Dynamic Properties of N and O $1s^{-1}\sigma_u^*$ Shape Resonances in N_2 and CO_2 Molecules

A. A. Pavlychev,[1] N. G. Fominykh,[1] N. Watanabe,[2,*] K. Soejima,[2,†] E. Shigemasa,[2] and A. Yagishita[2]

[1]*Institute of Physics, St. Petersburg University, St. Petersburg, 198904 Russian Federation*

[2]*Photon Factory, Institute of Materials Structure Science (KEK), Oho 1-1, Tsukuba, Ibaraki 305, Japan*

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An essential correlation between intramolecular interference of photoelectron waves and core-hole molecular relaxation is revealed by analyzing the partial wave composition of the calculated angular distribution of photoelectrons in the N and O $1s^{-1}\sigma_u^*$ shape resonances of aligned N_2 and CO_2. The dominance of coherent (N_2) and incoherent (CO_2) interference is revealed. pf and spd hybridization controls the main direction of photoelectron emission from the N and O K shell, respectively. [S0031-9007(98)07498-5]

K-shell excitations in N_2 and CO_2 molecules are of particular interest as prototypes of resonance phenomena in x-ray absorption and ionization of polyatomic systems. Intramolecular interference between emitted and multiply scattered photoelectron waves results in resonance features above the K edges. These features, which are observed in the σ channel [1–5], are regarded as either being associated with temporary trapping of ejected electrons by the molecular potential [1,6] or with promotion of core electrons into σ molecular orbitals (MO's) embedded in the K-shell continuum [7]. These quasistationary states can be assigned to the dipole allowed $1\sigma_{g,u} \rightarrow \varepsilon\sigma_{u,g}$ transitions to the virtual MO's belonging to the irreducible representations of the $D_{\infty h}$ point group [5,8]. On the other hand, in the quasiatomic model the shape resonances can be assigned to $1s \rightarrow \varepsilon\sigma$ transitions where the final state belongs to the irreducible representations of the $C_{\infty v}$ point group [9,10]. In this case the terminal atoms in the excited molecules are no longer equivalent and the inversion symmetry is broken due to dynamic localization of the core hole.

The analysis of angular distributions of photoelectrons (ADP), arising from resonance states in molecules aligned parallel to the electric vector of the incident light, is a promising candidate for studies of their symmetry features. If the inversion symmetry is broken, the odd and even harmonics are involved in the creation of the shape resonance resulting in asymmetry in the photoelectron ejection. An average over a molecular ensemble restores the equivalence of the θ and $\pi - \theta$ directions in the photoelectron current, but differences in its partial-wave composition will persist. To examine this, here we refer to the results of our previous works [2–4]. We used in Refs. [2–4] the ADP expansion derived by Dill [11]

$$d\sigma/d\boldsymbol{k} = \sum_{K=0}^{2l_{max}} A_K P_K(\cos\theta), \qquad (1)$$

where $\boldsymbol{k} = \{\theta, 0\}$ is the photoelectron ejection direction measured in the molecular frame, and P_K is a Legendre polynomial. Analysis of the experimental data shows

evidence of a significant contribution from the f harmonic to the signals at the σ_u^* resonance in N_2 and weaker contributions from other odd and even harmonics with $l \leq 5$ [2,3]. This decomposition supports the predictions of Dehmer and Dill [5] based on multiple-scattering method calculations in the framework of the $D_{\infty h}$ point group, although these calculations overestimated the f-wave contribution. In contrast to the N_2 case, the ADP decomposition for the σ_u^* resonance in CO_2 indicates a noticeable presence of both odd and even harmonics [4]. This difference can be seen in the expansion coefficients A_K for N_2 and CO_2, which are shown in Table I. The enhancement of the A_6 coefficient, which is associated with the $f\sigma$ partial wave, for the photoelectron current at 419 eV ($3\sigma_u^*$) can be clearly seen, whereas at 559 eV ($4\sigma_u^*$) the A_2 dominates the current and A_6 retains rather small. This different composition is caused primarily by the intense photoelectron current along the directions lying close to $\theta = \pi n \pm \pi/3$ ($n = 0, 1$), which can be seen clearly in the experimental ADP at 419 eV for N_2 [2,3] [Fig. 1(a)]. These directions are not pronounced for the current at 559 eV for CO_2 [4], which is directed mainly along $\theta = 0$ and π [Fig. 1(c)]. Quasiatomic calculations, carried out on the assumption that the total photoelectron flux is built up from two independent fluxes outgoing from the left and right oxygen atoms of CO_2, provide reasonable agreement with the experimental data [4]. The calculations point out the intense hybridization of the continuum s-, p-, and d-partial waves of the core-excited atom at the $5\sigma_g^*$ and $4\sigma_u^*$ resonances in CO_2. The degree of hybridization varies monotonously with photoelectron kinetic energies and is $s(31\%)$ $p(50\%)$ $d(19\%)$ at 559 eV ($4\sigma_u^*$).

The equivalence of atomic sites in a polyatomic system implies their equal probability of excitation (the value averaged over time) but not simultaneous core excitation. This means that one-photon absorption of the quasidegenerate K-shell levels occurs in one of the equivalent atoms in a molecule, and the relevant molecular photoelectron wave function Ψ should be presented as a symmetry-adapted linear combination of atomic wave functions ϕ_l

TABLE I. Expansion coefficients A_k of Eq. (1) (A_0 is normalized to unity), which are taken from Refs. [3,4].

$\hbar\omega$ (eV)		A_0	A_2	A_4	A_6	A_8	A_{10}
419	$3\sigma_u^*(N_2)$	1.0	0.26	−0.30	0.96	0.10	0.02
559	$4\sigma_u^*(CO_2)$	1.0	1.14	−0.18	−0.16	0.03	0.01

and ϕ_r, which describe photoelectrons emitted from left and right atoms in a molecule, respectively. To take this dynamic localization into account, we assume a different time dependence for the atomic wave functions in this superposition:

$$\Psi(t) = \phi_l(t - t_1) \pm \phi_r(t - t_2). \tag{2}$$

Because t_1 and t_2 are essentially different $|t_1 - t_2| \gg T$, where T is a time characterizing the interaction of photoelectrons with the anisotropic molecular potential), interference of the ϕ_l and ϕ_r waves becomes so insignificant that the parity of core-excited molecules disappears and the signs in Eq. (2) do not play any role in the photoelectron flux. This means that it is composed from two independent currents outgoing from both equivalent atoms: $d\sigma^{\mathrm{in}}/d\mathbf{k} \sim |\phi_l|^2 + |\phi_r|^2$. This particular formulation

FIG. 1. ADP at the $1s^{-1}\sigma_u^*$ resonance in N_2 (a), and above it (447 eV) (b), and at the $1s^{-1}\sigma_u^*$ resonance in CO_2 (c), and above it (579 eV) (d). Molecules are aligned along the $0°–180°$ axis. Filled circles: experimental points; thin solid line: their fitting of Eq. (1); dash-dotted line: $d\sigma^{\mathrm{in}}/d\mathbf{k}$; dashed line: $d\sigma/d\mathbf{k}$ [Eq. (5) with $D = 0.76$ for N_2 and $D = 0.30$ for CO_2]. The curves are normalized at $\theta = 0°$. ADP from right O atom of CO_2 ($0°$ direction) is also indicated by a bold solid line. Experimental data and fitting curves are taken from Refs. [2–4].

of ADP was successfully applied in Ref. [4]. Presuming that the average over an ensemble of molecules in the gas phase is equivalent to the average over time, one can assign the ϕ_l and ϕ_r functions to incoherent waves [12] emitted from different molecules.

A quasistationary description supposes that equivalent atoms must be treated as equivalent sources of electron waves, and the relevant MO-like photoelectron wave function is given by Eq. (2) with $t_1 = t_2$. The emission occurs simultaneously in both terminal atoms in a molecule with equal probability, and the process is described as being quasistationary. Since both left and right sources are located in the same molecule, the ϕ_l and ϕ_r waves are coherent and give $d\sigma^{\mathrm{co}}/d\mathbf{k} \sim |\phi_l \pm \phi_r|^2$. The interference term $\eta_0 = \pm 2\,\mathrm{Re}\,\phi_l^*\phi_r$ makes the difference between the g and u states.

A question now arises: Are equivalent atoms in a molecule coherent or incoherent sources of photoelectron waves? From our ADP analysis it follows that at the σ_u^* shape resonance they behave coherently in N_2 and incoherently in CO_2. To understand the difference we introduce another time (τ) dependence associated with core-hole molecular relaxation. The ADP then depends on the correlation between times T and τ; core-hole electronic relaxation τ_e and atomic rearrangement τ_a. These characteristic times ($t_1 - t_2, T, \tau$) are shown schematically in Fig. 2. Let us take the relaxation into account and consider the channels of $1s$-photoelectron emission from equivalent atoms in the molecules. For CO_2,

$$\hbar\omega + CO_2 \rightarrow$$

$$O_{1s}^*CO \rightarrow \begin{cases} (CO_2)^{+2} + e_{\mathrm{ph}} + e_A \cdots (channel\ 1) \\ (OCO)^{+2} + e_{\mathrm{ph}} + e_A \cdots (channel\ 2). \end{cases}$$

In addition, the corresponding equation for the equally probable reaction $\hbar\omega + CO_2 \rightarrow OCO_{1s}^*$ should be considered. Similar equations can be written for N_2. Postcollision interaction between the photoelectrons (e_{ph}) and the subsequently emitted Auger-electrons (e_A) is ignored here. The reaction serves to demonstrate the interaction between the photoelectron and the residual molecular ions with different symmetries. The ion possessing the $D_{\infty h}$ point group is denoted $(CO_2)^{+2}$ and the $C_{\infty v}$ group as $(OCO)^{+2}$.

In the limit of short interaction time ($T \ll \tau_e$ and $T \ll \tau_a$), the photoelectron leaves the ion mainly with initially ionized $1s^{-1}$ state for which the effective potential possesses $C_{\infty v}$ symmetry. During this short period the

FIG. 2. Correlation of photoelectron emission from a core-excited homonuclear molecule with its relaxation. Photoabsorption occurs in one of the constituent atoms at t_1 and t_2. T is an interaction time of photoelectrons with the molecular potential. τ is a core-hole relaxation time. Outgoing photoelectrons are shown by arrows with inclusion of multiple scattering.

terminal atoms in the core-ionized molecule are not equivalent. But if $T \gg \tau_e$ the photoelectron moves mostly in the potential of molecular ion with delocalized valence vacancies and its point group is restored to $D_{\infty h}$. In this case the electronic decay gives rise to the photoelectron current in *channel 1*. The molecular ion rearrangement with asymmetric motion of atoms reduces the initial molecular geometry. If the motion starts simultaneously with the creation of core hole, it keeps the broken inversion symmetry and gives rise to the current in *channel 2*. The competition between T and τ controls the molecular core hole relaxation effect on photoelectron wave function, the symmetry of which in the field of the relaxing ion acquires a dynamic character and cannot be unambiguously assigned to a fixed point group. Then, both coherent ($D_{\infty h}$) and incoherent ($C_{\infty v}$) photoelectron fluxes reproduce only a part of the real ADP pattern. Which part dominates in the photoelectron emission depends on the dynamical properties of the excited states.

Channel 1 does not differ essentially for the case of N and O K-shell excitations (see, e.g., [13]). But *channel 2* leads to a major difference in the symmetries (core-hole localization) for these two cases. High-resolution measurements [14] have revealed that the O K-shell photoelectron line in CO_2 at 554 eV is dominated by the antisymmetric stretching mode with a frequency of 307 ± 3 meV. The antisymmetric mode in CO_2 appears simultaneously with O K-shell ionization and keeps the dynamic breaking of the inversion symmetry. The photoelectron current in *channel 2* in N_2 does not appear simultaneously with the core-hole creation as its generation needs charge separation and large elongation of the internuclear distance. We hence infer that antisymmetric vibrations in CO_2 provide a long-time violation of the inversion symmetry that leads to large τ ($\gg T$). In contrast to CO_2, in N_2 fast electronic decay leads to effective restoration of the inversion symmetry and to short τ ($<T$). On this basis, the correlation of photoelectron emission with molecular relaxation becomes important for the description of ADP.

To obtain the relation of photoelectron waves outgoing from terminal atoms in a molecule to its symmetry behavior, Eq. (2) can be rewritten by adding terms depend on τ,

$$\Psi(t) \sim \phi_l(t - t_1) \pm \phi_r(t - t_1 - \tau) + \phi_r(t - t_2) \pm \phi_l(t - t_2 - \tau). \quad (3)$$

The time evolution of the K-shell photoelectron emission is shown schematically in Fig. 2. Assuming, as before, that t_1 and t_2 are essentially different, we have

$$d\sigma/d\mathbf{k} \sim |\phi_l|^2 + |\phi_r|^2 \pm \eta(\tau). \quad (4)$$

The interference term $\eta = \langle \Sigma_{i=1,2} \, \mathrm{Re} \, \phi^*_l(t - t_i) \times \phi_r(t - t_i - \tau) \rangle$ (where $\langle \rangle$ denotes an average over time) depends on the relaxation, and its variation makes it possible to bring together the localized and delocalized ADP descriptions given by Eqs. (3) and (4) via $\eta(\tau) \to 0$ for $\tau \gg T$ and $\eta(\tau) \to \eta_0$ for $\tau \ll T$.

To calculate the ADP on the basis of Eq. (4), the quasiatomic $\phi_{l,r}(t)$ functions must take electronic decay and rearrangement into account. To simplify these time-dependent calculations, we approximate the distribution Eq. (4) by mixing the ADP's related to the different stationary configurations. With only *channels 1 and 2* as linear configurations, this results in $d\sigma^{in}/d\mathbf{k} \sim |\phi_l|^2 + |\phi_r|^2$ and $d\sigma^{co}/d\mathbf{k} \sim |\phi_l \pm \phi_r|^2$. These distributions can be computed with time-independent potentials and with the $\phi_l(\mathbf{k})$ and $\phi_r(\mathbf{k})$ functions expressed as $\Sigma_L C_{pL\sigma} e^{+i(kr - L\pi/2 + \gamma)} Y_{L\sigma}(\theta, \varphi)$ and $\Sigma_L C_{pL\sigma} e^{+i(kr - L\pi/2 + \gamma)} Y_{L\sigma}(\pi - \theta, \varphi)$ outgoing waves for $r \gg R_{mol}$, where R_{mol} is the radius of the molecular region and γ is a Coulomb phase shift. But the mixture of the ADP's depends on the competition between T and τ. To obtain their weights, let us define a branching ratio D pertaining to inversion symmetry in the photoemission reactions; $D \equiv \zeta_1/(\zeta_1 + \zeta_2)$ where ζ_j is the photoelectron current in the channel j. If $D \to 1$ the photoelectron wave function possesses inversion symmetry and the $d\sigma^{co}/d\mathbf{k}$ distribution describes its current independent on which terminal atom is ionized. If $D \to 0$ the ADP is determined by $d\sigma^{in}/d\mathbf{k}$. In the general case $0 < D < 1$, and the incoherent ("atomic") and coherent ("molecular") distributions are mixed,

$$d\sigma/d\mathbf{k} \approx D \, d\sigma^{co}/d\mathbf{k} + (1 - D) d\sigma^{in}/d\mathbf{k}. \quad (5)$$

These differential cross sections as a function of the parameter D are calculated for the σ^*_u shape resonances. The $C_{pL\sigma}(k)$ amplitudes of the $\phi_{l,r}(\mathbf{k})$ functions are obtained via a multiple scattering model, and are equal to $[\mathbf{T}(\mathbf{1} - \mathbf{BS})^{-1}]_{pL\sigma}$ [4,15] where $\mathbf{T}$ and $\mathbf{B}$ are the matrices for transmission and reflection from the surrounding potentials and $\mathbf{S}$ is the scattering matrix of the core-excited atom. The calculated results show a strong dependence of the ADP on D. As a consequence of an

increase in D the hybridization degree of odd atomic partial (L) waves is magnified and higher odd harmonics become involved in the composition of the photoelectron current. In particular, at the shape resonance the spd hybridization for $D \approx 0$ changes to the pf (or pfh) for $D \approx 1$. Comparison of the experimental and calculated polar plots demonstrates that the large D regime applies for the resonance at 419 eV (the best fit is observed for $D \approx 0.76$) and the small D regime ($D \approx 0.30$) for the resonance at 559 eV [Figs. 1(a) and 1(c)]. For comparison, the incoherent ($D = 0$) ADP patterns are shown, too. The different ADP decompositions (Table I) reflects the essentially different dynamic properties of these shape resonances which can be explained by mixing the incoherent and coherent signals. Their contributions to the experimental ADP make it possible to approximately interpret the shape resonances at 419 eV (N_2) and 559 eV (CO_2) as the ones belonging to the $D_{\infty h}$ and $C_{\infty v}$ point groups, respectively.

In CO_2, the asymmetric motion of the absorber and the opposite oxygen atom relative to the central atom does not allow the coherent intramolecular interference of photoelectron waves. This asymmetric vibration mode is excited via vibronic coupling [16]. Its frequency was predicted in agreement with the experimental value [14] by calculating a potential energy surface for the O $1s^{-1}$ hole molecular state [17]. Owing to the asymmetric motion, asymmetry in the absorber during T time leads to a symmetry breaking in the photoelectron moving. The calculated ADP for a core-excited right atom in CO_2 (i.e., without averaging over a molecular ensemble) clearly reveals this asymmetry [Fig. 1(c)]. In contrast to forward-backward asymmetry in the ADP of CO [18], this asymmetry is a dynamic effect. Dynamic dipole momentum of the O K-shell excited CO_2 molecule [4] allows the hybridization of odd and even partial waves, which gives rise to this asymmetry, and is responsible for the correlation of the spd hybridization with the asymmetric vibration in the O $1s$ photoelectron line. As the T time is shortened with increasing photoelectron velocity, the dynamic effect on ADP is expected to be weaker at higher $\hbar\omega$. The similarity of the experimental ADP's at 447 eV for N_2 [Fig. 1(b)] and at 579 eV for CO_2 [Fig. 1(d)] supports this conclusion.

In conclusion, the analysis of the partial-wave composition in the experimental and calculated ADP at the N and O $1s^{-1}\sigma_u^*$ shape resonances of N_2 and CO_2 shows evidence of an essential correlation between intramolecular interference of the photoelectron waves and molecular relaxation. The ADP description is based on the supposition that the inversion symmetry of the ground state is being broken simultaneously with photoexcitation. Electronic relaxation tends to restore the inversion symmetry, while asymmetric atomic motion tends to keep the broken symmetry. The dominance of the coherent intramolecular interference of pf-hybridized photoelectron waves in N_2 and of the incoherent interference of spd-hybridized waves in CO_2 is identified.

*Permanent address: The Institute of Low Temperature Science, Hokkaido University, Sapporo, Hokkaido 060, Japan.

†Permanent address: Graduate School of Science and Technology, Niigata University, 8050 Igarashi, Niigata 950-21, Japan.

[1] J. L. Dehmer, D. Dill, and A. C. Parr, *Photophysics and Photochemistry in the Vacuum Ultraviolet,* edited by S. McGlynn, G. Findly, and R. Huebner (D. Reidel Publishing Company, Dordrecht, 1985), p. 341.

[2] E. Shigemasa, J. Adachi, M. Oura, and A. Yagishita, Phys. Rev. Lett. **74**, 359 (1995).

[3] E. Shigemasa, J. Adachi, M. Oura, N. Watanabe, K. Soejima, and A. Yagishita, *Atomic and Molecular Photoionization,* edited by A. Yagishita and T. Sasaki (Universal Academy Press, Inc., Tokyo, 1996), p. 69.

[4] N. Watanabe, J. Adachi, K. Soejima, E. Shigemasa, A. Yagishita, N. G. Fominykh, and A. A. Pavlychev, Phys. Rev. Lett. **78**, 4910 (1997).

[5] J. L. Dehmer and D. Dill, J. Chem. Phys. **65**, 5327 (1976).

[6] V. I. Nefedov, J. Struct. Chim. (USSR) **11**, 292 (1970).

[7] F. A. Gianturco, M. Guidotti, and U. Lamanna, J. Chem. Phys. **57**, 840 (1972).

[8] N. Padial, G. Csanak, B. V. McKoy, and P. W. Langhoff, Phys. Rev. A **23**, 218 (1981).

[9] A. A. Pavlychev and A. S. Vinogradov, Opt. Spectrosc. (USSR) **65**, 329 (1987).

[10] A. A. Pavlychev, A. Barry, and A. S. Vinogradov, Phys. Scr. **44**, 399 (1991).

[11] D. Dill, J. Chem. Phys. **65**, 1130 (1976).

[12] W. H. Flygare, *Molecular Structure and Dynamics* (Prentice-Hall, Englewood Cliffs, NJ, 1978).

[13] M. P. Miranda, C. E. Bielschowsky, and M. A. C. Nascimento, J. Phys. B **28**, L15 (1995).

[14] A. Kivimäki, B. Kempgens, K. Maier, H. M. Köppe, M. N. Piancastelli, M. Neeb, and A. M. Bradshaw, Phys. Rev. Lett. **79**, 998 (1997).

[15] A. A. Pavlychev and N. G. Fominykh, J. Phys. Condens. Matter **8**, 2305 (1996).

[16] W. Domcke and L. S. Cederbaum, Chem. Phys. **25**, 189 (1977).

[17] D. Clark and J. Müller, Chem. Phys. **23**, 429 (1977).

[18] F. Heiser, O. Geßner, J. Viefhaus, K. Wieliczek, R. Hentges, and U. Becker, Phys. Rev. Lett. **79**, 2435 (1997).