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Vibrationally resolved C and O 1s photoelectron spectra of carbon monoxides

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Abstract

Vibrationally resolved C and O 1s photoelectron spectra of carbon monoxide have been measured in the photon energy range between 300 and 440 eV and between 550 and 702 eV, respectively. The intensity ratios of the vibrational components vary slowly, approaching the sudden limit. From the spectra in the sudden limit, the information about the potential curves for the C 1s and O 1s ionized states are extracted. The experimental potential curves thus obtained are reproduced well by the present ab initio calculations based on the symmetry adapted cluster-configuration interaction method.

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', and are independent of the photon energy.

High photon fluxes with very narrow photon bandwidths via high-resolution soft X-ray monochromators installed in high-brilliance synchrotron radiation light sources invoked renewal of interest in core-level photoelectron spectroscopy [1,2]. In the core-level photoionization, shape resonances often appear [3,4]. The shape resonances can be described as trapping of the ejected photoelectron by a potential barrier of the molecular ion with subsequent tunnelling into the continuum, and often cause photon energy dependence of the vibrational structure [2,3,5]. Here, a question arises. Where can one assume that the vibrational structure is independent of the photon energy, i.e., a so-called sudden limit? One heuristically assumes that one can reach the sudden limit at about 40 eV above the ionization threshold, which is above the shape resonances as well.

In the present work, we have investigated the energy dependence of the vibrational structure of the C 1s and O 1s photoelectron spectra of the CO molecule, one of the best studied molecules [5–12] as a showcase example. Our results illustrate that the vibrational structure can vary slowly up to ~100 eV above the threshold. From the photoelectron spectra recorded in the region where the vibrational structure becomes nearly the independent of

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the photon energy, we have extracted the information about the potential energy curves 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 [13–15]. The SAC/SAC-CI method has been successfully applied to various molecular spectroscopic techniques including photoionization processes. In the series of applications, the SAC-CI general-*R* method [16,17] has clarified the fine details of the main and satellite spectra (e.g., [18,19]) in the outer- and inner-valence regions. In the present work, we demonstrate that this method can reproduce very precisely the observed C 1s and O 1s photoelectron spectra at the sudden limit.

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 is horizontally polarized. The half-integer (i.e., 0.5th,1.5th,...) harmonics provide vertically polarized light [20]. 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 [21,22]. The ejected electrons were analyzed with an SES-2002 electron energy analyzer (Gammadata-Scienta) equipped with a gas cell: the analyzer was mounted with its lens axis in the horizontal direction [23]. With the photoelectron kinetic energy up to ~60 eV, both horizontally and vertically polarized light from the undulator was used; the angle-independent electron emission intensity was obtained as $I(0°) + 2 \times I(90°)$, with $I(0°)$ and $I(90°)$ being the spectral intensity of the electron emission measured for the horizontal and vertical polarization, respectively. For higher kinetic energy photoelectrons, the photoemission perpendicular to the polarization plane became negligible and only horizontal polarization was used.

3. Theoretical

Potential energy curves of the ground, C 1s and O 1s core ionized states were calculated in the region of $R_{CO} = 0.9-1.45$ Å. The extensive basis sets were used to allow the description of the orbital reorganization and electron correlations; i.e., triple zeta (VTZ) (10s6p)/[6s3p] GTOs for C and O [24], augmented with two polarization d-functions [25]. 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. 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 [26]. The threshold of the linked terms for the ground state was set to $\lambda_g = 1.0 \times 10^{-6}$ 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 0.0 for the *R*- and *S*-operators, respectively.

The calculated potential energy curves were fit with the extended Rydberg 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 GAUSSIAN 03 suite of programs [27] with some modifications for calculating the inner-shell ionization spectra.

4. Results and discussion

C and O 1s photoelectron spectra of carbon monoxide, measured at a photon energy $h\nu = 440$ and 702 eV, respectively, are shown in Fig. 1 together with a least-squares curve fitting decompositions [28] into a vibrational progression. In the curve fit, the PCI-distorted line profile is convoluted with the Gaussian profile. The positions of the individual vibrational components and their intensities, as well as Lorentzian and Gaussian widths common for all the vibrational components, were treated as fitting parameters.

About 20 C 1s and O 1s photoelectron spectra were measured over a photon energy range between 300 and 440 eV and between 550 and 702 eV, respectively, and were decomposed into the vibrational components by the curve fit. The Gaussian widths extracted from the fittings, which represent a convolution of the monochromator bandwidth, electron analyzer bandwidth and Doppler broadening, are ~65 meV or less depending of the kinetic energy for both C 1s and O 1s. The averaged values of the Lorentzian widths extracted from the curve fit are 95(2) and 167(5) meV for C 1s and O 1s photoelectron spectra, respectively. These values very well agree with the previous values, 95(5) meV [8] for C 1s and 162(6) meV for O 1s [12].

The intensity ratios of the $v = 1$ peak to the main $v = 0$ peak, $I(v = 1)/I(v = 0)$, for the C 1s and O 1s photoelectrons are plotted in Fig. 2(a) and (b), respectively, as a function of photoelectron kinetic energy. The ratios measured by some other groups are also plotted in the figure. The agreements between the different measurements are reasonable. The shape resonances appear at kinetic energies below 10 eV for both C 1s and O 1s photoionizations and thus the lowest energy points in Fig. 2 are within the

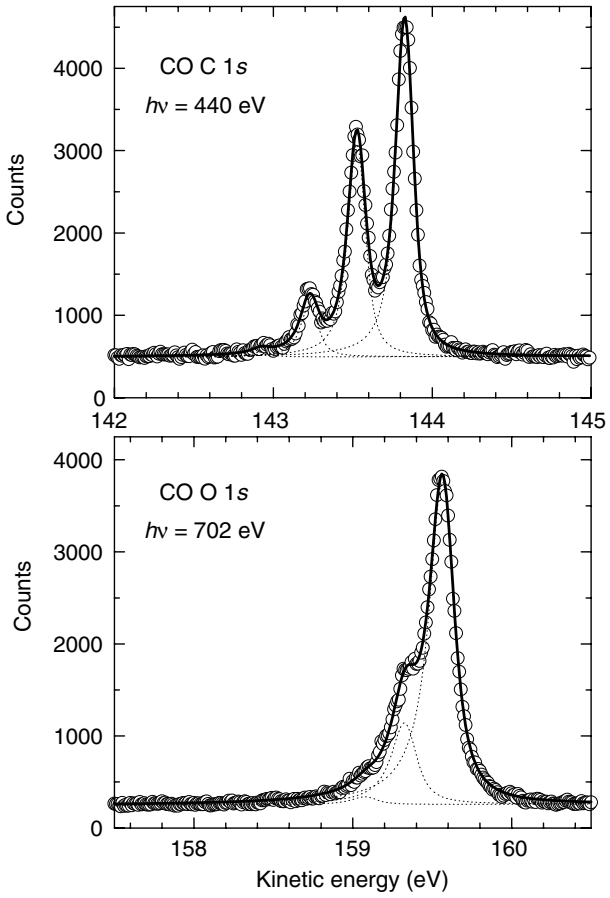

Fig. 1. C 1s and O 1s photoelectron spectra of carbon monoxide taken at $h\nu = 440$ and 702 eV, respectively. Circles – experiment, think solid lines – modelled spectrum, thin dotted lines – individual peaks.

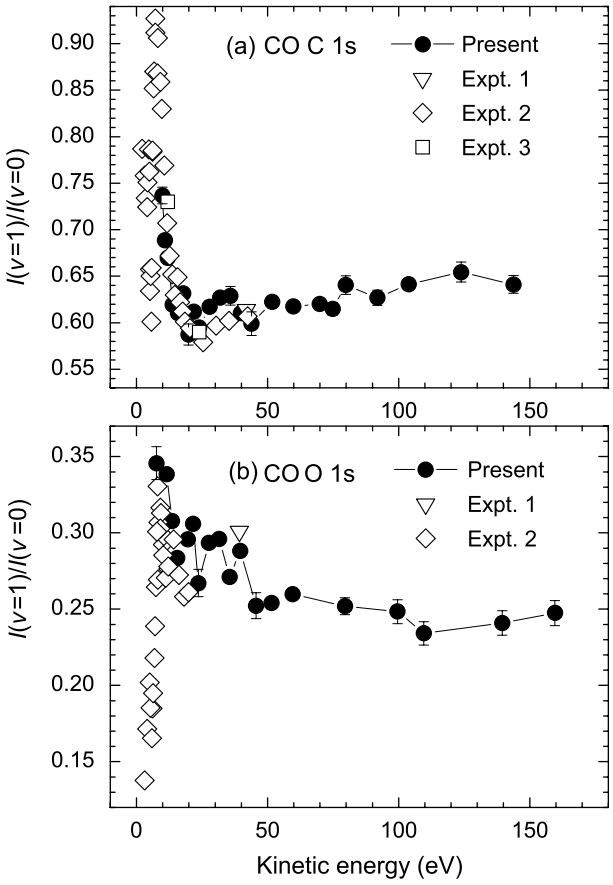

Fig. 2. Intensity ratios of the $v = 1$ peak to the main $v = 0$ peak, $I(v = 1)/I(v = 0)$, in (a) C 1s and (b) O 1s photoelectron spectra as a function of photoelectron kinetic energy. Expt. 1, Kempgens et al. [7]; Expt. 2, Kugeler et al. [12]; Expt. 3, Carroll et al. [8].

shape resonances. Let us focus on the C 1s photoionization. The ratio sharply drops as the kinetic energy increases from 10 to 20 eV, takes the minimum value at ~20 eV, and then gradually increases as the kinetic increases. It seems to reach the asymptotic value ~0.64, at kinetic energy of ~80 eV. Let us turn to the O 1s photoionization. The ratio monotonously decreases as the kinetic energy increases. It seems to reach the asymptotic value ~0.25, at a kinetic energy of ~80 eV. Usually, it is tacitly assumed that the vibrational structure is independent of the photon energy 40 eV above the ionization threshold. The present observations, however, suggest that the sudden limit seems to be at ~80 eV above the ionization threshold for carbon monoxide, though the shape resonances appear only below 10 eV. The intensity ratio observed in [2] shows a similar trend in the low energy region for both C 1s and O 1s photoionizations. However, the ratio measured as ~0.61 at ~40 eV for C 1s photoionization in [2] seems to be still increasing to the sudden limit. For O 1s photoionization, although the intensity ratio was ~0.26 at ~20 eV [2], the ratio in the energy region of 20–50 eV is still fluctuating in the present observation.

Let us consider that the vibrational structure is independent of the kinetic energy above 80 eV. The intensity ratios in the sudden limit directly reflect the ratios of the Franck–Condon factors. Then one can obtain the information about the potential curves of the core-ionized states.

We extracted the spectroscopic parameters of the core-ionized state from the photoelectron spectra in the sudden limit, assuming that the line-shape of each vibrational component can be described by a convolution of a Gaussian profile with a PCI-distorted line profile and that the intensity distribution among these components is given by the Franck–Condon factors between the ground and core-ionized states. We then performed a least-squares fit [28] to the spectrum, taking as adjustable parameters the Gaussian width W (representing the photon bandwidth), the Lorentzian width Γ (representing the natural lifetime width), the level of a constant background and the energy and height of the first peak in the progression. The positions and heights of all other peaks in the progression are determined by the potential energy curves and nuclear wavefunctions of the ground and core-excited states. The accurately known literature values of the Morse parameters, – vibrational frequency $\omega_e = 2169.8\ \mathrm{cm}^{-1}$, anharmonicity $\omega_e x_e = 13.3\ \mathrm{cm}^{-1}$ and equilibrium distance $r_e = 1.1282$ Å – were used for the ground state [29], whereas for the core-ionized state, ω_e, $\omega_e x_e$ and the difference of

the equilibrium distances in the ground and core-ionized states, Δr_e, were treated as free parameters. Thus, the number of free parameters required to model the entire experimental spectrum is reduced to eight. The decomposition based on the present potential model describes the spectrum as good as the fit in Fig. 1; there are no statistically significant discrepancies.

The averaged values of the individual spectroscopic constants extracted from the fit to several different photoelectron spectra are summarized in Table 1. The results for C $1s^{-1}$ are compared with the values extracted from the lower-energy photoelectron spectra by Kempgens et al. [7], Kugeler et al. [12] and Carroll et al. [8]. The agreements are reasonable. The present experimental spectroscopic constants and the intensity ratios at the sudden limit ~80 eV can be reasonably compared with the theoretical values derived from the potential energy curves.

We calculated the potential energy curves of the ground and both C 1s and O 1s ionized states and performed the vibrational analysis. The calculated spectroscopic constants of the ground state, $\omega_e = 2176\ \mathrm{cm}^{-1}$ and $r_e = 1.126$ Å, are in excellent agreement with well-known experimental values $\omega_e = 2169.8\ \mathrm{cm}^{-1}$ and $r_e = 1.1282$ 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 C 1s ionized state by Thiel et al. [10] by means of ADC(4). The geometry relaxations Δr_e estimated by the exact core–hole SCF calculations [9] are also given in Table 1. The agreements among the theories are reasonable. Detailed comparisons between the experiments and theories, however, reveal that the present experiments and present SAC-CI calculations agree better than other combinations briefly described below.

In the C 1s ionized state, the calculated CO bond length decreases by $\Delta R = -0.051$ Å from that of the ground state, exhibiting very good agreement with the experimental estimate of $\Delta R = -0.0514(4)$ Å. The shrink of the bond length is explained by the shrink of the electron distribution over the molecule and results in larger vibrational frequency than that of the ground state. The calculated frequency $\omega_e = 2444\ \mathrm{cm}^{-1}$ and anharmonicity $\omega_e x_e = 25\ \mathrm{cm}^{-1}$ are in reasonable agreement with the measurement ones $\omega_e = 2479(6)\ \mathrm{cm}^{-1}$ and $\omega_e x_e = 23(4)\ \mathrm{cm}^{-1}$. These theoretical values can be well compared with the experimental values derived from the sudden limit.

On the other hand, the CO bond length in the O 1s ionized state is predicted to be longer by +0.028 Å than that in the ground state and this prediction is fair agreement with the experimental estimate of $\Delta R = +0.037(2)$ Å. This elongation sharply contrasts to the shrink of the CO bond by the C 1s ionization. This can be explained by the redistribution of the electron density in which the electrons surrounding the C atom relax to the direction of the O atom and thus, in the longer bond length, the oxygen core–hole is better shielded [2,9]. The elongation of the CO bond causes a decrease of the vibrational frequency of the O 1s ionized state compared to that of the ground state. The calculated frequency $\omega_e = 1928\ \mathrm{cm}^{-1}$ and anharmonicity $\omega_e x_e = 9\ \mathrm{cm}^{-1}$ are in reasonable agreement with the measured ones $\omega_e = 1864(32)\ \mathrm{cm}^{-1}$ and $\omega_e x_e = 7(5)\ \mathrm{cm}^{-1}$, respectively.

The Franck–Condon factors (FCF) between the ground and core-ionized states are also calculated from the vibrational wavefunctions. For the C 1s ionized state, the calculated FCF ratios are 0.626, 0.133 and 0.012 for 0–1, 0–2, and 0–3 transitions, respectively, relative to the 0–0 transition. These values are in good agreement with the experimental values of 0.640(10), 0.161(3), and 0.019(5). The very reasonable agreement illustrates that the calculated potential curve of the C 1s ionized state is reliable. The FCF ratios calculated for the O 1s ionized states are 0.160 and 0.015 for 0–1 and 0–2 transitions, respectively, while the measured ones are 0.248(5) and 0.030(6), respectively. The agreement is not satisfactory. This suggests that the description of orbital relaxation of O 1s ionization is less accurate than that of C 1s ionization in the present cal-

Table 1
Spectroscopic constants and intensity ratios of the C 1s ionized and O 1s ionized states of CO

Spectroscopic constant	Experimental				Theoretical		
	Expt. 1 [7]	Expt. 2 [2]	Expt. 3 [8]	Present	SCF [9]	ADC(4) [10]	SAC-CI
C $1s^{-1}$							
ω_e (cm^{-1})	2420(33)	2457(18)	2452(8)	2479(6)		2437	2444
$\omega_e x_e$ (cm^{-1})		10(7)	10.5(3.0)	23(4)			25
ΔR_e (Å)	−0.049(2)	−0.0493(4)	−0.0485(5)	−0.0514(4)	−0.0631	−0.044	−0.051
$I(v=1)/I(v=0)$	0.61	0.607(6)	0.60	0.640 (10)		0.521	0.626
$I(v=2)/I(v=0)$	0.14	0.135(3)	0.14	0.161 (3)		0.101	0.133
$I(v=3)/I(v=0)$	0.02	0.011(2)	0.014	0.019 (5)		0.009	0.012
O $1s^{-1}$							
ω_e (cm^{-1})	1823(34)	1887(24)		1864(32)			1928
$\omega_e x_e$ (cm^{-1})				7(5)			9
ΔR_e (Å)	0.039(4)	0.0339(6)		0.037(2)	0.0372		0.028
$I(v=1)/I(v=0)$	0.30	0.259(8)		0.248 (5)			0.160
$I(v=2)/I(v=0)$	0.06	0.040(5)		0.030 (6)			0.015

ΔR_e is the difference of the bond lengths between the neutral and ionic species.

culation. Since the higher R-operators describe orbital relaxation as well as electron correlation in the present method, the description of deeper core-ionized state is more difficult. The details of the potential energy curve and FCF are sensitive to the accuracy of describing orbital relaxation, which was seen in the present results of C 1s and O 1s ionizations.

In conclusion, we have measured C and O 1s photoelectron spectra of carbon monoxide in the photon energy range between 300 and 440 eV and between 550 and 702 eV, respectively, at the unprecedented resolution, and found that the intensity ratios of the vibrational components vary slowly, approaching the sudden limit at ~80 eV above the thresholds. Usually, it is tacitly assumed that the vibrational structure is independent of the photon energy 40 eV above the ionization threshold. The present observations illustrate that this is not always the case. Approximating the potential curves of the core-ionized states by the Morse-potential function and performing the fit of the FC factors to the observed spectra at the sudden limit, the spectroscopic parameters for C 1s and O 1s ionized states are extracted. The parameters thus obtained are in excellent (reasonable) agreement for C (O) 1s ionized state with the ab initio calculations based on the SAC-CI method. Examinations of the intensity ratio for other molecules are now in progress and we will summarize these results in a future publication.

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