

# Vibrationally resolved C and O 1s photoelectron spectra of carbon dioxide

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## Abstract

Vibrationally resolved C 1s and O 1s photoelectron spectra of carbon dioxide have been measured with photon energies up to 500 and 700 eV, respectively. Vibrational branching ratios are nearly constant for the C 1s and O 1s photoelectron spectra recorded with the photon energies in the regions 400–500 and 600–700 eV, respectively, where neither shape resonance effect nor photoelectron recoil effect is significant. The information about the potential curves for the C 1s and O 1s ionized states are extracted from these spectra, using the Franck–Condon approximation. The experimental potential curves thus obtained are well reproduced by the present *ab initio* calculations based on the symmetry adapted cluster-configuration interaction (SAC-CI) method.

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## 1. Introduction

Vibrational excitation is often associated with photoionization of a molecule. The degree of vibrational excitation can be inferred by assuming the nuclei to be fixed during the process of photoionization. The vibrational excitation probabilities can then be calculated as an overlap integral between ground and excited state vibrational wavefunctions, i.e., ‘Franck–Condon factor’. High photon fluxes with very narrow photon bandwidths via high-resolution soft X-ray monochromators installed in high-brilliance synchrotron radiation light sources [1] invoked renewal of interest in core-level photoelectron spectroscopy study of free molecules [2]. Indeed both Franck–Condon analysis of the experimental core-level spectra and simulation of the spectra based on the *ab initio* potential surfaces using the Franck–Condon approximation have been carried out extensively for some small molecules [3–10].

In the present work, using unprecedented resolution achieved by the combination of the state-of-the-art soft X-ray beam

line at SPring-8 and the state-of-the-art electron spectroscopy apparatus, we have measured vibrationally resolved C 1s and O 1s photoelectron spectra of the CO<sub>2</sub> molecule and obtained spectroscopic parameters of the C 1s and O 1s ionized states. Furthermore, the C 1s and O 1s ionized states are investigated theoretically by means of the SAC/SAC-CI method [11–13]. The SAC/SAC-CI method has been successfully applied to various molecular spectroscopies including photoionization processes. In the series of applications, the SAC-CI general-*R* method [14] has clarified the fine details of the main and satellite spectra (e.g., [15–17]) in the outer- and inner-valence regions. In the present work, we compare the present experimental and theoretical spectroscopic parameters with those values reported so far [3–6].

## 2. Experimental

The measurements were carried out at the c-branch of the beam line 27SU at SPring-8, a third generation synchrotron radiation facility with an 8-GeV storage ring in Japan. The figure-8 undulator installed in this beam line produces high-intensity linearly polarized soft X-rays. When integer order (i.e., 1st, 2nd, ...) harmonics of the undulator radiation are chosen, the light

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is horizontally polarized. The half-integer (i.e., 0.5th, 1.5th, . . .) harmonics provide vertically polarized light [18]. The radiation was guided to a high-resolution soft X-ray monochromator installed in the c-branch. A more detailed description of the beam line and the monochromator can be found elsewhere [19,20]. The ejected electrons were analyzed with an SES-2002 electron energy analyzer (Gammadata-Scienta) equipped with a gas cell: the analyzer was mounted with lens axis in horizontal direction [21]. In the region of interest, the photoemission perpendicular to the polarization plane became negligible and only horizontal polarization was used.

### 3. Theoretical

Two dimensional (2D) potential energy surfaces of the ground, C 1s and O 1s core ionized states were calculated in the region of  $R_{CO} = 1.0 - 1.35 \text{ \AA}$ . The basis sets were correlation-consistent polarized core-valence double zeta basis set (cc-pCVDZ) [4s3p1d] GTOs for C and O [22]. The core-ionized states were calculated by the SAC-CI general- $R$  method. The different sets of  $R$ -operators were used for C 1s and O 1s ionizations. In the SAC-CI, the  $R$ -operators up to quadruples were included in the general- $R$  calculation; these higher order operators are necessary for describing orbital relaxations as well as electron correlations, especially for O 1s ionization. For the reference orbitals, the ground-state Hartree-Fock with canonical MOs was used. All MOs were included in the active space to describe core-hole relaxation. To reduce the computational requirements, the perturbation selection procedure was adapted [23]. The threshold of the linked terms for the ground state was set to  $\lambda_g = 1.0 \times 10^{-7}$  a.u. and the unlinked terms were adapted as the products of the important linked terms whose SDCI coefficients were larger than 0.005. For the inner-shell ionized states, the thresholds of the linked terms were set at  $\lambda_e = 1.0 \times 10^{-7}$  a.u. The thresholds of the CI coefficients for calculating the unlinked operators in the SAC-CI method were 0.05 and 0.001 for the  $R$  and  $S$  operators, respectively.

The calculated 2D potential energy surfaces were fit with the 2D Morse functions and the vibrational analysis was performed. For calculating the spectrum, vibrational wave functions and the Franck-Condon factors were obtained by the grid method, in which Lanczos algorithm was adapted for the diagonalization.

The SAC/SAC-CI calculations were executed with the Gaussian03 suite of programs [24] with some modifications for calculating the inner-shell ionization spectra.

### 4. Results and discussion

C 1s and O 1s photoelectron spectra of carbon dioxide, measured at a photon energy  $h\nu = 500$  and 700 eV, respectively, are shown in Fig. 1 together with a least-squares curve fitting decompositions [25] into a vibrational progression. In the curve fit, the post-collision-interaction-distorted line profile is convoluted with the Gaussian profile. For both C 1s and O 1s photoelectron spectra, only one progression was necessary to take into account. The progression in the C 1s photoelectron spectrum is assigned to the symmetric stretching vibrations ( $\nu_1', 0, 0$ ) [3,6],

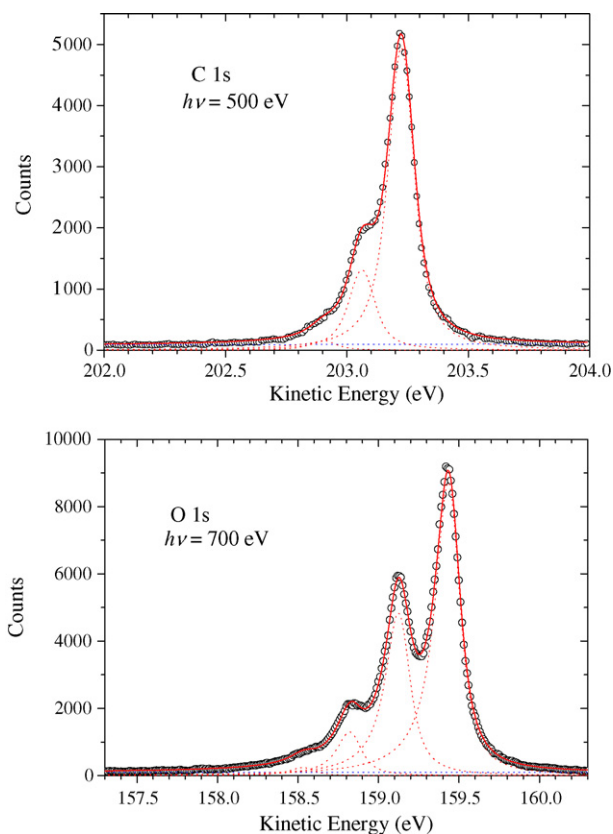


Fig. 1. C 1s and O 1s photoelectron spectra of carbon dioxide taken at  $h\nu = 500$  and 700 eV, respectively. Circles—experiment, thick solid lines—modeled spectrum and thin dotted lines—individual peaks.

whereas the progression in the O 1s spectrum is assigned to the antisymmetric stretching vibrations ( $0, 0, \nu_3'$ ) [3–5]. Antisymmetric stretching vibration is excited via vibronic coupling and provides a mechanism of dynamic core-hole localization [5,26].

C 1s and O 1s photoelectron spectra were measured with photon energies up to 500 and 700 eV, respectively, and were decomposed into the vibrational components. Values for the intensity ratio of the  $\nu = 1$  peak to the main  $\nu = 0$  peak,  $I(\nu = 1)/I(\nu = 0)$ , for the C 1s photoelectrons are between 0.257 and 0.266, in the photon energy range of 400–500 eV. Those for O 1s photoelectrons are between 0.546 and 0.560 in the photon energy range of 600–700 eV. In these photon energy ranges, the shape resonance effect [27,28] dies out, whereas the photoelectron recoil effect [29] is still negligible. We thus extracted the spectroscopic parameters of the C 1s and O 1s ionized states from the C 1s and O 1s photoelectron spectra in these photon energy regions. To do it, we employed different approaches for C 1s and O 1s. For C 1s, we assumed the Morse potential energy curves for the symmetric stretching coordinate and employed the intensity fitting described in Ref. [9]. For O 1s, we employed harmonic oscillator approximation. The averaged values of the individual spectroscopic constants extracted from the fit to several different photoelectron spectra are summarized in Table 1. The table also includes the experimental values extracted by Carroll et al. [6] for C 1s and by Kivimäki et al. [3] for O 1s. The agreements are reasonable.

Table 1  
Vibrational constants, ratios of the Franck–Condon factors,  $R(v'_1, v'_3) \equiv I(v'_1, v'_3)/I(0, 0)$ , and differences of the equilibrium bond lengths between the neutral and ionic species,  $\Delta R_{C-O}$  and  $\Delta R_{C-O^+}$ , for the C and O 1s ionized states of CO<sub>2</sub>

Spectroscopic constant	Experimental			Theoretical			
	Expt.1 [6]	Expt.2 [3]	Present	MP2 [4]	SDCI[5]	SAC-CI	ECA CC-SD(T)
<b>C 1s<sup>-1</sup></b>							
$\Gamma$ (meV)	99(2)		95(2)				
$\omega_{e1}$ (meV)	165.6(7)		164(1)			175	169
$\omega_{e1x_{e1}}$ (meV)			0.2(1)			0.2	
$R(1, 0)$	0.241(2)		0.262(4)			0.278	1.139
$R(2, 0)$	0.016(1)		0.028(4)			0.016	0.536
$\Delta R_{C-O}$ (Å)	-0.0195(1)		-0.0212(1)			-0.020	-0.049
<b>O 1s<sup>-1</sup></b>							
$\Gamma$ (meV)			163(4)				
$\omega_{e3}$ (meV)		307(3)	309(1)	292	319	330	302
$R(0, 1) + R(2, 0)$			0.553(6)		0.576	0.956	0.534
$R(0, 2) + R(2, 1)$			0.151(4)		0.161	0.349	0.127
$R(0, 3) + R(2, 2)$			0.028(4)		0.030	0.057	0.020
$\Delta R_{C-O^+CO}$ (Å)		0.042	0.0427(3)	0.0339		0.031	0.040
$\Delta R_{C-O}$ (Å)		-0.042	-0.0427(3)	-0.0395		-0.049	-0.043

We have performed the vibrational analysis for the ab initio potential energy curves of the ground and both C 1s and O 1s ionized states. The calculated spectroscopic constants of the ground state,  $\omega_{e1} = 171$  meV,  $\omega_{e3} = 301$  meV and  $R_{C-O} = 1.162$  Å, are in good agreement with well-known experimental values  $\omega_{e1} = 165$  meV,  $\omega_{e3} = 276$  meV and  $R_{C-O} = 1.162$  Å. The calculated spectroscopic constants of the C 1s and O 1s ionized states are summarized in Table 1. Table 1 also includes the relevant theoretical values for the O 1s ionized state by Hahne et al. with the MP2 method [4] and by Dobrodey et al. with the SDCI method [5].

In the C 1s ionized state, the calculated C–O bond length decreases by  $\Delta R_{C-O} = -0.020$  Å from that of the ground state, exhibiting very good agreement with the experimental estimate of  $\Delta R_{C-O} = -0.0212(1)$  Å. The calculated frequency  $\omega_{e1} = 175$  meV and anharmonicity  $\omega_{e1x_{e1}} = 0.2$  meV are in reasonable agreement with the measurement ones  $\omega_{e1} = 164(1)$  meV and  $\omega_{e1x_{e1}} = 0.2(1)$  meV. The C–O<sup>+</sup> bond length with a core hole site is, on the other hand, predicted to be longer by 0.031 Å than that in the ground state, whereas the other C–O bond length is predicted to be shorter by  $-0.049$  Å than that in the ground state. The estimated change of the bond length is in fair agreement with the experimental estimate of  $\Delta R_{C-O} = \pm 0.043(1)$  Å. The calculated frequency  $\omega_{e3} = 330$  meV is in reasonable agreement with the measured one  $\omega_{e3} = 309(1)$  meV. The potential barrier between the two local minima of O 1s ionized states are calculated to be as low as 160 meV at the lowest point, which is below the zero point energy.

The Franck–Condon factors (FCF) between the ground and core-ionized states are also calculated from the vibrational wavefunctions and the calculated FCF ratios relative to the 0–0 transition are listed also in Table 1 together with the experimental values. Dobrodey et al. concluded that the vibrational motion of the O 1s ionized states can be considered on the potential energy surfaces of the localized core-hole states separately: we followed this method in the present calculation. The calculated values are in good agreement with the experi-

mental values for C 1s while the agreement becomes worse for O 1s.

We also performed the CCSD(T) calculation with cc-pVTZ basis set within the equivalent core approximation (ECA) [30,31]. The FCFs of the O 1s ionized state by this method agree well with the experimental values, though the agreement is worse for the C 1s ionization. It is worth to consider the reason why the SAC-CI general-*R* method gave better result than the ECA-CCSD(T) method for C 1s and vice versa for O 1s. The SAC-CI general-*R* method can be applied to wide varieties of core excitation/ionization processes and usually provides reliable results. However, since it employs the ground-state Hartree-Fock MOs, higher order *R*-operators are necessary for describing orbital relaxation. Thus, this method may give less accurate results for the system that exhibits large orbital relaxation. Orbital relaxation for O 1s ionization in CO<sub>2</sub> is more significant than that of C 1s ionization. Because of it, the FCF of O 1s ionization of CO<sub>2</sub> were calculated less accurately than that of C 1s ionization. The ECA-CCSD(T) method is generally less reliable than the SAC-CI general-*R* method, because the ECA-CCSD(T) method does not directly calculate the core-hole state, relying on the ECA. One can see this deficiency in the FCF calculations in C 1s ionization of CO<sub>2</sub>. The ECA-CCSD(T) method is, however, free from the orbital relaxation problem as a natural consequence of the ECA. Also, one can easily use larger basis set at the expense of the ECA. Thus, for the system that exhibits large orbital relaxation, such as O 1s ionized CO<sub>2</sub> concerned here, this method can give better result than the SAC-CI general-*R* method.

## 5. Conclusions

We have measured C and O 1s photoelectron spectra of carbon dioxide in the photon energy range up to 500 and 700 eV, respectively. Vibrational branching ratios are nearly constant in the photon energy regions 400–500 and 600–700 eV, for C 1s and O 1s photoelectrons, respectively, where neither shape resonance effect nor photoelectron recoil effect is significant. The

information about the potential curves for the C 1s and O 1s ionized states has been extracted from these sudden-limit spectra, using the Franck–Condon approximation. The spectroscopic constants thus obtained are in excellent (fair) agreement for C 1s (O 1s) ionized state with the ab initio calculations based on the SAC-CI method. The origin of relatively poor agreement by the SAC-CI calculation for the O 1s ionized state is attributed to the large orbital relaxation effect of the O 1s ionized state, in comparison with the ECA-CCSD(T) calculation that is free from orbital relaxation effect.

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