ω_i are the GS vibrational frequencies. Thus, if only the quadratic expansion is used, the method of calculating the f values based on the geometry changes in the ionized state relative to the reference GS [Eq. (11)] contains a hidden renormalization of the linear coupling constants. We, therefore, refer to the approach based on Eq. (11) as the *renormalized linear vibronic coupling model*. Strictly speaking, for potential-energy surfaces containing non-negligible bilinear and higher-order mixed terms one cannot explicitly define renormalized linear coupling constants, but in many cases we nevertheless expect the renormalized linear model to serve as a good approximation. Comparing the f_g and f_u values obtained at the SCF and SDCI levels using the renormalized linear model (Table V) with those calculated numerically (Table IV) we see that for CO_2 the renormalized linear model works rather well despite considerable anharmonicity in the potential-energy surfaces of both the ground and ionized states.

TABLE V. The positions ΔQ_g and ΔQ_u of the minimum of the O $1s$ ionic potential-energy surfaces of the CO_2 molecule relative to the GS reference configuration obtained by the SCF and SDCI methods for different numbers of terms in the polynomial expansions. Listed are also the f values obtained using these minimum positions, see Eq. (11).

	4th order	3rd order	SCF 3rd order without $Q_gQ_u^2$	2nd order	2nd order without the bilinear term	Strict linear model
ΔQ_g	−0.12953	−0.12722	−0.39342	−0.40978	−0.33442	−0.32770
ΔQ_u	−1.19126	−1.20676	−1.24540	−1.26123	−1.24818	−1.35720
f_g	0.0083	0.0081	0.0774	0.0839	0.0559	0.0537
f_u	0.7095	0.7280	0.775	0.795	0.7789	0.9210
			SDCI			
ΔQ_g	−0.02945	−0.02555	−0.24983	−0.25633	−0.18094	−0.17660
ΔQ_u	−1.06765	−1.08128	−1.09493	−1.09860	−1.08940	−1.16970
f_g	0.0004	0.0003	0.0312	0.0328	0.0163	0.0156
f_u	0.5699	0.5845	0.5994	0.6034	0.5934	0.6841

D. The role of electron relaxation and correlation

Although the strict linear model is not highly accurate for CO_2 it is of sufficient quality to be used to trace out general trends in the intensity changes when going from the frozen orbital approximation, i.e., using derivatives of GS orbital energies, to the case of SDCI. It should be noted that the SCF calculations of core ionized states cannot be considered to incorporate only electron relaxation. We use here a localized orbital basis to calculate the O 1s core-ionized states and, therefore, some important correlation contributions with respect to a symmetry-adapted (delocalized orbitals) calculation are already incorporated into the calculation [20–22]. The f_g and f_u values calculated at the level of FOA are 0.4737 and 0.5065, respectively, see Table VI. Here, for the construction of the dimensionless normal coordinates we used the frequencies ω_g and ω_u calculated for the SCF GS (0.1850 and 0.3132 eV, respectively). The values of f_g and f_u reported in Ref. [2] were 0.32 and 0.98, respectively, and have been computed using experimental GS frequencies. These values, when recalculated for the dimensionless normal coordinates used in the present paper, become 0.262 and 0.784, respectively, and are very different from ours. This difference should be entirely related to the relatively small basis set ($[4s,2p]$) used for the electronic structure calculations in Ref. [2]. We note that the basis set dependence is particularly strong for the f_g values calculated at the FOA level. The calculations performed in the $[5s,3p,2d]$ basis set show that f_g is within 30% of its value obtained in the better-quality cc-pVTZ basis set ($[4s,3p,2d,1f]$) used in the present paper. In contrast, the f_u values obtained in these two basis sets are almost identical. This different behavior of f_g and f_u with respect to the extension of the basis set is not surprising. Within FOA the cut of the potential-energy surface along the totally symmetric stretching mode is calculated in the basis of symmetry-adapted delocalized orbitals. Obviously, such a delocalized description should be more sensitive to the basis set extension than a localized one. On the other hand, the cut along the nontotally symmetric stretching mode is obtained in the basis of localized orbitals as the symmetry of the molecule is lower in this asymmetrically distorted case. The above finding means that our SCF and SDCI results should not exhibit a substantial dependence on the choice of basis set since in both these cases we used a basis of localized orbitals. Indeed, the values of f_g and f_u calculated with the two basis sets are identical within 3%. Our calculations seem to have converged with respect to the basis set.

Comparing the f values calculated using the strict linear model at the levels of FOA, SCF, and SDCI, one can see that the f_g value dramatically decreases when going from FOA to SCF and then slightly decreases again when going to SDCI. The f_u value, in contrast, increases when going from FOA to SCF and then decreases when going from SCF to SDCI. Thus, electronic relaxation (with the reservations discussed in the beginning of this section) decreases f_g but increases f_u. Electronic correlation, on the other hand, rather decreases both f_g and f_u. To avoid misunderstanding we should note that the above discussion was based on the results of the strict linear model where the ''g'' and ''u'' modes do not interact with each other. The numerical f_g and

f_u values presented in Table IV exhibit a marginally different behavior from that obtained using the strict linear model: the f_g value slightly increases when going from SCF to SDCI. We surmise that this is related to the interaction (coupled oscillators) of ''g'' and ''u'' modes in our case.

V. DISCUSSION

The vibrational structure of the O 1s XPS of the symmetrical linear CO_2 molecule computed in the present paper is in a very good agreement with the experimental data [19]. We have shown that there is a strong excitation of the nontotally symmetric vibrational stretching mode in the spectrum whereas the excitation of the totally symmetric mode is almost completely suppressed. Qualitatively similar theoretical results were also reported in Refs. [2,4,9].

There is a point of view commonly accepted by the core-level spectroscopy community that the O 1s core-hole created upon ionization of CO_2 is localized and, consequently, the symmetry of the final O 1s ionized electronic states is lower than the symmetry of the ground electronic state. In other words, a symmetry breaking occurs upon ionization of the O 1s core levels of the highly symmetrical CO_2 molecule. The physical mechanism driving the created core hole to the localization is, however, very often misleadingly attributed to the ionization itself. Specifically, the core hole is thought of as localized due to the electronic relaxation accompanying the creation of the core hole. This notion is based on an observation that direct SCF core-hole-state calculations of highly symmetrical molecules give a substantial lowering of the total energy of the ionic state when the core hole is forced to be localized by choosing a localized orbital basis [4,23–25]. There is, however, no purely electronic physical mechanism leading to a molecular symmetry breaking upon ionization of highly symmetrical molecules. It has been conclusively shown in Refs. [20,21] that the energy lowering of the core-hole state obtained in the localized basis is due to the fact that an important fraction of the electron correlation is effectively incorporated into the electron relaxation when the symmetry restrictions imposed on the orbital basis in a delocalized representation are abandoned. A consistent many-body treatment of the problem immediately reveals the complete equivalence of the localized and delocalized representations. Recent x-ray emission investigations of the O_2 molecule experimentally proved that the creation of the core hole alone does not lead to the symmetry breaking in this symmetrical molecule [26]. The mechanism responsible for the symmetry breaking and core-hole localization in CO_2 is the vibronic coupling mechanism [2]. There are actually two delocalized ionic electronic states of different symmetry (Σ_g and Σ_u) that interact vibronically with each other via the nontotally symmetric stretching mode. This vibronic interaction intermixes the delocalized electronic states resulting in localized core holes. Thus, a prerequisite to the symmetry breaking and localization in the ionized states of highly symmetrical molecules is the presence of several energetically closely placed electronic states of different symmetry that can vibronically interact via nontotally symmetric modes. These nearly degenerate electronic states, in principle, can be observed directly in XPS experiments since the selection rules in this case allow for final

ionic states of different symmetries. For those molecules with equivalent atoms where the core states are not nearly degenerate, for instance, N_2 [12] and C_2H_2 [11], dynamical localization is either not present (N_2) or incomplete (C_2H_2) and two individual states can be observed experimentally [11]. This by itself already proves that core states cannot be considered localized.

Dynamical localization in symmetrical systems manifests itself differently in different experiments. In ionization and absorption experiments the pictures of localized and delocalized core states are essentially equivalent if core states are nearly degenerate [2]. Starting from the more basic symmetry-adapted formulation, a transformation of the Hamiltonian to a localized representation can be given. Most importantly, this transformation also transforms the expression for the observed spectrum to an expression for the spectrum with *a priori* localized core states [2]. The situation is different for emission spectra like Auger and x-ray emission spectra [27,28]. Here, in particular, in x-ray emission, the above-mentioned transformation of the Hamiltonian does not bring the expression for the observed spectrum into the form of spectra of *a priori* localized core states. The final result is that the spectrum does depend on the details of the vibronic coupling between the nearly degenerate core states. In other words, there is some coherence of emission from the equivalent atoms and the strength of this coherence depends on the vibronic coupling constant as well as on temperature. This leads to a violation of the usual optical selection rules and this violation depends on the nuclear dynamics [28]. This has been confirmed experimentally and further discussed theoretically for CO_2 [29] and not observed in O_2 [26] where vibronic coupling cannot be present.

In our calculations we used a localized representation. In this representation the nuclear and electronic motions are decoupled (see Sec. II). This decoupling should not be confused with the adiabatic or BO separation: in the adiabatic (delocalized in our case) representation the nuclear and electronic motions are coupled. Obviously, one can use also the delocalized representation but the localized one is evidently more convenient in our case.

Our calculations on the vibrational structure of the O $1s$ XPS of CO_2 unequivocally show that the anharmonicity of the potential-energy surfaces of the GS and O $1s$ ionized states significantly affects the intensity distribution within the vibrational progression of the O $1s$ spectrum.

On the other hand, the renormalized linear model provides rather good results on the intensities of the vibrational lines in the spectrum. At first glance it would seem that there is some contradiction as the linear model deals with harmonic vibrational wave functions only. The reason that the results of the renormalized linear model agree quite well with those of our anharmonic numerical treatment is that the vibronic excitations in the case of O $1s$ XPS of CO_2 are not very strong. The largest overlap between the vibrational wave function of the GS and those of the O $1s$ ionized state is for states in the vicinity of the minimum of the potential surfaces where the anharmonic terms do not contribute significantly to the surface polynomial expansion. In this case the vibrational wave functions to a good accuracy can be approximated by the harmonic oscillator wave functions. The renormalized linear model simply places the harmonic

wave functions of the ionized state to the right minimum position of the ionized state potential-energy surface relative to the GS one. Thus, in principle, the renormalized linear model may be used in situations where the ground- and excited-state potential-energy surfaces are appreciably anharmonic but with one important reservation: the vibrational excitations should not be very strong. If the vibrational excitations were very strong the renormalized linear model would give significantly wrong results. In such a case the region of large overlaps between the vibrational wave functions covers that part of the ionic surface that is far away from its minimum and where strong contributions of anharmonic terms are present. The wave functions of the vibrationally excited states that have the maximum amplitudes in this region should also significantly deviate from the harmonic wave functions. By inspection of our results one can see that the larger the distance between the minima positions of the GS and O $1s^{-1}$ potential-energy surfaces, the larger the deviation between the f_u values obtained from the renormalized linear model (Table V) and those of the full numerical anharmonic treatment (Table IV). The value of ΔQ_u is -1.191 for the SCF calculations and f_u obtained from the renormalized linear model is 0.709, whereas the respective numerical value is 0.755. On the other hand, ΔQ_u is smaller in the case of the SDCI calculations (-1.067) and the difference between f_u obtained from the renormalized linear model and the numerical anharmonic treatment (0.569 and 0.576, respectively) is smaller than that of the SCF. At the end of this paragraph we would like to mention that in the case of strong vibrational excitation there are arguments in favor of the strict linear model as a good estimate of the intensity distribution [30]. While the renormalized linear model may be somewhat superior for weak excitations and tends to fail for strong excitation, the strict linear model retains its quality.

As we have already mentioned in Sec. IV B the anharmonic terms in the expansion of the ionic potential-energy surface are very similar to those of the GS surface. This finding implies that the anharmonicity of the ionic surface, which plays an important role in the correct description of the intensity distribution of the O $1s$ XPS of CO_2 is rather *ground-state-induced anharmonicity*. We surmise that by investigating the ground-state potential-energy surface one can get an idea whether or not it is possible to use the linear model (strict or renormalized) or whether or not a calculation of the vibrational structure of a core-level spectrum should be performed at a more sophisticated level. Here we should note that this finding is not specific to CO_2, but is of rather general importance for other symmetrical and nonsymmetrical molecules.

To describe properly the vibrational structure of the O $1s$ XPS of CO_2 it is important to incorporate electron correlation into the calculation of the potential-energy surfaces. The f values and the vibrational frequencies of the ground and ionic states become considerably closer to the respective experimental data when electron correlation is taken into account (in our case, at the level of SDCI). Interestingly, electron correlation affects the f_g and f_u values in opposite directions. The value of f_g calculated at the SDCI level increases compared to the case of the SCF calculation, whereas f_u decreases.

TABLE VI. The f values obtained by different methods and comparison with the experimental data. Listed are the results obtained by the FOA, SCF, and SDCI with and without using the ECA and MP2 with the use of ECA. The theoretical literature values (in parentheses) have been recalculated for the dimensionless normal coordinates of the ground state used in the present paper (see text). Our SCF and SDCI results with and without the use of ECA have been obtained from the numerical calculations on the coupled quartic anharmonic oscillators.

	FOA	FOA[a]	SCF	SCF[b]	ECA SCF	ECA SCF[c]	ECA MP2[c]	ECA SDCI	SDCI	Experiment[d]
f_g	0.473	(0.262)	0.004	(0.0)	0.025	(0.005)	(0.005)	0.007	0.011	<0.02
f_u	0.506	(0.784)	0.755	(1.318)	0.613	(0.716)	(0.423)	0.570	0.576	0.56

[a]Reference [2].
[b]Reference [4].
[c]Reference [9].
[d]Reference [8].

It is worthwile to compare our results for the vibrational line intensities with the data available in the literature. Such a comparison is presented in Table VI. Our results listed have been obtained by solving numerically for the coupled anharmonic quartic oscillators. Because the absolute values of f_g and f_u depend rather strongly on the respective frequencies used for the construction of the dimensionless normal coordinates, it is desirable for the sake of comparison to have a unified normal coordinate scale for the values obtained by similar methods. For this purpose we recalculated the f values obtained in Refs. [2,4,9] at the one-particle level using our GS frequencies for the "g" and "u" vibrational modes calculated by the SCF method. The MP2 f values from Ref. [9] have been recalculated using our SDCI GS frequencies. The reason for the descrepancy between our FOA values and those reported in Ref. [2] has already been discussed in Sec. IV D. This is due to the small basis set used for the electronic structure calculations in Ref. [2]. The f values reported in Refs. [4,9] were calculated using the geometry change in the O $1s$ ionized state relative to the reference GS nuclear configuration or, in our nomenclature, using the renormalized linear model. Surprisingly, the f_u value calculated with the O-C bond length changes reported in Ref. [4] and our SCF vibrational frequency ($\omega_u = 0.3132$ eV) deviates drastically from that presented in Ref. [4]. The f_u reported in Ref. [4] is 0.936, whereas the value calculated using the geometry change reported in Ref. [4] and our SCF vibrational frequences is 1.318. This deviation cannot be associated with the different frequencies since ω_u used in Ref. [4] is 0.32 eV (for the ionic state), which is very close to our frequency $\omega_u = 0.3132$ eV. The analogous value to that of Ref. [4] obtained from our SCF calculations using the renormalized linear model (see Table V) $f_u = 0.779$ is rather similar to that listed in Table VI (0.755). Thus, we assume that there is a misprint in Ref. [4].

The f values reported in Ref. [9] are in reasonable agreement with the respective experimental data (Table VI). They have been computed using the SCF within the equivalent core approximation. The MP2 calculations of Ref. [9] have also been performed within the equivalent core approximation. The results are in worse agreement with the experiment (Table VI). The reason for this is not clear. In an attempt to clarify this point we have performed in addition to our calculations discussed in the preceding sections SCF and SDCI calculations, but now using the equivalent core approxima-

tion. The results obtained are also reported in Table VI. It is seen that the SCF results are in reasonable agreement with the experimental data. Moreover, the inclusion of electron correlation in the calculations improves the agreement with the experiment. The f values obtained by SDCI with and without using the equivalent core approximation are almost identical indicating that this approximation works rather well in the case of O $1s$ ionization of CO_2. The individual energies and intensities of the vibrational lines in the spectrum computed using ECA are slightly different from those obtained from the direct core-hole calculations (see Table III). Here we should note that the f_u value obtained at the SCF level within ECA is closer to the experimental one than that obtained from the direct core-hole SCF calculations (Table VI). Moreover, the difference between f values obtained with and without ECA depends on the method used for the electronic structure calculations (SCF, MP2, and SDCI). Apparently, there is an uncontrolled error compensation in ECA that makes this approach not robust. The quality of the results obtained using ECA depends also on the molecule studied [31].

Our analysis explains why the rather simple approach used in Ref. [9] gives reasonable results on the vibrational structure of the O $1s$ ionization spectrum of the CO_2 molecule. First, the linear model used in Ref. [9] works rather well in this particular case because it uses the geometry change as input data and, therefore, contains a hidden renormalization of the coupling constants (remember that the vibrational excitations are not very strong, $f < 1$). Second, there is an error compensation in ECA at the SCF level that decreases f_u in this case. This is borne out by the numerical anharmonic oscillators' calculations using the full 4th-order polynomial expansion of the potential-energy surface that are compared with and without ECA, in columns 3 and 5 of Table VI.

VI. CONCLUSIONS

Our *ab initio* calculations of the vibrational structure of the O $1s$ XPS of the CO_2 molecule confirm previously reported results that core-hole localization and symmetry breaking occurs upon ionization of the O $1s$ electrons. The physical mechanism that drives the O $1s$ core holes to localization is dynamical in its origin [2]: the two almost degenerate Σ_g and Σ_u electronic delocalized core-hole states

interact vibronically via the nontotally symmetric stretching mode, which leads to their intermixing and consequently to the localization of the core holes. The SCF and SDCI calculations show that electron reorganization and correlation effects strongly influence the vibrational intensity distribution of the O $1s$ XPS of CO_2. The vibrational structure of the O $1s$ XPS of CO_2 computed at the SDCI level is in very good agreement with the respective high-resolution experimental spectrum.

The anharmonicity of the potential-energy surface of the O $1s$ ionized electronic states has been shown to play a crucial role in a proper description of the vibrational structure of the XPS. This anharmonicity is mostly a replica of the ground-state anharmonicity. This ground-state-induced anharmonicity substantially affects the position of the minimum of the ionic potential-energy surface relative to that of the ground state. As a result, the linear vibronic coupling model in its strict formulation gives intensities of the ``g'' and ``u'' vibrational modes in the spectrum that strongly deviate from their experimental values. The linear model, which employs the geometry changes in the ionized state relative to the GS equilibrium configuration, is equivalent to the strict linear model if the GS and ionic potential-energy surfaces are harmonic in the vicinity of the GS reference configuration. Our analysis shows that the former model contains a hidden renormalization of the linear coupling constants in the case where the ionic- and ground-state potential-energy surfaces exhibit considerable anharmonicity. This hidden renormalization, which actually provides the right position of the minimum of the ionic surface relative to the GS one within the framework of the linear model, is the main

reason why this renormalized linear model gives rather good results for the vibrational line intensities in the spectrum. Another reason why the renormalized linear model works well in the case of the O $1s$ XPS of CO_2 is that the vibrational excitations in the spectrum are not very strong. In this case the largest overlaps between the vibrational wave functions of the ground and ionic electronic states fall within the region where the anharmonic terms do not significantly distort the harmonic shape of the surfaces. As a consequence the vibrational wave functions, to a good accuracy, can be approximated by the harmonic ones. This explains why the renormalized linear model employing the harmonic vibrational wave functions for the ground and ionic electronic states gives rather good results in our case.

We have presented results with and without using the equivalent core approximation. This approximation has been shown to be a good approach for calculating the vibrational structure of the core-hole spectrum at the SDCI level. The f values for the O $1s$ core-hole states of CO_2 obtained within this approximation at the SDCI level are almost identical to those obtained at the same level of treatment of the electron correlation, but without using this approximation.

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