

Vibrationally Resolved O 1s Photoelectron Spectrum of CO₂: Vibronic Coupling and Dynamic Core-Hole Localization

A. Kivimäki,* B. Kempgens, K. Maier, H. M. Köppe, M. N. Piancastelli,† M. Neeb, and A. M. Bradshaw

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

(Received 12 November 1996)

The C and O 1s photoelectron lines of the CO₂ molecule in the gas phase have been measured with vibrational resolution in the threshold region. The vibrational fine structure on the O 1s line is completely dominated by the antisymmetric stretching mode with a frequency of 307 (± 3) meV. This mode can be excited only via vibronic coupling, as predicted by Domcke and Cederbaum [Chem. Phys. **25**, 189 (1977)], and provides a mechanism for dynamic core-hole localization. Relaxation effects are found to affect strongly the vibrational intensity distribution of the photoelectron line. [S0031-9007(97)03784-8]

PACS numbers: 33.80.Eh, 33.60.Fy

Electronic transitions in molecules are generally accompanied by vibrational excitations. In the Born-Oppenheimer approximation they are usually considered to be strictly separated in time, although this fundamental axiom is violated when vibronic coupling occurs, i.e., when degenerate or nearly degenerate electronic states are coupled via a nontotally symmetric vibration. Vibronic coupling thus opens up channels in photoabsorption or photoionization which would otherwise be dipole forbidden. These channels can make a substantial contribution to the excitation process, as has been shown in valence level photoionization [1,2]. As a consequence of the Franck-Condon principle, normally only totally symmetric modes are observed in electronic spectra. In inner shell photoionization of CH₄, for example, the pronounced vibrational structure on the C 1s line first observed by Gelius *et al.* [3] contains only the symmetric C-H stretching mode. Nontotally symmetric vibrations have, however, been observed recently in the core absorption spectra of C₆H₆ [4] as well as of C₂H₄ and its isotopomers [4–6]. Such an observation in photoionization would be of fundamental importance since vibronic coupling gives rise to symmetry breaking and leads to a dynamic localization of the core hole in molecules with equivalent atoms. This was predicted by Domcke and Cederbaum [7] who considered specifically O 1s photoionization in CO₂ and showed that vibronic coupling should lead to a strong excitation of the antisymmetric stretching mode. Vibrationally resolved electron spectroscopy has so far been hampered at the O 1s threshold by the insufficient photon energy resolution and photon flux available on soft x-ray monochromators at synchrotron radiation sources. In the present study, we present measurements of both the C and O 1s photoelectron spectra of CO₂ with vibrational resolution and demonstrate for the first time the importance of vibronic coupling in core level photoionization, thus confirming the prediction of Domcke and Cederbaum [7].

The photoelectron spectra of the CO₂ molecule were measured on the X1B undulator beamline [8] at the

National Synchrotron Light Source, Brookhaven National Laboratory. Recently, the mechanically ruled blazed grating (800 lines/mm) has been replaced by a holographically manufactured laminar grating (also 800 lines/mm) which has resulted in a considerable improvement in resolution and flux, particularly at photon energies above 500 eV. The O 1s photoelectron spectra were recorded with the entrance and exit slit of the monochromator set to 5 μ m, which corresponds to resolution of about 100 meV. Pass energies of 10–15 eV were used for the angle-resolving magic-angle cylindrical mirror analyzer (CMA) [9], giving an electron kinetic energy resolution between 80 and 120 meV. The C 1s photoelectron spectrum of CO₂ was measured with a photon energy resolution of ~ 80 meV and electron energy resolution of ~ 60 meV. All measurements were normalized with respect to the photon flux and target gas pressure.

The vibrationally resolved O 1s photoelectron line of CO₂ measured at a photon energy of 554 eV is shown in Fig. 1 (points). The spectrum has been fitted with a non-linear least-square fit procedure, the intrinsic line shape of which derives its asymmetry from the phenomenon of post-collision interaction (PCI) between the outgoing slow photoelectron and the subsequently emitted Auger electron. This asymmetry can be seen in the dashed lines which represent individual vibrational components before convolution with the CMA and monochromator functions. The final fit curve is shown as a solid line in Fig. 1. From the fit of several spectra measured at different photon energies a lifetime broadening of 165 (± 10) meV is obtained for the O 1s core-ionized state in CO₂. The vibrational energy is found to be 307 (± 3) meV. The linear CO₂ molecule (point group $D_{\infty h}$) has four normal vibrations: the totally symmetric stretching mode (ν_1) of σ_g symmetry, the antisymmetric stretching mode (ν_3) of σ_u symmetry, and the two degenerate bending modes (ν_2) of π_u symmetry. In the molecular ground state ν_1 (σ_g) and ν_2 (π_u) have considerably lower vibrational energies: 165 and 83 meV [10], respectively. On the other hand, the

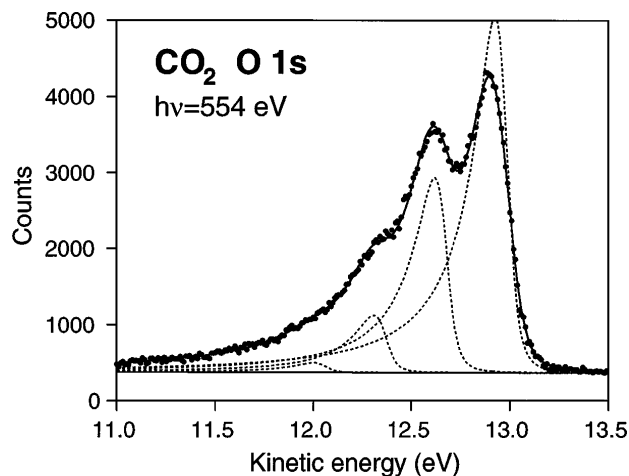


FIG. 1. The vibrationally resolved O $1s$ photoelectron spectrum of CO_2 measured at a photon energy of 554 eV (points). Dashed lines show the individual fitted vibrational lines before convolution with the instrumental function. The solid line represents the final fit.

ground-state frequency of ν_3 is 291 meV [10]. In keeping with the observation that vibrational energies change only marginally upon core ionization [11–14] we attribute the vibrational fine structure of the O $1s$ line to the *antisymmetric stretching mode*. Self-consistent field (SCF) calculations for the O $1s^{-1}$ state of CO_2 also give a similar vibrational energy (320 meV) for the antisymmetric stretch [15]. The two O $1s$ orbitals give rise to a bonding and antibonding pair of molecular orbitals $\phi_{1s}(\sigma_g)$ and $\phi_{1s}(\sigma_u)$, the separation of which is actually only 1.5 meV [7]. In addition to the coupling to the totally symmetric stretching mode expected for the dipole-allowed Franck-Condon transition, Domcke and Cederbaum [7] show that the σ_g and σ_u core orbitals themselves may be coupled via the antisymmetric stretch of σ_u symmetry. Because of this nonadiabatic coupling process the total symmetry between the initial state, dipole operator, and the final state is still conserved but the ν_3 mode also appears in the vibrational fine structure.

Figure 1 also shows that the vibrational fine structure on the O $1s$ line can be described very well with only one vibrational mode. In a fit allowing two vibrational progressions the $\nu = 1$ components of the symmetric stretch ν_1 , fixed to have a vibrational energy of 170 meV, acquires only a very low intensity (2% or less of the intensity of the $\nu = 0$ line). Moreover, the decomposition of the experimental line shape with a maximum entropy program package [16] gave no indication of the totally symmetric stretching mode. Thus, the vibrational envelope of the O $1s$ photoelectron line appears to be completely dominated by the antisymmetric stretching mode which becomes dipole allowed via vibronic coupling. Nordgren *et al.* [17] have already obtained experimental evidence for vibronic coupling in CO_2 by measuring x-ray emission spectrum from the O $1s^{-1}$ state. From a Franck-Condon

fit they concluded indirectly the excitation of the antisymmetric stretching mode in the core-ionized intermediate state. By measuring the vibrationally resolved O $1s$ photoelectron spectrum, however, the vibronic coupling between the two O $1s$ core orbitals can be observed immediately, giving quantitative information on the coupling strength, vibrational energy, cross section, and asymmetry parameter. The photon energy dependence of the absolute cross section and asymmetry parameter β for the individual vibrational components will be reported in a later paper [18].

The vibrational coupling constants and other parameters calculated by Domcke and Cederbaum [7] are compared with the experimental ones in Table I. Whereas the experimental spectrum has its highest intensity in the vibrational ground state of the core-ionized molecule, the calculated spectrum would peak at the first vibrational component ($V_{\sigma_u} = 1$) and is characterized by a broader vibrational envelope. The difference can be explained by the strength of relaxation: A more effective relaxation reduces the vibrational coupling constant and, consequently, the intensity of higher vibrational components [19]. The experimentally determined coupling constant $f_u = 0.56$ is indeed much smaller than the calculated one (0.98). The dominance of the antisymmetric stretching was correctly predicted, but the symmetric stretching mode still acquired considerable intensity in the calculations ($f_g = 0.32$). Since the latter were based on a one-particle approximation, relaxation effects were not included. Using the harmonic potential approximation and the Franck-Condon factors, we determine the geometry shift in the antisymmetric stretching direction to be $0.055 \pm 0.005 \text{ \AA}$ (see Table I), confirming the previous result obtained from the x-ray emission spectrum [17].

In contrast to the calculations of Domcke and Cederbaum [7], Clark and Müller [15] did not take into account vibronic coupling. Instead, they assumed that the core hole itself breaks the symmetry of the molecule, resulting in an excitation of the antisymmetric vibration which is symmetry allowed in the point group of the ion. Recently, however, Glans *et al.* [20] have demonstrated in a study of the x-ray emission spectra of the O_2 molecule that the creation of the core hole alone does not break the symmetry. They observed that the selection rules based on the inversion symmetry of homonuclear diatomic molecules are still valid even when the core hole is filled by the x-ray emission process. In contrast to core ionization in O_2 , vibronic coupling in CO_2 can occur simultaneously with ionization and provides the mechanism for the breaking of the inversion symmetry. This may be understood in a simple way as follows: In the sudden approximation O $1s$ ionization implies that both the $1\sigma_g$ and $1\sigma_u$ derived states are simultaneously created. As described above, they are coupled via the nontotally symmetric mode. If this coupling were neglected the states could be treated independently, and

TABLE I. Spectroscopic constants for the O $1s^{-1}$ state in CO₂.

	Theory	Experiment
Lifetime broadening [meV]	–	165 ± 10
Vibrational energy [meV]	320^a	307 ± 3
Change in equilibrium bond distance along the σ_u coordinate [\AA]	0.12^b	0.055 ± 0.005
Vibrational coupling constants $f_{\sigma_u}, f_{\sigma_g}$	$0.98, 0.32^b$	$0.56, <0.02$
Franck-Condon factors (%)	$38/37/18/6/1^b$	$58/32/9/2/0$
O $1s^{-1}(v_{\sigma_u} = 0/1/2/3/4) \leftarrow \text{GS}(v = 0)$		

^aRef. [15].^bRef. [7].^cRef. [17].

the ionization transition would lead to the excitation of totally symmetric modes in the usual way. Owing to the coupling, however, the antisymmetric stretching vibration leads to dynamical symmetry breaking of the CO₂ molecule. Asymmetric forces are exerted on the nuclei and all three begin to move asymmetrically relative to the former inversion point. The local symmetry is reduced from $D_{\infty h}$ to $C_{\infty v}$, the two oxygen atoms are no longer equivalent, and the vacancy localizes on one atom. Formally, the very nearly degenerate $1\sigma_g$ and $1\sigma_u$ orbitals separate into the nondegenerate 1σ and 2σ orbitals within the $C_{\infty v}$ point group. The molecular ion will therefore be left in a more stable state when ionization formally occurs from the $1\sigma_u$ orbital, which transforms nominally into the “anti-bonding” 2σ orbital. This is confirmed by the vibrational energy which is higher in the ionic state than in the molecular ground state. However, the full symmetry of the resulting vibronic eigenstates of the ion remains $D_{\infty h}$: We encounter a (incoherent) superposition of two asymmetric motions, one in the state with the vacancy on the left oxygen and one in the state with the vacancy on the right oxygen. Because of this dynamical localization, the antisymmetric mode is excited as if it were totally symmetric.

Vibronic coupling is expected to occur only in ionization from nearly degenerate equivalent core orbitals: The C $1s$ photoelectron spectrum of CO₂ should reveal only the symmetric stretching mode. The high resolution C $1s$ spectrum, measured at $h\nu = 313$ eV, is shown in Fig. 2. Despite the higher overall resolution, the vibrational fine structure is far less distinct than in the O $1s$ spectrum, implying a much lower vibrational frequency. From the fit a lifetime broadening of $\Gamma = 78 (\pm 15)$ meV and a vibrational spacing of $161 (\pm 7)$ meV are determined for the C $1s^{-1}$ state. The former is in good agreement with the $\Gamma = 70 \pm 20$ meV obtained by Nordgren *et al.* [17]. The measured vibrational energy (161 meV) lies close to both the frequency of the totally symmetric stretching mode in the molecular ground state (167 meV) and the calculated value of 170 meV [15]. As expected, there is no indication of a second vibrational progression.

The bending modes (ν_2) have quite a low vibrational frequency (83 meV in the molecular ground state), but

should not appear anyway in the O $1s$ and C $1s$ photoelectron spectra: The core orbitals in CO₂ are of pure σ symmetry and thus cannot couple with the bending modes which transform under π symmetry [7]. If, however, a $1s$ electron is excited into a degenerate orbital of π symmetry the excitation of the bending mode becomes allowed through vibronic coupling in the valence orbital space. This Renner-Teller effect [21] removes the degeneracy of the excited $2\pi_u$ orbital in CO₂ and results in the bending of the molecule. In the O $1s \rightarrow 2\pi_u$ excitation of CO₂ all four vibrational modes may appear due to the degeneracy of both the valence ($2\pi_u$) and O $1s$ core orbitals ($1\sigma_g, 1\sigma_u$), whereas in the C $1s \rightarrow 2\pi_u$ transition the antisymmetric stretching mode should not be excited. So far, we have not been able to distinguish any vibrational fine structure in the C or O $1s^{-1}2\pi_u$ absorption lines even under high resolution conditions, probably indicating the complexity of the vibrational excitations in the absorption profile.

In conclusion, we have measured the C and O $1s$ photoelectron lines of the CO₂ molecule with vibrational

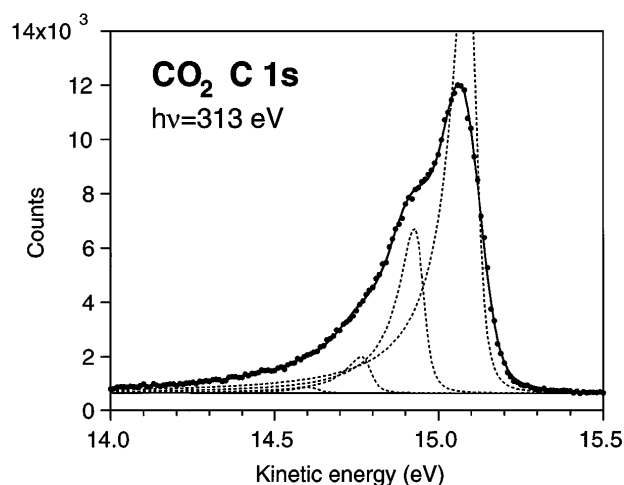


FIG. 2. The C $1s$ photoelectron spectrum of CO₂ measured at a photon energy of 313 eV (points). Dashed lines show the individual fitted vibrational lines before convolution with the instrumental function. The solid line represents the final fit.

resolution. The O 1s spectrum is completely dominated by the antisymmetric stretching mode with a vibrational frequency of 307 ± 3 meV. This mode would normally be dipole forbidden, but is observed as a result of vibronic coupling which effectively breaks the symmetry of the molecule and leads to dynamic core-hole localization. The electronic relaxation is found to be much stronger than predicted.

We are grateful to L.S. Cederbaum for stimulating discussions during the preparation of this paper. Further, we sincerely thank F. Loeb for assistance in setting up the new grating on the X1B beamline. Part of this work has been financed by the Deutsche Forschungsgemeinschaft. The National Synchrotron Light Source at Brookhaven National Laboratory is supported by the U.S. Department of Energy under Contract No. DE-AC02-76CH00016.

*Permanent address: University of Oulu, Department of Physical Sciences, 90570 Oulu, Finland.

†Permanent address: University "Tor Vergata," Department of Chemical Sciences and Technologies, 00133 Rome, Italy.

- [1] P.M. Dehmer, J.L. Dehmer, and W.A. Chupka, *J. Chem. Phys.* **73**, 126 (1980).
- [2] J.H.D. Eland, *Photoelectron Spectroscopy* (Butterworths, London, 1984), 2nd ed.
- [3] U. Gelius, S. Svensson, H. Siegbahn, E. Basilier, Å Faxälv, and K. Siegbahn, *Chem. Phys. Lett.* **28**, 1 (1974).
- [4] Y. Ma, F. Sette, G. Meigs, S. Modesti, and C.T. Chen, *Phys. Rev. Lett.* **63**, 2044 (1989).
- [5] F.X. Gadea, H. Köppel, J. Schirmer, L.S. Cederbaum, K.J. Randall, A.M. Bradshaw, Y. Ma, F. Sette, and C.T. Chen, *Phys. Rev. Lett.* **66**, 883 (1991).
- [6] B. Kempgens, B.S. Itchkawitz, K.J. Randall, J. Feldhaus, A.M. Bradshaw, H. Köppel, F.X. Gadea, D. Nordfors, J. Schirmer, and L.S. Cederbaum, *Chem. Phys. Lett.* **246**, 347 (1995).
- [7] W. Domcke and L.S. Cederbaum, *Chem. Phys.* **25**, 189 (1977).
- [8] K.J. Randall, J. Feldhaus, W. Erlebach, A.M. Bradshaw, W. Eberhardt, Z. Xu, Y. Ma, and P.D. Johnson, *Rev. Sci. Instrum.* **63**, 1367 (1992).
- [9] J. Feldhaus, W. Erlebach, A.L.D. Kilcoyne, K.J. Randall, and M. Schmidbauer, *Rev. Sci. Instrum.* **63**, 1454 (1992).
- [10] T. Shimanouchi, *Tables of Molecular Vibrational Frequencies*, National Standard Reference Data Series, 39 (National Bureau of Standards, Washington, 1972), Consolidated Vol. I.
- [11] L.J. Medhurst, P.A. Heimann, M.R.F. Siggel, D.A. Shirley, C.T. Chen, Y. Ma, S. Modesti, and F. Sette, *Chem. Phys. Lett.* **193**, 493 (1992).
- [12] K.J. Randall, A.L.D. Kilcoyne, H.M. Köppe, J. Feldhaus, A.M. Bradshaw, J.-E. Rubensson, W. Eberhardt, Z. Xu, P.D. Johnson, and Y. Ma, *Phys. Rev. Lett.* **71**, 1156 (1993).
- [13] H.M. Köppe, A.L.D. Kilcoyne, J. Feldhaus, and A.M. Bradshaw, *J. Chin. Chem. Soc.* **42**, 255 (1995).
- [14] B. Kempgens, A. Kivimäki, M. Neeb, H.M. Köppe, A.M. Bradshaw, and J. Feldhaus, *J. Phys. B* **29**, 5389 (1996).
- [15] D.T. Clark and J. Müller, *Chem. Phys.* **23**, 429 (1977).
- [16] S.F. Gull and J. Skilling, Maximum Entropy Data Consultants Ltd., 33 North End, Meldreth, Royston SG8 6NR, England.
- [17] J. Nordgren, L. Selander, L. Pettersson, C. Nordling, K. Siegbahn, and H. Ågren, *J. Chem. Phys.* **76**, 3928 (1982).
- [18] K. Maier, B. Kempgens, A. Kivimäki, H.M. Köppe, M.N. Piancastelli, M. Neeb, and A.M. Bradshaw (to be published).
- [19] W. Domcke and L.S. Cederbaum, *Chem. Phys. Lett.* **31**, 582 (1975).
- [20] P. Glans, K. Gunnelin, P. Skytt, J.-H. Guo, N. Wassdahl, J. Nordgren, H. Ågren, F. Kh. Gel'mukhanov, T. Warwick, and E. Rotenberg, *Phys. Rev. Lett.* **76**, 2448 (1996).
- [21] G. Herzberg and E. Teller, *Z. Phys. Chem. B* **21**, 410 (1933); R. Renner, *Z. Phys.* **92**, 172 (1934).