

Vibrational effects on the shape resonance energy in the K -shell photoionization spectra of COD. A. Mistrov,¹ A. De Fanis,² M. Kitajima,³ M. Hoshino,³ H. Shindo,³ T. Tanaka,³ Y. Tamenori,² H. Tanaka,³
A. A. Pavlychev,^{1,4} and K. Ueda^{4,*}¹*Institute of Physics, St. Petersburg State University, 198504 St. Petersburg, Russia*²*Japan Synchrotron Radiation Research Institute, Sayo-gun, Hyogo 679-5198, Japan*³*Department of Physics, Sophia University, Tokyo 102-8554, Japan*⁴*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan*

(Received 10 April 2003; published 28 August 2003)

O $1s$ single-hole ionization cross sections of CO have been measured for $v' = 0 - 2$. The O $1s^{-1}\sigma^*$ shape resonance moves up in energy with an increase in v' , opposite to the C $1s^{-1}\sigma^*$ shape resonance observed previously. Theoretical calculations beyond the fixed-nuclei approximation reproduce these experimental results. The relationship between the v' -dependent characteristic internuclear distance in the residual ion and the shape resonance energy is discussed.

DOI: 10.1103/PhysRevA.68.022508

PACS number(s): 33.60.Fy, 33.15.Bh, 33.20.Rm, 33.20.Wr

I. INTRODUCTION

Shape resonances, often described as a temporal trapping of the photoelectron by the molecular potential box, are the most intriguing features in molecular photoionization [1]. Recent progress of the soft x-ray monochromators invoked renewal of interest in the shape resonance phenomena in core-level photoemission and indeed vibrationally resolved core-level photoelectron spectroscopy studies of small molecules revealed complex nuclear dynamics at the shape resonance (see, for example Ref. [2]). A typical example can be seen in the carbon monoxide molecule CO [3,4]. Köpfe *et al.* [3] found that the broad C $1s^{-1}\sigma^*$ shape resonance, which appears at $h\nu \sim 305$ eV in the photoabsorption spectrum, is present also in the C $1s$ single-hole ionization (SHI) cross sections for the individual vibrational components v' , but the energy of the shape resonance varies anomalously from ~ 307 eV for $v' = 0$ to ~ 302 eV for $v' = 3$.

Previously, Dehmer and co-workers [1] predicted, for diatomic molecules, that the energy of the shape resonance is dependent on the vibrational states of the residual ion core. The reason is as follows. The SHI cross sections for the individual vibrational states of the molecular ion can be expressed, within the independent-particle and Born-Oppenheimer approximations, as

$$\sigma_{iv'}^+(E) \sim \left| \int X_{iv'}^*(R) D_E(R) X_0(R) dR \right|^2, \quad (1)$$

where E is the kinetic energy of the photoelectron and X_0 and $X_{iv'}$ are the wave functions of the nuclear motion in the ground ($v = 0$) and ionic (iv') states, respectively. The electronic transition dipole moment D_E is given by

$$D_E(R) = \int \psi_E^*(r, R) r \psi_{\text{core}}(r, R) dr, \quad (2)$$

where ψ_E and ψ_{core} are the electronic wave functions of the photoelectron and the core electron, respectively. The photoelectron wave function ψ_E in the shape resonance region varies significantly when the nuclear distance R varies, and results in the dependence of the resonance energy on the internuclear distance R . The R dependence of the resonance energy is a natural consequence of the intramolecular interference, i.e., the interference of the photoelectron waves within the molecular potential box. It is clear from Eq. (1) that a different vibrational component v' samples a different range of the internuclear distances R within the Franck-Condon region where the zero-point vibrational motion is confined. As a result, $\sigma_{iv'}^+(E)$ for different v' exhibits a shape resonance at different energy. Although the prescription described above is rather straightforward, the dependence of the shape resonance energy on the final vibrational states have never been examined in the core-level photoemission. Indeed most of the elaborated theories published so far use the fixed-nuclei approximation (see, for example, [5,6]).

In the present work, we investigate the relationship between the shape resonance in the core-level photoemission and the vibrational excitation in the residual ion core. For that purpose, we first describe new measurements for the cross sections $\sigma_{01sv'}^+(E)$ of the individual vibrational components in the O $1s$ photoelectron mainline of CO. This measurement confirms an important role of the vibrational excitations in the spectral dependence of molecular photoionization and reveals new site-selective properties of the vibrational effect on the σ^* shape resonance. To rationalize this effect, the intramolecular interference is examined beyond the fixed-nuclei approximation. Strong dependence of the shape resonance energy on the internuclear distance found through the present work casts some doubts on the use of the conventional fixed-nuclei approximation in the description of the shape resonance phenomena.

II. EXPERIMENT AND RESULTS

The experiment was carried out on the C branch of the soft x-ray photochemistry beam line 27SU [7,8] at SPring-8,

*Email address: ueda@tagen.tohoku.ac.jp

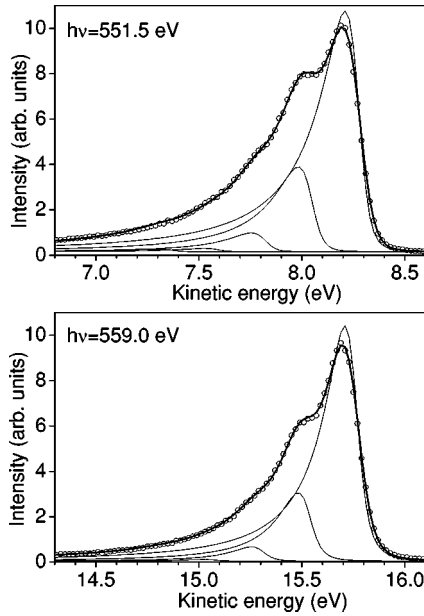


FIG. 1. Angle-integrated O $1s$ photoemission spectra of CO recorded at 551.5 eV (at the peak of the shape resonance) and 559 eV (above the shape resonance). The thick lines represent the least χ^2 fits, whereas the thin lines are the individual components.

the 8-GeV synchrotron radiation facility in Japan. The radiation source is a figure-8 undulator, whose emitted radiation is linearly polarized either in the horizontal plane of the storage ring (1st order) or in the vertical plane perpendicular to it (0.5th order) [9]. The degree of linear polarization was measured by observing Ne $2s$ and $2p$ photoline and confirmed to be larger than 0.98 with the present setting of optics. In the analysis, we thus assume the complete polarization. Angle-resolved electron emission measurements were performed only by changing the undulator gap, without rotations of the electron analyzer. The electron spectroscopy apparatus consists of a hemispherical electron analyzer (Gammadata-Scienta SES-2002), a gas cell, and a differentially pumped chamber [10]. The transmission function of the analyzer was measured by observing the Ar $2p$ line at kinetic energies concerned.

The O $1s$ photoelectron spectra are recorded at photon energies across the σ^* shape resonance region. Figure 1 shows an example of the spectra, where the spectra are presented in the angle-integrated form, $I = I(0) + 2 \times I(90)$ with $I(0)$ and $I(90)$ being spectra recorded for parallel and perpendicular polarizations. The spectra exhibit a vibrational progression with the separation of $\omega_e = 226$ meV [4]. To extract the intensity of each vibrational component, we carry out the least χ^2 fit to all the recorded spectra similar to the ones in Fig. 1, describing each vibrational component as a convolution between a profile distorted by the post-collision interaction [11], with the lifetime width of ~ 165 meV [4], and the measured Gaussian profile corresponding to the experimental resolution, with the width of ~ 80 meV. The fitted functions are also included in Fig. 1. The O $1s$ SHI cross sections thus extracted for the individual vibrational components $v' = 0, 1$, and 2 are plotted in Fig. 2(a). The energy of

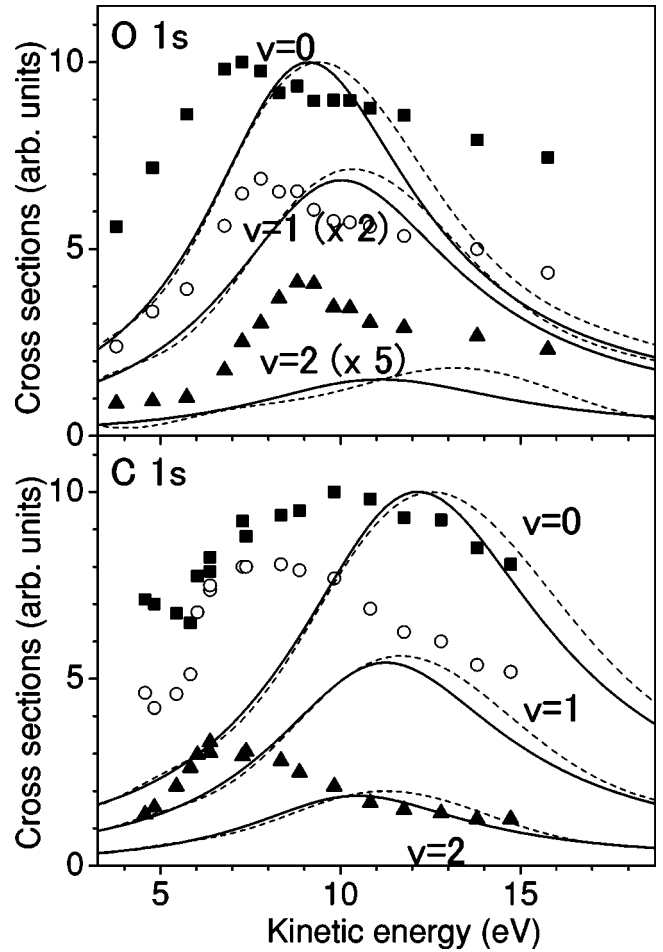


FIG. 2. Single-hole ionization cross sections σ_{iv}^+ , for the vibrational components $v' = 0, 1$, and 2 , for (a) present measurement and calculation for $i = \text{O } 1s$, (b) measurement by Köppe *et al.* [3] and present calculation for $i = \text{C } 1s$. The cross sections computed beyond the fixed-nuclei approximation [Eq. (9)] and within the v' -dependent fixed-nuclei approximation [Eq. (17)] are shown with the solid and dotted lines, respectively.

the O $1s^{-1}\sigma^*$ shape resonance increases with an increase in v' . The C $1s$ SHI cross sections $\sigma_{\text{C}1s v'}^+$ for $v' = 0, 1$, and 2 measured by Köppe *et al.* are included in Fig. 2(b) for comparison. We find that the shape resonance energy exhibits the opposite v' dependence for the C $1s$ and O $1s$ SHI cross sections.

III. THEORY AND DISCUSSION

To understand the site selectivity of the σ^* shape resonance, we pay our attention to the influence of the vibrational excitations accompanying the K -shell photoionization on the intramolecular interference. For that purpose, Eq. (1) is rewritten by exchanging the order of integration for dr and dR :

$$\sigma_{iv\Gamma}^+(E) \sim \left| \int \psi_{iv\Gamma}^*(E, r) r \psi_{\text{core}}(r) dr \right|^2, \quad (3)$$

where

$$\psi_{iv'\Gamma} = \int X_0^*(R) \psi_{E\Gamma}(r, R) X_{iv'}(R) dR \quad (4)$$

describes the primary photoelectron leaving the residual ion core in the vibrational state v' and Γ labels the irreducible representation of the symmetry group for the continuum state consisting of a residual ion core and a photoelectron ($\Gamma = \Sigma$ or Π). The function $\psi_{iv'\Gamma}$ is a superposition of the partial waves $\phi_{i\ell\Gamma}^\pm$ outgoing from and incoming to the core-ionized atom:

$$\begin{aligned} \psi_{iv'\Gamma} = & \sum_{\ell} C_{i\ell\Gamma}^+(E, v') \phi_{i\ell\Gamma}^+(E, r) \\ & + \sum_{\ell} C_{i\ell\Gamma}^-(E, v') \phi_{i\ell\Gamma}^-(E, r). \end{aligned} \quad (5)$$

Here the coefficients $C_{i\ell\Gamma}^\pm(E, v')$ can be written as

$$C_{i\ell\Gamma}^\pm(E, v') = \sum_{\mu \geq 0} S^\mu \Theta_{i\ell\Gamma}^{(\mu+\alpha)}(E, v'), \quad (6)$$

where

$$\Theta_{i\ell\Gamma}^{(\mu+\alpha)} = \int X_{iv'}^*(R) B_{i\ell\Gamma}^{\mu+\alpha} X_0(R) dR, \quad (7)$$

S and B are the scattering and reflection matrices, μ designates multiplicity of the scattering, and α is 0 for $C_{i\ell\Gamma}^+$ and 1 for $C_{i\ell\Gamma}^-$. The elements of the reflection matrix,

$$B_{i\ell\Gamma}(R) = |B_{i\ell\Gamma}(R)| e^{i[2kR + \varphi_{i\ell\Gamma}(R)]}, \quad (8)$$

describe the $1s$ -photoelectron waves backscattered by the neighboring atom and can be obtained by solving the variable phase equation [12,13]. Examining the flux of the photoelectrons through the sphere surrounding the core-ionized molecule, the SHI cross section is expressed as

$$\sigma_{iv'\Gamma}^+ = \sigma_i^+ M_{i\Gamma}(E, v'), \quad (9)$$

where σ_i^+ is the atomic cross section and

$$M_{i\Gamma} = \sum_{\ell} [|C_{i\ell\Gamma}^+(E, v')|^2 - |C_{i\ell\Gamma}^-(E, v')|^2] \quad (10)$$

describes the intramolecular interference beyond the fixed-nuclei approximation. Because the function $M_{i\Gamma}$ depends on v' , the SHI cross section for each vibrational channel exhibits a different spectral behavior. To simplify our study on the vibrational effects, we adopted an independent particle description of the SHI cross sections. Besides, we neglected the coupling between the photoelectron and vibrations of the residual ion core, which could be significant for the low-energy photoelectron scattering.

To demonstrate the vibrational effect on the shape resonance energy, the $\sigma_{iv'\Gamma}^+(E)$ cross sections of CO are computed using Eq. (9) for different v' components above the C and O $1s$ thresholds. In the calculations, harmonic-oscillator wave functions are used for the functions $X_{iv'}$ and X_0 . The

equilibrium internuclear distances for the neutral ground, O and C $1s$ ionized states, $R_0 = 1.128 \text{ \AA}$, $R_{O1s}^+ = 1.167 \text{ \AA}$, and $R_{C1s}^+ = 1.079 \text{ \AA}$, and the vibrational spacings $\omega_0 = 269 \text{ meV}$, $\omega_{C1s} = 302 \text{ meV}$, and $\omega_{O1s} = 226 \text{ meV}$ are taken from Ref. [4]. The cross sections are calculated only for the $\Sigma \rightarrow \Sigma$ transition where the σ^* shape resonance appears. $B_{i\ell\Gamma}(R)$ of Eq. (8) is determined within the quasi-atomic model [12,13]. We take a summation over μ in Eq. (6) up to $\mu_{\max} = 7$ as it is found that the terms with higher μ do not contribute noticeably to the result of the calculation.

The cross sections $\sigma_{O1sv'\Sigma}^+$ and $\sigma_{C1sv'\Sigma}^+$ thus calculated for $v' = 0, 1$, and 2 are plotted by solid lines in Figs. 2(a) and 2(b), respectively. The results of the calculations show that the spectral behavior of the cross sections strongly depends on the final vibrational state, illustrating that the intramolecular interference is significantly influenced by the vibrational excitation of the residual ion core. The calculations reproduce well the observed upward and downward energy shifts, with an increase in v' , of the σ^* shape resonance above the O $1s$ and C $1s$ thresholds, respectively.

To rationalize the vibrational effect on the shape resonance energy in more detail, we analyze the linkage between the intramolecular interference and the nuclear distance R in CO. We notice that both $|B_{i\ell\Gamma}|$ and $\varphi_{i\ell\Gamma}$ vary only slightly with R within the zero-point vibrational motion. Neglecting this minor variation leads to

$$\Theta_{i\ell\Sigma}^{(\mu+\alpha)}(v') \simeq B_{i\ell\Sigma}^{(\mu+\alpha)}(R_i^+) \int X_{iv'}^* e^{i2(\mu+\alpha)ku} X_0 du, \quad (11)$$

where u is the displacement of the nuclear separation from the equilibrium distance R_i^+ of the ionic state i (O $1s$ or C $1s$). Expanding $e^{i2\mu ku}$ for small displacements, we have

$$\Theta_{i\ell\Sigma}^{(\mu+\alpha)} \simeq F_{0v'}^{\mu+\alpha} B_{i\ell\Sigma}^{\mu+\alpha}(R_i^+) e^{2i(\mu+\alpha)ku_i(v')}, \quad (12)$$

where

$$F_{0v'} = \int X_{iv'}^*(R) X_0(R) dR \quad (13)$$

and the effective displacement $u_i(v')$ is defined as

$$u_i(v') \equiv F_{0v'}^{-1} \int X_{iv'}^*(u) u X_0(u - \Delta_i) du, \quad (14)$$

with

$$\Delta_i = R_0 - R_i^+ \quad (15)$$

being the difference in the equilibrium distance between the neutral ground and ionic states. Comparison between Eqs. (7) and (8) and (11)–(14) leads to $B_{i\ell\Sigma}(R) \simeq B_{i\ell\Sigma}(R_i^+(v'))$ within the zero-point vibrational motion. Hence we can describe the vibrational effect on the SHI cross section by introducing the v' -dependent fixed nuclear distance:

$$R_i(v') = R_i^+ + u_i(v'). \quad (16)$$

Within this v' -dependent fixed-nuclei approximation, the $\sigma_{iv'\Sigma}^+$ cross section of Eq. (9) can be rewritten as

$$\sigma_{iv'\Sigma}^+ \approx \sigma_i^+ |F_{0v'}|^2 \operatorname{Re} \left(\frac{1 + B_{iv'} S}{1 - B_{iv'} S} \right)_{\ell=1 \ell=1\Sigma}, \quad (17)$$

where $|F_{0v'}|^2$ is the Franck-Condon factor and the elements of $B_{iv'}$ are determined within the v' -dependent fixed-nuclei approximation. The SHI cross sections thus calculated and plotted by dotted lines in Figs. 2 (a) and 2(b) are in good agreement with the ones obtained beyond the fixed-nuclei approximation (solid lines).

According to Eq. (14) for the O $1s$ photoionization, the displacements $u_{O1s}(v')$ from the equilibrium value R_{O1s}^+ are -0.020 , -0.074 , and -0.109 Å for $v'=0, 1$, and 2 , respectively. These numbers clearly indicate that the O $1s$ photoelectron is trapped by the compressed ion and that the compression increases with an increase in v' . An opposite situation is observed for the C $1s$ photoionization. The computed displacements $u_{C1s}(v')$ are $+0.025$, $+0.068$, and $+0.111$ Å for $v'=0, 1$, and 2 , respectively. These values show that the C $1s$ photoelectron is trapped by the elongated ion and that the elongation increases with an increase in v' .

Once we establish the relationship between the vibrational excitation of the residual ion core and the characteristic internuclear distance $R_i^+(v')$, it is straightforward to understand the v' dependence of the σ^* shape resonance energy. From the quasiatomic view [13], the energy of the σ^* shape resonance decreases and the energy of the π^* resonance increases, toward the atomic O (or C) $1s^{-1}2p$ resonance, with increasing R . Hence the compression (elongation) of $R_i^+(v')$ results in the upward (downward) energy shift of the σ^* shape resonance. This explains why the O $1s^{-1}\sigma^*$ shape resonance energy increases, while the C $1s^{-1}\sigma^*$ shape resonance energy decreases, with an increase in v' .

Within the approximations used here, the condition for the SHI cross section to take the maximum, $dM_{\Sigma}/dE=0$, at the shape resonance energy leads to

$$E_0 - E_{v'} \approx \frac{2E_0 \Delta u_i(v')}{R_i^+}, \quad (18)$$

where E_0 and $E_{v'}$ are kinetic energies of the $v'=0$ and $v' \neq 0$ components of the main photoline. Equation (18) shows that the energy shift $E_0 - E_{v'}$ is directly related to the change of the effective displacement

$$\Delta u_i(v') = u_i(0) - u_i(v'). \quad (19)$$

The compression $\Delta u_{O1s} < 0$ and elongation $\Delta u_{C1s} > 0$ result in upward and downward shifts of the σ^* shape resonance, respectively.

In the present analysis, multielectron effects were neglected. In the experimental SHI cross sections, characteristic structures appear at 8.3 eV and 5.8 eV for $\sigma_{O1sv'=0}^+$ and $\sigma_{C1sv'=0}^+$, respectively, illustrating multielectron effects [14].

IV. CONCLUDING REMARK

We have measured the vibrationally resolved O $1s$ SHI cross section of CO in the region of the σ^* shape resonance and found that the resonance energy moves up from 7 eV for $v'=0$ to 9 eV for $v'=2$. This shift is in the direction opposite to that observed previously for the C $1s^{-1}\sigma^*$ shape resonance in CO. Our theoretical analysis has shown that these site-selective v' dependencies stem from the compression (or elongation) of the characteristic internuclear distance in the O (or C) $1s$ -ionized molecule that traps the photoelectron. The characteristic internuclear distance $R_i(v')$ varies significantly with v' . These findings cast some doubts on the use of the conventional (v' -independent) fixed-nuclei approximation in the description of the shape resonance phenomena in the molecular core-level photoionization.

ACKNOWLEDGMENTS

This experiment was carried out with the approval of the SPring-8 program advisory committee and supported in part by Grants-in-Aid for Scientific Research from the Japan Society for the Promotion of Science. A.A.P. appreciates the hospitality of Tohoku University and the financial support for his stay there. We are also grateful to the staff of SPring-8 for excellent operations of the ring.

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