

Direct Probe of the Shape Resonance Mechanism in $2\sigma_g$ -Shell Photoionization of the N_2 Molecule

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Angular distributions of photoelectrons from a $2\sigma_g$ shell of fixed-in-space N_2 molecules have been measured for left- and right-elliptically polarized and for linearly polarized light at several photon energies in the region of σ^* shape resonance. That allowed the determination of a set of dipole matrix elements and phase shift differences characterizing the process. These data clearly show the enhancement of the $f\sigma_u$ partial cross section in the resonance simultaneously with an abrupt increase of the corresponding phase shift by π , which is the first experimental demonstration of the nature of the σ^* shape resonance in homonuclear diatomic molecules.

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The first theoretical investigation of the angular distribution of photoelectrons (ADP) ejected from fixed-in-space molecules was done in 1976 [1,2], keeping in mind an application to molecules adsorbed on surfaces. After that a long time passed until the relevant experimental data for the gas phase molecules appeared [3,4] obtained by the angle-resolved electron-ion coincidence technique. In that method a photoelectron is detected in coincidence with a fragment ion produced in dissociative photoionization. This allowed one to select the processes corresponding to a certain direction of molecular axis in space, provided the dissociation is much faster than the period of molecular rotation, and opened a new horizon in photoelectron spectroscopy [5,6]. In particular, it allowed the extraction of the sets of dipole matrix elements and phase shift differences for C and O K -shells of a CO molecule from the measured data [7,8]. Nevertheless, due to the use of only linear polarization of light the relation between the subsets of matrix elements and phase shifts for the $\sigma \rightarrow \sigma$ and $\sigma \rightarrow \pi$ transitions remained undetermined.

Although equations derived by Dill [1] are general and applicable to any polarization of incident light, the advantages of using different light polarizations were not explored by him. It was later realized that oriented molecules are optically active [9–12] and, in particular, that oriented linear molecules reveal circular (and linear) dichroism in the angular distribution (CDAD and LDAD), which is a difference between the photoelectron currents ejected at a definite angle by light of right- and left-circular polarization (or of two mutually perpendicular linear polarizations). Investigations of CDAD and LDAD proved to be fruitful in studies of adsorbed molecules [13,14] and molecules in aligned excited states [15]. However, experiments on the ADP from oriented molecules in a gas phase were up to now limited to those performed with linearly

polarized light, except for two publications on CDAD by Heiser *et al.* and Jahnke *et al.* [16].

In this Letter we report the first experimental study of the ADP of $2\sigma_g$ photoelectrons from oriented N_2 molecules obtained with right- and left-elliptically, as well as linearly, polarized light. From the combination of these data we determined the dipole matrix elements and phase shift differences for the partial waves with $l = 1$ and 3; that is, we performed the complete experiment in this approximation. That allowed the investigation of the nature of a σ^* shape resonance appearing in the photoionization cross section of this shell. According to the generally accepted explanation [17], the σ^* shape resonance is formed by a predominant contribution of a σ continuum wave function with $l = 3$. For low energies near the ionization threshold this wave function is concentrated outside the molecule due to the centrifugal barrier, but at a kinetic energy of about 0.5 a.u. it rapidly penetrates into the molecular core region. This penetration leads to the appearance of a broad maximum in the cross section which is called a σ^* shape resonance. Simultaneously the phase shift of this partial wave is increasing by $\sim \pi$ radians. In contrast to that, the first complete experiment performed in the σ^* shape resonances of C and O K -shells of a CO molecule [7,8] demonstrated that not one but several partial waves, at least with $l = 1, 2, 3$, are giving comparable contributions. Therefore, it is of principal interest to check whether the simple model of Dehmer and Dill [17] is adequate at least in the case of a homonuclear molecule, where the dipole selection rule restricts the orbital angular momenta of photoelectrons by odd values. Dehmer and Dill originally studied the σ^* shape resonance in the K shell of the N_2 molecule and showed that the resonance appears only in the $1\sigma_g$ shell. But in N_2 the energy splitting of $1\sigma_g$ and $1\sigma_u$ shells is smaller than the widths of the corresponding

photoelectron lines, and it is very hard to resolve them [18]. Without resolving them there is no possibility to perform the complete experiment and to extract the matrix elements and phase shift differences from the measured angular distributions. Therefore, we selected the $2\sigma_g$ shell of N_2 where this problem does not exist.

The experiment has been performed at the helical undulator [19] beam line BL-28A equipped with the constant deviation monochromator [20] of the Photon Factory in Tsukuba, by applying the angle-resolved photoelectron-photoion coincidence method [7]. Both a photoelectron and an ion spectrometer are placed in the plane perpendicular to the photon beam. The ion spectrometer has a fixed position which defines the direction of molecular axis. The photoelectron spectrometer is rotated about the photon beam to measure the molecular frame ADP. We studied photoionization of the $2\sigma_g$ inner valence shell of the N_2 molecule at five photon energies in the region 45–65 eV (bandwidth 0.2 eV). The photoelectron spectrometer is set to transmit electrons corresponding to the maximum of the broadband (reflecting a steep repulsive potential) around binding energy 38 eV. This broadband has the strongest intensity among several lines corresponding to the $2\sigma_g$ shell [21] and carries the largest single-particle contribution compared to other satellite lines as it follows from calculations [22,23]. As a result, the use of a single-particle picture for interpretation of photoionization in this broadband seems to be justified. The pass energy of the ion spectrometer is set to transmit the fragment N^+ ions having 5–6 eV kinetic energy.

In the photon coordinate frame with the Z axis facing the photon beam, the light polarization is characterized by the Stokes parameters S_i . $S_1 = +1$ (-1) corresponds to linear polarization along the X (Y) axis, $S_2 = +1$ (-1) to linear polarization along the direction making the angle $+45^\circ$ (-45°) with the X axis, and $S_3 = +1$ (-1) to right- (left-) circular polarization, described by the spherical function Y_{1-1} (Y_{11}). We imply in the following that the photon coordinate system is defined in a way that the major axis of the polarization ellipse is taken as the X axis of the photon frame. With this choice of the coordinate system the Stokes parameter S_2 is zero. Three measurements have been made at every photon energy with different light polarizations, namely, with right- and left-elliptically polarized, and with linearly polarized, light having the polarization vector perpendicular to the molecular axis. The Stokes parameter S_1 and the direction of the major axis of the polarization ellipse were determined from the photoelectron angular distributions for He which were measured during the same run of the storage ring as the coincidence measurements. The Stokes parameter S_3 was estimated assuming that there is no unpolarized component in the helical undulator radiation.

Figure 1 shows our experimental results and the fitting curves for ADP's at photon energy 58.2 eV. The results of calculations in the random phase approximation (RPA) using the method described in [24] are also shown. The

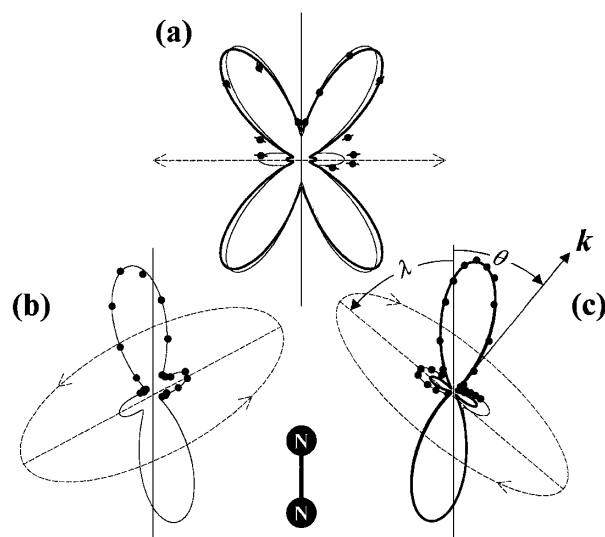


FIG. 1. ADP in the plane perpendicular to the photon beam for photon energy 58.2 eV and for different light polarizations. The molecular axis is directed along the vertical line; the angles θ and λ introduced in Eq. (2) are shown in (c). (a) Linearly polarized light, $S_1 = 0.97 \pm 0.01$, $S_3 = 0$, $\lambda = 90^\circ \pm 0.3^\circ$. (b) Left-elliptically polarized light, $S_1 = 0.42 \pm 0.01$, $S_3 = -0.91 \pm 0.01$, $\lambda = 120^\circ \pm 0.4^\circ$. (c) Right-elliptically polarized light, $S_1 = 0.50 \pm 0.01$, $S_3 = 0.87 \pm 0.01$, $\lambda = 50^\circ \pm 0.3^\circ$. Dashed lines show the photon polarization ellipse. Thin solid lines in (b) and (c) are the fitting curves, and that in (a) is calculated with the experimentally determined parameters given in Table I. The thick solid line shows the RPA calculation.

ADP's are strongly dependent on the light polarization properties. For light which is linearly polarized perpendicular to the molecular axis there is a reflection symmetry with respect to the molecular axis, with zero intensities along the molecular axis, as was observed in our previous works [4–8]. The ADP's for right- and left-elliptically polarized light do not have that reflection symmetry, but one of them is a mirror image of the other one.

For a detailed analysis of the experimental data the following procedure has been applied. The ADP for arbitrary polarization of incident light can be written as an incoherent sum of four contributions corresponding to light linearly polarized along the X and Y axes of the photon frame defined above (polarization vectors \mathbf{e}_x and \mathbf{e}_y , respectively), and to right- and left-circularly polarized light, as given below:

$$\begin{aligned}
 I(\mathbf{p}, S_1, S_3) &= d\sigma_{\text{obs}} \\
 &= \frac{1}{2} (d\sigma_{\mathbf{e}_x} + d\sigma_{\mathbf{e}_y}) + \frac{S_1}{2} (d\sigma_{\mathbf{e}_x} - d\sigma_{\mathbf{e}_y}) \\
 &\quad + \frac{S_3}{2} (d\sigma_r - d\sigma_l), \quad (1)
 \end{aligned}$$

where $d\sigma_i \equiv d\sigma_i/d\Omega_p$ is the differential photoionization cross section for a given light polarization, and $d\Omega_p$ is the angle of the photoelectron ejection with \mathbf{p} being the photoelectron momentum. Using Dill's [1] expression for the differential cross sections and performing the

TABLE I. Two sets of ratios of dipole matrix elements and phase shift differences (in degrees), determined from the experimental data for right-elliptically polarized light, and the corresponding theoretical values calculated in the Hartree-Fock (HF) and RPA approximations. Photon energy is 58.2 eV.

	$d_{p\sigma}/d_{f\pi}$	$d_{p\pi}/d_{f\pi}$	$d_{f\sigma}/d_{f\pi}$	$\delta_{p\sigma} - \delta_{f\pi}$	$\delta_{p\pi} - \delta_{f\pi}$	$\delta_{f\sigma} - \delta_{f\pi}$
Set 1	0.35 ± 0.08	0.51 ± 0.07	1.79 ± 0.22	308 ± 17	118 ± 5	52 ± 11
Set 2	0.35 ± 0.08	0.51 ± 0.07	1.79 ± 0.22	209 ± 17	242 ± 5	186 ± 11
HF	0.51	0.71	1.78	285	96	82
RPA	0.62	0.58	1.83	284	133	94

transformations as described in [1,11], we finally arrive at the following equation for ADP for our geometry of the experiment shown in Fig. 1 (atomic units are used in this Letter):

$$I(\mathbf{p}, S_1, S_3) = \frac{1}{4\pi} \sigma(\omega) \sum_{L=0}^{2l_{\max}} \left\{ \frac{3}{B} \left[\left(\frac{1}{2} A_L + C_L \right) + \left(\frac{1}{2} A_L - C_L \right) S_1 \cos 2\lambda \right] P_L(\cos\theta) + \sqrt{\frac{3(2L+1)}{L(L+1)}} [iS_3 A_{L1}^1 + S_1 \sin 2\lambda A_{L1}^2] P_L^1(\cos\theta) \right\}. \quad (2)$$

Here $\sigma(\omega)$ is the photoionization cross section, λ is the angle between the major axis of the polarization ellipse and the molecular axis, $P_L(\cos\theta)$ and $P_L^1(\cos\theta)$ are the Legendre and associated Legendre polynomials, respectively, and θ is the angle of electron ejection relative to the molecular axis (see Fig. 1). The dynamical parameters A_{LM}^J, A_L, C_L, B contain products of the dipole matrix elements and sine or cosine functions of the phase shift differences and have been defined in [7,8].

Assuming that four channels, namely, $2\sigma_g \rightarrow \varepsilon p \sigma_u, \varepsilon f \sigma_u, \varepsilon p \pi_u, \varepsilon f \pi_u$, where ε is the photoelectron energy, are sufficient for an adequate description of the ADP, that is, $l_{\max} = 3$, we come to the condition that L in Eq. (2) is even, and $L \leq 6$. Our calculations both in the HF and RPA approximations support the validity of this assumption. In this case, considering the coefficients in front of the Legendre and associated Legendre polynomials in Eq. (2) as fitting parameters, we obtain six fitting parameters (apart from the normalization constant) from one measurement with elliptically polarized light. This allows the extraction of three ratios of dipole matrix elements and three phase shift differences. However, since the parameters A_{LM}^J, A_L, C_L are quadratic in matrix elements, this procedure gives eight different sets of solutions, four sets for the ratios of dipole matrix elements, and for each of them the two sets of phase shift differences (see [8] for a more detailed discussion). The measurements for both left- and right-elliptically polarized light having approximately equal magnitudes of the Stokes parameters do not give any new information. But a measurement with linearly polarized light does give additional information and allows the reduction of the number of possible sets of solutions to two. Indeed, using the parameters extracted from the measurement with elliptically polarized light, we calculated the angular distributions for linearly polarized light and compared them with the corresponding experimental angular distributions. Only one set of ratios of dipole matrix elements correctly reproduces the measured angular

distribution (see Fig. 1a). But in that way we could not distinguish between the two sets of the phase shift differences. The single set can be obtained by fitting the CDAD with these parameters. Unfortunately, our set of data does not allow the determination of CDAD because the opposite elliptical light polarizations contain also the linearly polarized components characterized by different angles λ . As a result, the difference between the two measured ADP's contains always a sum of CDAD and LDAD which does not allow the resolution of the ambiguity in defining the set of phase shift differences. Then the only way to select a single solution is by comparing with corresponding theoretical values. In Table I we compare the two sets extracted from the experiment, with the theoretical values calculated in the RPA approximation described in [24]. The comparison between the experimental and theoretical phase shift differences shows that set 1 is a correct solution. The situation at all other photon energies is similar.

We performed measurements at five photon energies in the region of the photoionization cross section maximum, which for the first time allowed the probing of the shape resonance mechanism unambiguously. For that purpose we need to calibrate our matrix elements. Since our ADP's are not absolute but relative, we can derive from our experimental data only the ratios of the dipole matrix elements. On the other hand, there are the data for the absolute cross section obtained in [21]. Using them, we can derive also the absolute values of the matrix elements. After that it is straightforward to calculate the partial photoionization cross sections. Since the matrix elements and phase shift differences obtained with left- and right-elliptically polarized light are not identical, we took the mean values for these two polarizations. The results of such a procedure are shown in Fig. 2a together with theoretical data. The cross section corresponding to the $2\sigma_g \rightarrow \varepsilon f \sigma_u$ transition gives the dominant contribution around the maximum, in accord with the general

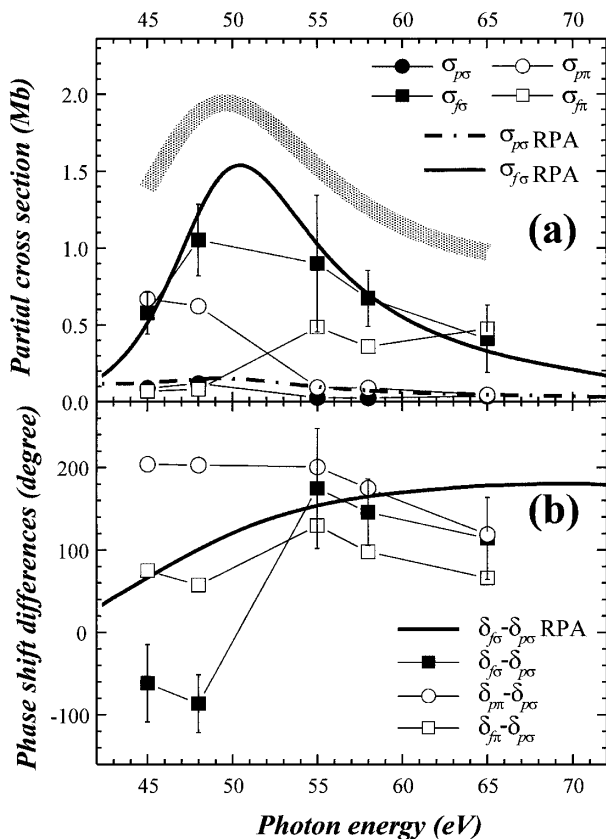


FIG. 2. (a) Partial cross sections deduced from the experiment and calculated in the RPA. The total cross section of [21] used for normalization of experimental data is also shown by the shaded line. (b) Phase shift differences (without the Coulomb phases) deduced from the experiment and calculated in the RPA. Experimental points correspond to the mean values for two elliptical polarizations; the error bars are the sum of the fitting errors for two polarizations.

prediction of Dehmer and Dill [17]. Simultaneously, the phase shift difference ($\delta_{f\sigma} - \delta_{p\sigma}$) shown in Fig. 2b is increasing approximately by π , as it must be in the resonance (provided there is no resonance in the $2\sigma_g \rightarrow \varepsilon p\sigma_u$ channel). There is a qualitative agreement between the experimentally deduced values and the results of our *ab initio* RPA calculations. The RPA cross sections in Fig. 2a were multiplied by a scaling factor 0.72 to take into account the transition of intensity to two-electron processes [21]. The cross sections for the $2\sigma_g \rightarrow \varepsilon\sigma_u$ and $2\sigma_g \rightarrow \varepsilon\pi_u$ channels published in [23] agree reasonably well with our experimentally deduced values.

In conclusion, we have measured the ADP's for the $2\sigma_g$ shell of fixed-in-space N_2 molecules by the angle-resolved electron-ion coincidence technique using elliptically and linearly polarized light. The set of measured data was sufficient for extracting the ratios of dipole matrix elements and phase shift differences corresponding to four main continuum channels, $\varepsilon p\sigma_u$, $\varepsilon f\sigma_u$, $\varepsilon p\pi_u$, and $\varepsilon f\pi_u$, assuming the validity of a single-particle description. By normaliza-

tion to the experimentally measured partial cross section it was possible to deduce also the absolute values of the matrix elements. We showed that the main contribution to the photoionization cross section in the resonance is given by the $f\sigma_u$ partial wave, with the phase shift difference ($\delta_{f\sigma} - \delta_{p\sigma}$) increasing in that region by approximately π radians. This is the most direct confirmation of the general theoretical picture of the σ^* shape resonance given in [17].

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