Direct Determination of Partial Wave Contributions in the σ^* Shape Resonance of CO Molecules

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The first complete experiment for the C K-shell of CO molecules in the region of the σ^* shape resonance has been performed by detecting photoelectrons in coincidence with fragment ions. Four ratios of dipole matrix elements and four phase shift differences have been extracted from the experimental data. Their analyses show that, in the σ^* shape resonance due to the l mixing, d and f partial waves give the main contribution to the cross section, and f and g waves give the main contribution to a rapid increase of phase shift by π. [S0031-9007(97)05279-4]

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It is well known [1] that the K-shell photoabsorption spectra in diatomic molecules exhibit broad resonances above the ionization thresholds and, owing to that, strongly differ from monotonically decreasing atomic K-shell spectra. Dehmer and Dill [2] showed that though the molecular K shells remain essentially atomiclike, the p-wave photoelectrons ejected from them interact with an anisotropic molecular field and are scattered into states with another angular momentum, for example, with $l = 3$. As follows from their calculations for N_2 molecules, the σ continuum wave function with $l = 3$, which for low energies is concentrated outside the centrifugal barrier, can penetrate into the molecular core region at a kinetic energy of about 1 Ry. This penetration is rapid and leads to the appearance of a broad maximum in the cross section which is called a σ^* shape resonance. Simultaneously the corresponding phase shift is increased by $\sim\pi$ radians. This means that the molecular field can support a quasi-bound f state oriented along the molecular axis. The fact that the resonances appear only in σ channels has recently been proved experimentally for several molecules [3,4] by measuring the partial σ and π channel cross sections separately using angle-resolved photoion spectroscopy.

The calculations in Ref. [2] were relatively simple and gave only a qualitative description of the experimental σ^* shape resonances. But the majority of more recent and more sophisticated calculations [5] are still giving much sharper and stronger resonances than those observed experimentally. Therefore a so-called complete experiment is needed from which it would be possible to extract directly the dipole matrix elements and phase shift differences describing the process and to establish the origin of the σ^* resonances. Measurements of the angular distribution of photoelectrons ejected from fixed-in-space molecules reported in this paper are just the kind of experiment which is able to give this information.

The possibility to perform a complete experiment in photoionization was first discussed for atoms (see [6] and references therein) where the orbital angular momentum l of bound states is a good quantum number. The continuous spectrum wave function containing at large distances a plane wave propagating in the direction of photoelectron emission is represented as an infinite expansion in partial waves. The dipole selection rules restrict the number of partial waves in this expansion by only two terms with $l' = l \pm 1$ where l is the orbital angular momentum of an initial state. As a result, for a complete experiment in closed shell atoms one needs to determine at most five parameters. This can be done by measuring the angular distribution of photoelectrons with defined spin polarization ejected from unpolarized atoms [6], or by measuring the angular distribution of photoelectrons ejected from polarized atoms without spin analysis of photoelectrons [7]. In molecules the orbital angular momentum l is not a good quantum number, and the ground state wave function could not be characterized by a single value of l. Therefore, the dipole selection rules could not restrict the summation over partial waves in continuous spectrum which extends to infinity, and the complete experiment is impossible. But in practice the partial wave expansions are converging, and to a good approximation one can restrict the corresponding summations by some finite number of terms. In this more restricted sense the complete experiment is possible also in molecules as it was demonstrated in [8] for laser excited NO molecules.

Equations for the angular distribution of photoelectrons ejected from fixed-in-space molecules has been derived by Dill [9], and the first calculations for CO molecules [10] demonstrated a rich structure of the corresponding angular distributions. But so far no complete experiment has been reported on photoionization from the ground state of molecules.

Photoionization of fixed-in-space molecules in a gas phase is realized here by detecting photoelectrons in coincidence with fragment ions as described in [11,12].

In order to improve the time resolution for ion detection as C^+ and O^+ ions are detected separately, the ion detector with a retarding grid was replaced with a parallel plate electrostatic analyzer, which was used to detect the fragment ions having the kinetic energy of 5 ± 2.5 eV. Details of the present experiment will be described in the forthcoming paper [13]. The direction of light polarization was parallel to the molecular axis so that only $\sigma \rightarrow \sigma$ transitions were contributing. This makes the process axially symmetric and allows one to present the general expression for the angular distribution, obtained in [9] as an expansion in spherical harmonics, as an expansion in Legendre polynomials,

$$d\sigma/d\hat{k} = C \sum_{i}^{K} A_i P_i(\cos\theta), \tag{1}$$

where $\hat{k} = \{\theta, \varphi\}$ is the photoelectron ejection direction in the molecular frame, C is a normalization constant, and the parameters A_i are presented below in Eq. (2). They can be obtained by fitting the experimental angular distribution by Eq. (1). In homonuclear molecules symmetry considerations limit the summation over i to even values, and the number of parameters A_i is always smaller than the number of matrix elements and phase shift differences entering the equations for these parameters. Therefore it was impossible to extract them from the angular distributions measured in [11]. In heteronuclear molecules both even and odd i contribute to (1). Because of that, for any even value of K the number of parameters A_i is just equal to the number of dipole matrix elements and phase shift differences entering the equations for A_i, provided the partial wave expansion of the photoelectron wave function is restricted by the maximal value $l_{\max} = K/2$. It means that in this approximation, one can perform the complete experiment and extract the dipole matrix elements and phase shift differences directly from the measured angular distributions. This opens the possibility of a direct probe of the orbital angular momentum composition of molecular photoelectrons and to establish the origin of the σ^* shape resonances. In a previous measurement for CO molecules [12] the time resolution of the ion detector was not sufficient to distinguish between O^+ and C^+ ions, and therefore the angular distributions were characterized by the terms with only even values of i in Eq. (1) as in homonuclear molecules.

Figure 1 shows the observed angular distributions of C K-shell photoelectrons at three photon energies, the lowest energy 304.1 eV is very close to the position of the C $1s \rightarrow \sigma^*$ shape resonance. It is interesting to mention that in the resonance photoelectrons from carbon atom are ejected predominantly in the direction of an oxygen atom, while above the resonance they are ejected mainly in the opposite direction. The latter can be easily explained as a backscattering of photoelectrons from the neighboring atom, while in the shape resonance the behavior of the angular distribution is defined by an interference between different partial waves.

The measured angular distributions have been fitted by Eq. (1) with $K = 8$. From the general equations presented in [9,14] one can find the parameters A_i for the case $l \leq 4$

$$\begin{aligned}
A_0 &= d_0^2 + d_1^2 + d_2^2 + d_3^2 + d_4^2, \\
A_1 &= 2\sqrt{3}\, d_1 d_0 \sin\Delta_{10} + \frac{4\sqrt{3}}{\sqrt{5}}\, d_2 d_1 \sin\Delta_{21} + \frac{18}{\sqrt{35}}\, d_3 d_2 \sin\Delta_{32} + \frac{8}{\sqrt{7}}\, d_4 d_3 \sin\Delta_{43}, \\
A_2 &= 2d_1^2 + \frac{10}{7} d_2^2 + \frac{4}{3} d_3^2 + \frac{100}{77} d_4^2 - 2\sqrt{5}\, d_2 d_0 \cos\Delta_{20} - \frac{6\sqrt{3}}{\sqrt{7}}\, d_3 d_1 \cos\Delta_{31} - \frac{12\sqrt{5}}{7}\, d_4 d_2 \cos\Delta_{42}, \\
A_3 &= -2\sqrt{7}\, d_3 d_0 \sin\Delta_{30} - \frac{8}{\sqrt{3}}\, d_4 d_1 \sin\Delta_{41} + \frac{6\sqrt{3}}{\sqrt{5}}\, d_2 d_1 \sin\Delta_{21} + \frac{8\sqrt{7}}{3\sqrt{5}}\, d_3 d_2 \sin\Delta_{32} + \frac{12\sqrt{7}}{11}\, d_4 d_3 \sin\Delta_{43}, \\
A_4 &= \frac{18}{7} d_2^2 + \frac{18}{11} d_3^2 + \frac{1458}{1001} d_4^2 + 6 d_4 d_0 \cos\Delta_{40} - \frac{8\sqrt{3}}{\sqrt{7}}\, d_3 d_1 \cos\Delta_{31} - \frac{120\sqrt{5}}{77}\, d_4 d_2 \cos\Delta_{42}, \\
A_5 &= \frac{20\sqrt{5}}{3\sqrt{7}}\, d_3 d_2 \sin\Delta_{32} - \frac{10}{\sqrt{3}}\, d_4 d_1 \sin\Delta_{41} + \frac{120}{13\sqrt{7}}\, d_4 d_3 \sin\Delta_{43}, \\
A_6 &= \frac{100}{33} d_3^2 + \frac{20}{11} d_4^2 - \frac{30\sqrt{5}}{11}\, d_4 d_2 \cos\Delta_{42}, \\
A_7 &= \frac{350\sqrt{7}}{143}\, d_4 d_3 \sin\Delta_{43}, \\
A_8 &= \frac{490}{143} d_4^2,
\end{aligned} \tag{2}$$

where d_i are the dipole matrix elements (which are assumed to be real and positive) and $\Delta_{ik} \equiv \delta_i - \delta_k$ are the phase shift differences corresponding to the transitions to the final state with orbital angular momentum $l = i$ or k. Extracting

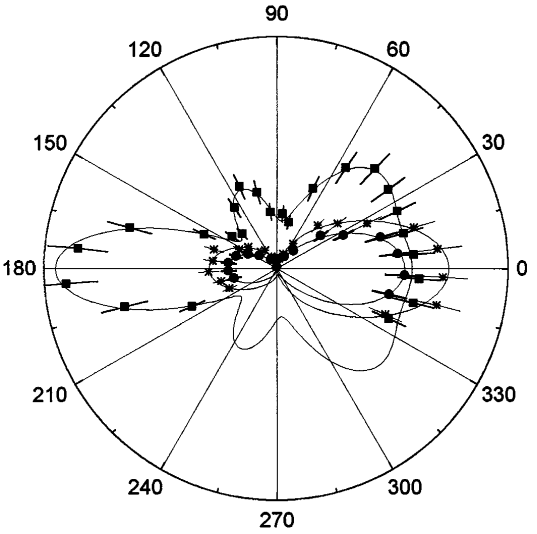

FIG. 1. Angular distributions of photoelectrons ejected from C K-shell of fixed-in-space CO molecules measured at three photon energies: 304.1 eV (■), 317.4 eV (*), and 333.7 eV (●) normalized to the total cross section measured in [4]. The positions of C and O atoms correspond to 0° and 180°, respectively. Light is linearly polarized along the molecular axis. Curves show the fit of experimental points by Eq. (1) with $K \leq 8$.

eight ratios A_i/A_0 from the fit of experimental angular distribution by Eq. (1) with $K = 8$, we can determine from Eqs. (2) four ratios of dipole matrix elements d_i/d_0 and four phase shift differences $(\delta_i - \delta_0)$, where $i = 1, 2, 3,$ and 4. But since Eqs. (2) are quadratic in dipole matrix elements, there are eight different solutions for four ratios of dipole matrix elements. Moreover, since the phase shifts enter the arguments of sine or cosine functions, there are two sets of phase shift differences corresponding to each set of dipole matrix elements, so that totally there are 16 different solutions at each photon energy. One could not select one of these solutions without additional information on photoionization process.

From the theory [2] it follows that in the σ^* resonance the f partial wave contribution to the cross section should be predominant. Therefore from the eight different solutions at 304.1 eV we have selected that one which gives the largest fraction for the $l = 3$ cross section (34%). The second largest contribution of the f partial wave is equal to 24% which seems to be not compatible with the theory. Then from the condition to have a smooth variation of dipole matrix elements with photon energy we must select probable solutions for the next points at photon energy 317.4 eV. At least four solutions presented in Table I can be taken as possible candidates at 317.4 eV, and at the moment there is no definitive argument to select one of them. On the other hand, the differences between them are not very essential, and for the following illustrations we shall use only row 1 of Table I.

The contributions of different partial waves to the C $1s \rightarrow \varepsilon l\sigma$ photoionization cross section obtained in that way are shown in Fig. 2. The curves show a possible reconstruction of the partial cross sections from the condition to correctly reproduce the cross section measured in [4]. The contributions of d and f partial waves could not be extracted unambiguously having only one point in the resonance; therefore their sum is also presented which is defined with much higher confidence. It is seen from Fig. 2 that the cross section maximum in the σ^* shape resonance is formed not by a predominant contribution of the $l = 3$ partial wave but by a joint contribution of d and f partial waves, with the d partial wave contribution being slightly larger. This is also evident from the view of the angular distribution shown in Fig. 1 which does not have a pattern characteristic for the f partial wave and differs strongly from the theoretical predictions [10]. From Table I it is seen that the phase shift differences Δ_{i0} for $i = 1$ and 2 are slowly varying between the first two measured points in photon energy while for $i = 3$ and 4 they are growing by $\sim\pi/2$ radians each. It means that three partial waves with $l = 2, 3,$ and 4, are participating in forming the σ^* shape resonance, d and f waves giving the main contribution to the cross section, and f and g waves giving the main contribution to a rapid increase of phase shift by π. This strong l mixing makes the σ^* shape resonance in CO essentially different from the analogous resonances in homonuclear molecules. In homonuclear molecules like N_2 the σ^* shape resonances occur in $1s\sigma_g \rightarrow \varepsilon l\sigma_u$ transitions where the partial waves with odd l are contributing, with the predominant contribution of only one f partial wave [2]. The d partial wave is

TABLE I. Dipole matrix elements (normalized by the condition $A_0 = 1$) and phase shift differences (in degrees) deduced with the help of Eqs. (1) and (2) from the measured angular distributions shown in Fig. 1.

Energy	No.	d_0	d_1	d_2	d_3	d_4	Δ_{10}	Δ_{20}	Δ_{30}	Δ_{40}
304.1 eV	1	0.152	0.436	0.654	0.580	0.149	57.5	−151.7	44.5	−140.4
	2						122.5	151.7	135.5	140.4
317.4 eV	1	0.234	0.840	0.380	0.276	0.136	71.9	−131.1	156.9	−57.1[a]
	2	0.217	0.752	0.561	0.233	0.136	169.0	183.9	229.8	271.3[a]
	3	0.315	0.872	0.261	0.230	0.136	183.7	−66.3	70.1	−152.2[a]
	4	0.436	0.868	0.114	0.160	0.136	23.0	−190.9	−69.9	34.5[a]

[a] The second set of phase shift differences is obtained by reversing the sign of differences with even i and by applying the equation $(\Delta_{i0})_2 = \pi - (\Delta_{i0})_1$ for odd i as is demonstrated in row 2 for photon energy 304.1 eV.

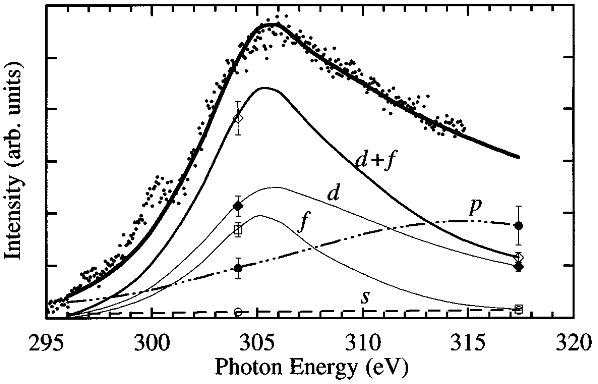

FIG. 2. Contributions of the s (○), p (●), d (◆), and f (□) partial waves and of the sum $(d + f)$ (◇) to the σ photoionization cross section deduced from the experimental angular distributions. Curves show a probable reconstruction of the corresponding contributions from the condition to reproduce the experimental cross section measured in [4] (points). The g cross section is smaller than the s one and is not shown in the figure.

contributing to the $1s\sigma_u \rightarrow \varepsilon l\sigma_g$ transition where there is no resonance at all. In heteronuclear molecules both even and odd partial waves contribute to the C $1s \rightarrow \varepsilon l\sigma$ transition as the inversion symmetry is gone, which makes l mixing rather strong. Unfortunately, there is no possibility to compare our data with the corresponding theoretical results because neither the dipole matrix elements nor the phase shifts are presented in [2,5,10].

Since even Legendre polynomials are symmetrical relative to the vertical line in Fig. 1, a gradual shift of the main maximum in the angular distributions from the direction to the neighboring atom at the shape resonance to the opposite direction at higher energies appears due to a variation of coefficients of odd Legendre polynomials in Eq. (1). The coefficients A_i with odd i contain only the products of matrix elements with odd and even l so that the interference of odd and even partial waves is responsible for that gradual shift. It also means that odd and even partial waves are giving equally important contributions.

In conclusion, we have for the first time performed the complete experiment by measuring the angular distributions of photoelectrons ejected from the C K-shell of fixed-in-space CO molecules in the region of the σ^* shape resonance. Four ratios of dipole matrix elements and four phase shift differences were determined from the measured data. The analyses of these data demonstrate that due to a strong l-channel mixing three partial waves with $l = 2, 3, 4$ are participating in forming the σ^* shape resonance in CO molecules. The first results obtained here clearly demonstrate that the complete experiment in molecules is now feasible, and that it enables one to perform the most stringent test of existing theories.

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[1] A. P. Hitchcock and D. C. Mancini, J. Electron Spectrosc. Relat. Phenom. **67**, 1 (1994), and references therein.
[2] J. L. Dehmer and D. Dill, Phys. Rev. Lett. **35**, 213 (1975); J. Chem. Phys. **65**, 5327 (1976).
[3] A. Yagishita, E. Shigemasa, J. Adachi, and N. Kosugi, in *Proceedings of the 10th International Conference on Vacuum Ultraviolet Radiation Physics,* edited by F. J. Wuilleumier, Y. Petroff, and I. Nenner (World Scientific, Singapore, 1993), p. 201.
[4] E. Shigemasa, T. Hayaishi, T. Sasaki, and A. Yagishita, Phys. Rev. A **47**, 1824 (1993).
[5] N. Padial, G. Csanak, B. V. McKoy, and P. W. Langhoff, J. Chem. Phys. **69**, 2992 (1978); D. L. Lynch and V. McKoy, Phys. Rev. A **30**, 1561 (1984); J. Schirmer, M. Braunstein, and V. McKoy, Phys. Rev. A **41**, 283 (1990); G. Bandarage and R. R. Lucchese, Phys. Rev. A **47**, 1989 (1993); I. Wilhelmy and N. Rosch, Chem. Phys. **185**, 317 (1994).
[6] N. A. Cherepkov, Adv. At. Mol. Phys. **19**, 395 (1983).
[7] H. Klar and H. Kleinpoppen, J. Phys. B **15**, 933 (1982).
[8] D. J. Leahy, K. L. Reid, H. Park, and R. N. Zare, J. Chem. Phys. **97**, 4948 (1992).
[9] D. Dill, J. Chem. Phys. **65**, 1130 (1976).
[10] D. Dill, J. Siegel, and J. L. Dehmer, J. Chem. Phys. **65**, 3158 (1976); J. W. Davenport, Phys. Rev. Lett. **36**, 945 (1976).
[11] E. Shigemasa, J. Adachi, M. Oura, and A. Yagishita, Phys. Rev. Lett. **74**, 359 (1995).
[12] P. A. Hatherly, J. Adachi, E. Shigemasa, and A. Yagishita, J. Phys. B **28**, 2643 (1995).
[13] E. Shigemasa *et al.* (to be published).
[14] N. A. Cherepkov and V. V. Kuznetsov, Z. Phys. D **7**, 271 (1987).