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Photoelectron Angular Distributions from O K Shell of Oriented CO Molecules: A Critical Comparison between Theory and Experiment

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The dynamical information (ten dipole matrix elements and eight phase differences) has been deduced from the measured angular distributions of photoelectrons from O K shell of oriented CO molecules near the ionization threshold in the region of a σ^* shape resonance. Light polarization parallel and perpendicular to the molecular axis has been used. An important contribution of six $l\sigma$ partial waves with $0 \leq l \leq 5$ to the σ^* shape resonance is demonstrated. A comparison with our calculations in the relaxed core Hartree-Fock approximation reveals only a qualitative agreement, therefore a more advanced theory is needed.

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For a long time there was a great distance between detailed information contained in theoretical dipole matrix elements, and general information available from experimental total or partial photoionization cross sections. In typical experiments random molecular orientations greatly reduce the information content. The ultimate goal for experimentalists is a so-called complete, or perfect, experiment from which one can extract, within some approximation, all matrix elements and phase differences necessary for the theoretical description of a process [1–3]. Only now a complete experiment with molecules is becoming possible due to availability of lasers and synchrotron radiation sources in combination with coincidence techniques.

For closed shell atoms, where l is a good quantum number, due to the dipole selection rules the photoionization is described theoretically by at most five dynamical parameters, three dipole matrix elements, and two phase shift differences. We assume in this paper that the electric dipole approximation is valid. We also imply that the complex dipole matrix elements are presented in a polar form as a product of a modulus and an exponent with the total (Coulomb plus short range) phase shift. In molecules the orbital angular momentum l is no longer a good quantum number, and both the initial and final state wave functions are presented as an infinite expansion in partial waves. The dipole selection rules cannot restrict these summations, and an infinite number of dipole matrix elements contribute to the process, making the complete experiment impossible. However, in practice, the partial wave expansions converge relatively rapidly, and, to a good approximation, one can restrict the corresponding summations to a limited number of terms.

In this more restricted sense the complete experiment is also feasible in molecules. That was demonstrated in [4] for laser excited states of NO molecules by $(1 + 1')$ resonantly enhanced multiphoton ionization technique, and in [5] for the ground state of molecules (which is much more important) by using the angle-resolved photoelectron-photoion coincidence technique (AR-PEPICO). In the AR-PEPICO technique, a photoelectron is detected in coincidence with a fragment ion produced in dissociative photoionization. That allows the selection of processes corresponding to a given direction of the molecular axis in space, provided the dissociation is much faster than the period of molecular rotation. In that way, one can measure the angular distribution of photoelectrons ejected from oriented molecules in the gas phase by detecting ions moving in a given direction. The AR-PEPICO technique also allows the measurement of the angular distribution of ions corresponding to a given direction of photoelectron emission, as was shown in [6].

The equation for the angular distribution of photoelectrons ejected from oriented molecules has been derived by Dill [7]. Subsequent calculations for CO molecules in a relatively simple Multiple Scattering (MS) approximation [8,9] demonstrated a rich structure of the angular distributions (see Fig. 1). In this Letter, we present for the first time the photoelectron angular distributions for O K shell of oriented CO molecules measured using the AR-PEPICO technique at several photon energies near the ionization threshold where a σ^* shape resonance occurs. From these data, we determined as many as 18 dynamical parameters, that is, we performed a complete experiment. We also report here the corresponding theoretical values calculated in a Relaxed Core Hartree-Fock (RCHF) approximation, and compare them with the values determined from the experiment. The analysis of our data allowed us a new insight into the nature of the σ^* shape resonance.

Consider the photoionization of $ns\sigma$ shell of an oriented diatomic molecule with a fixed direction of molecular axis taken as Z axis of a molecular coordinate system. When molecules are ionized by linearly polarized light with polarization vector $\boldsymbol{e}_z$ parallel to the molecular axis, the process acquires an axial symmetry about the molecular

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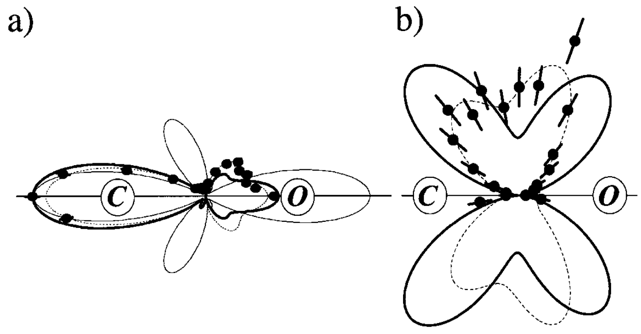

FIG. 1. Angular distributions of photoelectrons from O K shell of fixed-in-space CO molecules ejected by light linearly polarized parallel (a) and perpendicular (b) to the molecular axis. Photon energy is 552.3 eV, the angular distributions are normalized to unity at maximum. Dots: our experiment with error bars showing the statistical uncertainties; dotted line: the fit to the experimental data; thick solid line: our RCHF calculations; thin solid line: calculation in the MS approximation [8].

axis, and the angular distribution can be presented as an expansion in Legendre polynomials [7]

$$I(\boldsymbol{k}, \boldsymbol{e}_z) \sim \sum_{L=0}^{L_{\max}} A_L P_L(\theta_k), \tag{1}$$

where $\boldsymbol{k}$ is the photoelectron momentum, θ_k is its polar angle in the molecular frame, and as the measurements are relative, the value of a proportionality constant is not important. The parameters A_L, normalized by the condition $A_0 = 1$, are expressed through the moduli and phases of the dipole matrix elements by equations given in Ref. [5]. As expected from symmetry arguments, only the $\sigma \to \sigma$ transitions contribute to these parameters. Let us assume that the partial wave expansion of the photoelectron wave function is restricted by the maximal value $l_{\max} = L_{\max}/2$ where $L_{\max}$ is even. Then, for heteronuclear diatomic molecules, the number of parameters A_L in Eq. (1) is equal to the number of moduli of dipole matrix elements and phase differences, and they can be extracted from the measured angular distributions.

Suppose now that light is linearly polarized along the X axis of the molecular frame, and photoelectrons are detected in the XOZ plane, $\boldsymbol{k} = (\theta_k, \varphi_k = 0°)$. Then the angular distribution can be presented in the form similar to (1)

$$I(\boldsymbol{k}, \boldsymbol{e}_x) \sim \sum_{L=0}^{L_{\max}} C_L P_L(\cos\theta_k), \tag{2}$$

where parameters C_L (normalized by the condition $C_0 = 1$) contain only the moduli and phases of the dipole matrix elements of the $\sigma \to \pi$ transitions. Since the partial wave expansion for the $\sigma \to \pi$ transitions starts at $l = 1$, the number of parameters C_L is always larger by 2 than the number of matrix elements and phase differences provided $l_{\max} = L_{\max}/2$ and $L_{\max}$ is even. This means that not all of the parameters C_L are mutually independent. Indeed, one can find two linear relations between them,

$$\sum_{L=0}^{L_{\max}} C_L = 0, \qquad \sum_{L=0}^{L_{\max}} (-1)^L C_L = 0. \tag{3}$$

Therefore the number of independent coefficients C_L is equal to $L_{\max} - 2$, and in a complete experiment we can determine from them $L_{\max} - 2$ dynamical parameters. Inserting Eq. (3) into (2) we find that the electron intensity along the molecular axis is zero [see Fig. 1(b)].

Measurements for $\boldsymbol{e}_z \parallel \boldsymbol{n}$ and $\boldsymbol{e}_x \perp \boldsymbol{n}$ where $\boldsymbol{n}$ is the direction of molecular axis enable one to define separately two independent sets of matrix elements $d_{l\sigma}$ and $d_{l\pi}$, and phase shifts $\delta_{l\sigma}$ and $\delta_{l\pi}$, for the $l\sigma$ and $l\pi$ channels, respectively. That is a great advantage as compared to the experiment where the ion angular distribution is measured [6] and where such a separation is impossible. The ratios of moduli of the dipole moments belonging to different sets, for example, $d_{l\pi}/d_{0\sigma}$, can be defined from the relative cross sections corresponding to the σ and π ionization channels measured in [10]. For determining the phase differences $(\delta_{l\pi} - \delta_{0\sigma})$ one needs to perform at least one measurement under the condition different from ours, $\boldsymbol{e}_z \parallel \boldsymbol{n}$ and $\boldsymbol{e}_x \perp \boldsymbol{n}$. As this measurement has not been done yet, the differences $(\delta_{l\pi} - \delta_{0\sigma})$ remain undefined, which makes our experiment not quite complete.

For interpretation of the observed angular distributions we have performed numerical calculations using a relaxed molecular basis set called Transition State Approximation (TSA) proposed by Slater [11]. It consists of a self-consistent field calculation of an average electronic configuration where half an electron is removed from the inner shell under consideration. To avoid nonorthogonality problems this basis set is used for both the initial N-electron ground and the $(N - 1)$-electron final ion states. As described in [12,13], the photoelectron wave function is obtained in the RCHF approximation in the field of $(N - 1)$-electron ion state. The RCHF method gives relatively good results for the dipole transition moments and partial photoionization cross sections [12].

Photoionization of fixed-in-space molecules in the gas phase has been realized here by detecting photoelectrons in coincidence with fragment ions (AR-PEPICO) at the soft x-ray undulator beam line BL-2C of the Photon Factory [14]. The experimental apparatus described in detail elsewhere [15] consists of two electron-ion coincidence circuits (instead of one in [5]). Photoelectrons and ions emitted in the plane perpendicular to the photon beam are energy analyzed by parallel-plate energy analyzers with a $\pm 10°$ geometrical acceptance angle in the detection plane. Compared with previous measurements [5], we were now able to obtain simultaneously the angular distributions of photoelectrons for light polarization parallel and perpendicular to the molecular axis. As an example, Fig. 1 shows two angular distributions of photoelectrons measured at photon energy 552.3 eV (closest to the maximum of the σ^* shape resonance) compared to a previously available calculation [8] in the MS approximation, and the present RCHF result. Our calculation is in a much better agreement with the experiment, though discrepancies still remain.

Starting from the measured angular distributions, we proceed towards the complete experiment; that is, we defined the coefficients A_L of Eq. (1) with $L_{\max} = 10$ (the maximal number of terms compatible with the angular resolution of our experiment), and the coefficients C_L of Eq. (2) with $L_{\max} = 8$ (here the convergence is faster, and 8 terms is sufficient). Then, using the analytical expressions for these coefficients given in [5], we determined 5 ratios of dipole matrix elements $d_{l\sigma}/d_{0\sigma}$ and 5 phase differences $(\delta_{l\sigma} - \delta_{0\sigma})$ for the $1s\sigma \rightarrow \varepsilon l\sigma$ transitions with $0 < l \leq 5$. Also, we obtained 3 ratios of dipole matrix elements $d_{l\pi}/d_{1\pi}$ and three phase differences $(\delta_{l\pi} - \delta_{1\pi})$ for the $1s\sigma \rightarrow \varepsilon l\pi$ transitions with $1 < l \leq 4$. Then we normalized the relative experimental cross section for the $1s\sigma \rightarrow \varepsilon l\pi$ channels from [10] to our theoretical cross section at 561 eV photon energy. Using the relative cross sections for the $1s\sigma \rightarrow \varepsilon l\sigma$ and $1s\sigma \rightarrow \varepsilon l\pi$ channels measured in [10], we obtained from the experiment the absolute values of the dipole matrix elements. As a result, we have determined 18 values from the experimental data. But since the equations for the coefficients A_L and C_L are quadratic in dipole matrix elements, and the phase differences are arguments of sine or cosine functions, the solution is not unique. There are 32 different solutions for ten values (five ratios of dipole matrix elements and five phase differences) of the $1s\sigma \rightarrow \varepsilon l\sigma$ transitions, and eight different solutions for six values of the $1s\sigma \rightarrow \varepsilon l\pi$ transitions. One could not select unambiguously one of these solutions without additional information on the photoionization process. We used the results of the RCHF calculations to select one set of solutions giving the closest agreement with the theory.

Figure 2 shows the comparison between the dipole matrix elements for the first six $1s\sigma \rightarrow \varepsilon l\sigma$ transitions ($l \leq 5$) extracted from the experimental data and calculated in RCHF. At about 550 eV there is the σ^* shape resonance where, according to the MS calculation [16], the f-wave contribution to the cross section is expected to dominate. Both the RCHF calculation and experiment show that the situation is totally different and more complicated. Namely, the matrix elements with $l = 0, 1, 2, 3$ are large and almost equal, and the other matrix elements with $l = 4$ and 5 are of the same order of magnitude (only the theoretical matrix element with $l = 5$ is small). Among 32 solutions there is not one where the f-wave contribution to the cross section exceeds 50%. Two solutions with the largest f-wave contribution to the cross section (equal to 50% and 36%) correspond to a very small d-wave contribution, and therefore contradict to the RCHF result. The other solution with the 40% f-wave contribution gives the phase differences which deviate from the theory. The solution shown in Figs. 2 and 3 corresponds to the fourth largest f-wave contribution (equal to 28%), and

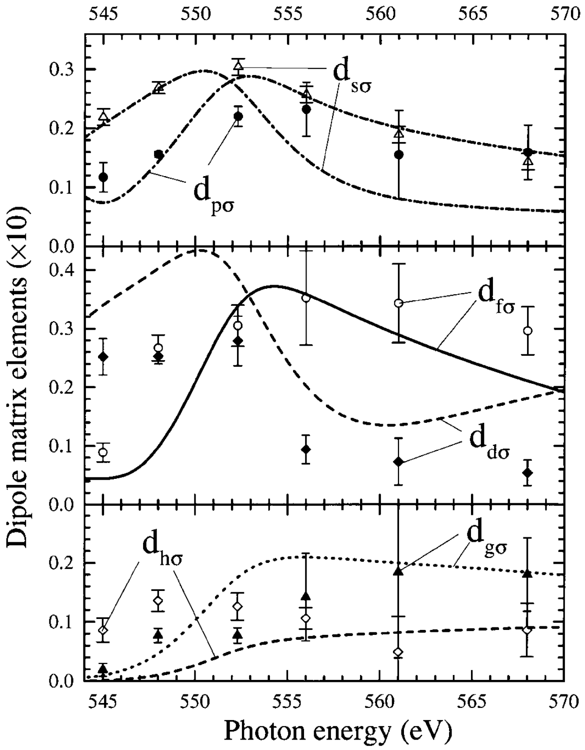

FIG. 2. Dipole matrix elements $d_{l\sigma}$ (in atomic units, multiplied by 10) for the $1s\sigma \rightarrow \varepsilon l\sigma$ transitions with $0 \leq l \leq 5$ extracted from the experimental data (points with error bars which come from the statistical uncertainties shown in Fig. 1) and calculated in the RCHF approximation (curves).

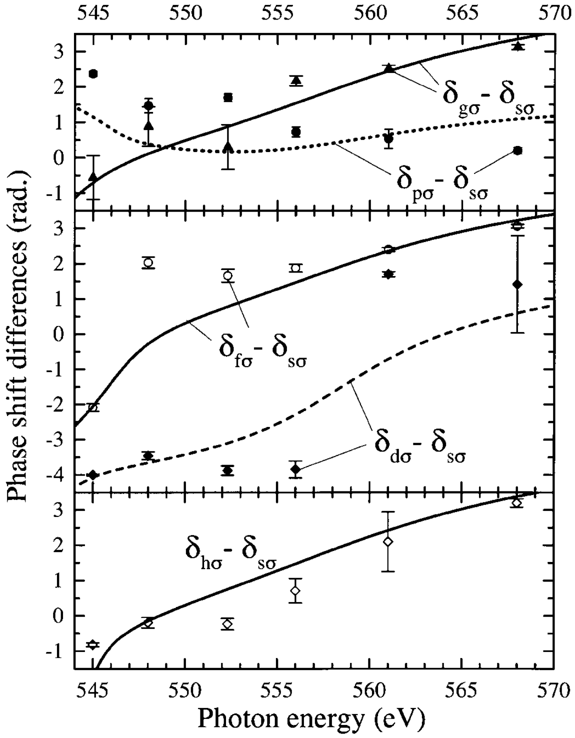

FIG. 3. Phase shift differences $\delta_{l\sigma} - \delta_{0\sigma}$ for the $1s\sigma \rightarrow \varepsilon l\sigma$ transitions with $l \leq 5$ (the same notations as in Fig. 2.

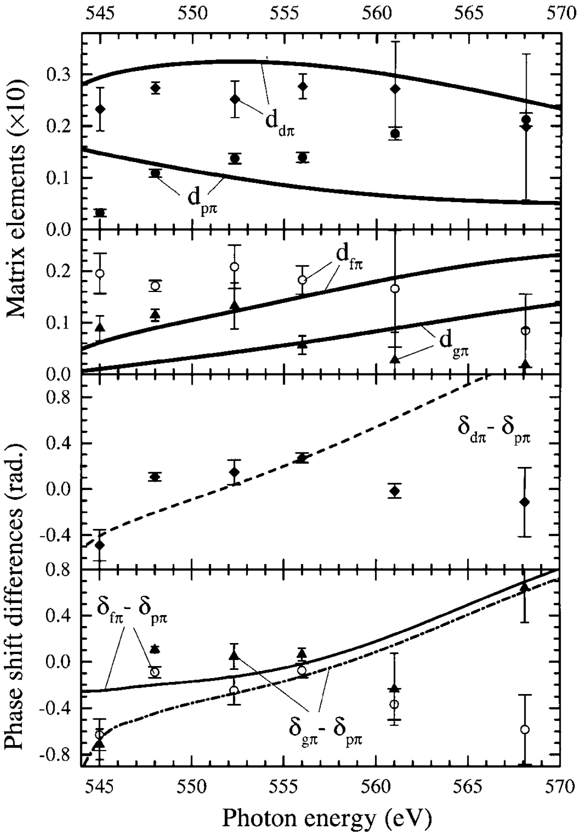

FIG. 4. Dipole matrix elements $d_{l\pi}$ and phase shift differences $\delta_{l\pi} - \delta_{1\pi}$ for the $1s\sigma \to \varepsilon l\pi$ transitions with $l \leq 4$ (the same notations as in Figs. 2 and 3).

is in the closest agreement with the RCHF result for both the matrix elements and phase differences (all solutions will be presented elsewhere [13]). Nevertheless, the discrepancies between theory and experiment are not small. Figure 4 displays the matrix elements and phase differences for the first four $1s\sigma \to \varepsilon l\pi$ transitions with $l \leq 4$. Theory and experiment are in a reasonable agreement, showing that the largest is the dipole matrix element with $l = 2$, though the energy dependencies of the matrix elements with $l = 1$ and $l = 3$ in theory and experiment are different. One should keep in mind that more advanced theory can differ from our RCHF results, and perhaps another set of dynamical parameters determined from our experiment will better fit that theory.

In conclusion, we demonstrated that the complete experiment in photoionization of diatomic molecules is now feasible, and that it gives unprecedentedly rich quantum-mechanical information on molecular structure and photoionization. From the 32 + 8 sets of the matrix elements and phase differences extracted from the experimental data we retained one set, the closest to the theoretical RCHF calculation. That set is still only in a qualitative agreement with the RCHF result, and therefore a more involved model including electron correlations is needed. For the first time we proved that the σ^* shape resonance is formed not by the f wave alone, as it was widely believed earlier, but by approximately equal contributions of four partial waves with $0 \leq l \leq 3$ with a rather substantial contribution of two other partial waves with $l = 4, 5$. A similar conclusion has been drawn earlier in [5] for the σ^* shape resonance in C K shell ionization, and in the theoretical work [17] for valence shell of CO.

Knowing the dipole matrix elements and phase shifts from a complete experiment, one can predict the result of any other photoionization experiment. For example, one can predict the angular distribution of ions for a given direction of photoelectron emission as demonstrated in [18]. One can also determine the direction of molecular axis relative to the surface normal for molecules adsorbed on surfaces [9,19].

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