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Ab initio calculation of the vibrationally resolved O 1*s* photoelectron spectrum of CO_2

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The oxygen 1*s* photoelectron spectrum for CO_2 has been calculated using *ab initio* electronic structure theory, a localized hole simulated by the equivalent-cores approximation, and the harmonic-oscillator approximation. The predicted spectrum is found to be in good agreement with a recently reported experimental spectrum, and is in better agreement with the experimental spectrum than is an earlier prediction by Domcke and Cederbaum. The equivalence of the approach taken here and that used by Cederbaum and Domcke is discussed, as well as the reasons for the differences in the calculated results. [S1050-2947(98)08906-9]

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Kivimäki *et al.* [1] have reported the vibrational structure in the oxygen 1*s* photoelectron spectrum of CO_2 as evidence for dynamic localization of the core hole, predicted by Domcke and Cederbaum [2]. Although the qualitative evidence for the effect is quite convincing, the quantitative agreement between the experimental results and the predictions of Domcke and Cederbaum is not good. The latter predict a more extensive vibrational progression in the antisymmetric mode than is observed and significant excitation of the symmetric mode, whereas no evidence for this mode is seen in the experimental results. The discrepancies between theory and experiment are thought to arise because of the use of a one-particle model by Domcke and Cederbaum to calculate the appropriate coupling constants. Such an approach ignores relaxation effects and overestimates the degree of vibrational excitation [1]. It is useful, therefore, to consider the results of calculations that do not suffer from this drawback. We have done this and find good agreement between our calculated spectra and the experimental data of Kivimäki *et al.*

Our calculations use GAUSSIAN94 [3] with the 6-311 G** basis set at both the Hartree-Fock (HF) and MP2 [4] levels. The core hole and its localization are simulated using the equivalent-cores approximation; that is, the core-ionized oxygen atom is replaced by an isovalent fluorine ion. Therefore, the calculations for the core-ionized species are done on FCO^+. The electrostatic effect of the oxygen 1*s* core, with only one electron, is simulated by the additional charge on the nucleus and two 1*s* electrons on the fluorine atom. This approach should give approximately the correct potential for the valence electrons, which determine the molecular geometry. Although we can expect failure of the equivalent-cores approximation when correlation between the core and valence electrons is important, it has been successful in predicting vibrational structure in inner-shell photoelectron spectra [5–7].

The calculations begin with geometry optimization of both CO_2 and FCO^+, followed by calculations of the vibrational frequencies and normal modes of these molecules. From the difference in geometry between the two molecules and the vectors describing the normal modes, we obtain the changes in normal coordinates between the two species [8]. Using these together with the harmonic oscillator approximation and the calculated frequencies, we determine Franck-Condon factors for the excitation of both the symmetric and antisymmetric stretching modes of the core-ionized molecule. Since such calculations are known to overestimate the vibrational frequencies, we have reduced our calculated frequencies according to the factors suggested by Scott and Radom [9] (90.5% for the HF calculations and 94.6% for the MP2 calculations). The bond lengths and vibrational frequencies (scaled) that we have calculated are compared with experimental values in Table I. The agreement between experiment and theory is quite good for the values of ν_3 (the antisymmetric stretching frequency for neutral CO_2) at both the Hartree-Fock and the MP2 levels. In the core-ionized species the two methods bracket the value of ν_3 reported by Kivimäki *et al.* [1] and both theoretical values are within 5% of their experimental value. Similarly, the values for the change in bond length on core-ionization bracket the value determined from the results of Kivimäki *et al.* [1,10].

To a first approximation, excitation of ν_1 (the symmetric stretching mode) depends on the sum of the changes in bond lengths, $\Delta r_{CO} + \Delta r_{CF}$. Since these are nearly equal and opposite in sign we expect negligible excitation of these modes, in agreement with the results of Kivimäki *et al.* Our calculations of the Franck-Condon factors for this mode are in agreement with this expectation, indicating that 99% of the ionization leads to the $v=0$ state of this mode. Excitation of

TABLE I. Results of electronic structure calculations for CO_2 and FCO^+.

	CO_2			FCO^+		
	HF	MP2	Expt.[a]	HF	MP2	Expt.[b]
r_{CO}, pm	113.51	116.81	116.01	108.52	112.85	
r_{CF}, pm				117.88	120.20	
ν_3, cm^{-1}	2347	2337	2349	2522	2357	2475
Δr_{CO}, pm				−4.98	−3.95	−4.2
Δr_{CF}, pm				4.38	3.39	4.2

[a] G. Herzberg and L. Herzberg, in *American Institute of Physics Handbook*, 3rd ed., edited by D. E. Gray (McGraw-Hill, New York, 1972), pp. 7–186 and 7–191.

[b] Refs. [1], [10].

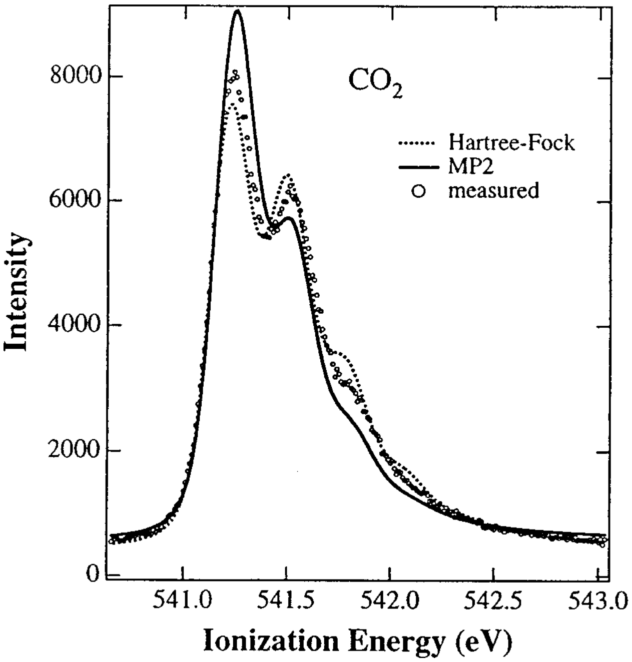

FIG. 1. Comparison of calculated and experimental photoelectron spectrum for oxygen 1s ionization of CO$_2$. The points represent measurements taken at a photon energy of 585 eV [1,13]. The solid line has been calculated as described in the text at the MP2 level and the dotted line has been calculated at the Hartree-Fock level.

ν_3 (antisymmetric stretch) depends on the difference, $\Delta r_{\mathrm{CO}} - \Delta r_{\mathrm{CF}}$, which is significant, in agreement with the predictions of Domcke and Cederbaum [2] and of Clark and Müller [11], and with the experimental results of Kivimäki *et al.* In our prediction of the photoelectron spectrum, we consider only this mode.

The measurements of Kivimäki *et al.* are made close to threshold, and the spectra are modified by postcollision interaction between the slow photoelectron and the fast Auger electron. We have used the theory of van der Straten, Morgenstern, and Niehaus [12] to calculate the shape of the photoelectron lines. For this we have used an intrinsic linewidth (resulting from the core-hole lifetime) of 165 meV, as found by Kivimäki *et al.* from fitting their data. These line shapes have been convoluted with a Gaussian resolution function with a width of 140 meV, and then convoluted with the Franck-Condon factors from the vibrational calculations to give predicted photoelectron spectra. These have been fit to the experimental data of Kivimäki *et al.* [1,13] with overall height, overall position, and a constant background as the only adjustable variables.

A comparison of the theoretical and calculated spectra is shown in Fig. 1, where we see that the agreement is quite satisfactory; the two theoretical curves closely bracket the experimental data. We see that, with a suitable calculation of the molecular parameters, there is good agreement between theory and experiment.

On the surface, it would appear that the approach we have taken is quite different from that used by Domcke and Cederbaum [2]. However, within the limits of the linear coupling model [14], the two methods are equivalent, differing only in the details of how the molecular structure parameters are determined. To illustrate this point, we consider a harmonic oscillator model in dimensionless coordinates: Q, the distance coordinate, is $R\sqrt{\mu\omega/\hbar}$, where R is the normal coordinate, μ is the reduced mass for this coordinate, and ω is the vibrational frequency (all in conventional units). Dimensionless energies are measured in units of $\hbar\omega$ and the potential energy is therefore equal to $Q^2/2$. We restrict ourselves to a model in which the vibrational frequencies are the same for the ground and core-ionized states; this restriction is implicit in the linear-coupling model.

In our approach, we determine the difference, ΔQ, between the locations of the potential energy minima for the ground and core-ionized states. From the harmonic oscillator wave functions, it can be shown that the Franck-Condon factors for the excitation from the ground vibrational state of the neutral molecule to any vibrational state of the core-ionized molecule are given by a Poisson distribution [15]:

$$I(0\rightarrow v)=\frac{f^v}{v!}\,e^{-f}, \tag{1}$$

where $f=\Delta Q^2/2$. This result is rigorous in the limit that the frequency of the excited state is the same as that of the ground state.

In the treatment of Domcke and Cederbaum [2], the expression for $I(0\rightarrow v)$ is the same as Eq. (1), but f is equal to κ^2 or λ^2 [16], where κ and λ are derivatives of the energy of the core-ionized molecule, E^*, with respect to the normal coordinates: $\kappa=(\partial E^*/\partial Q)_0/\sqrt{2}$. The derivative is evaluated at the equilibrium position of the ground-state molecule. In the harmonic approximation, $(\partial E^*/\partial Q)_0=\Delta Q$, with the result that $\kappa=\Delta Q/\sqrt{2}$ and $f=\Delta Q^2/2$, as before. Thus, at the level of the harmonic approximation the two approaches are equivalent, differing only in how they use molecular electronic structure theory to determine a value for the change in normal coordinate.

Domcke and Cederbaum have made two important approximations in evaluating κ and λ. The first is to equate the normal coordinates of the core-ionized state Q to the normal coordinates of the ground state Q'. The second is to replace $(\partial E^*/\partial Q)_0$ with $-(\partial\epsilon/\partial Q)_0$, where ϵ is an appropriate orbital energy. The second approximation ignores relaxation effects, which are significant, as has been noted [1,2]. The first leads to an overestimation of the value of κ, the coupling constant for the symmetric stretching mode. Our calculations of the normal modes for neutral and core-ionized CO$_2$ show that

$$Q_S'=1.04Q_S+0.17Q_A, \tag{2}$$

$$Q_A'=-0.30Q_S+1.01Q_A, \tag{3}$$

where the subscripts S and A refer to the symmetric and antisymmetric modes. The derivative of energy with respect to the symmetric normal coordinate is given by the expression

$$\frac{\partial E^*}{\partial Q_S}=\frac{\partial E^*}{\partial Q_S'}\frac{\partial Q_S'}{\partial Q_S}+\frac{\partial E^*}{\partial Q_A'}\frac{\partial Q_A'}{\partial Q_S} \tag{4}$$

with a similar expression for the other derivative. From Domcke and Cederbaum, $\partial E^*/\partial Q_S' = 0.098$ eV and $\partial E^*/\partial Q_A' = 0.288$ eV. Taking these, together with the appropriate coefficients from Eqs. (2) and (3), we find that $\partial E^*/\partial Q_S = 0.015$ eV, which is considerably smaller than the value of $\partial E^*/\partial Q_S'$. This result is in agreement with both the experimental observation and our theoretical calculation that the symmetric mode is negligibly excited.

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