# SPIN POLARIZED PHOTOELECTRONS FROM $CO_2$ AND $N_2O$

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The photoelectrons emerging from unpolarized $CO_2$ and $N_2O$ molecules exposed to circularly polarized synchrotron radiation are spin polarized After a brief description of the apparatus the polarizations measured at the ionization threshold are presented and compared. in the case of $CO_2$, with a calculated. in an ab initio theory obtained value Using the spin density matrix formalism a general expression for the spin polarization as a function of the dipole matrix elements is presented

One of the novel results in the interactions of photons with atoms and solid states is the experimental evidence for spin polarization of photoelectrons produced by circularly polarized light (called Fano effect [1], for a summary see ref. [2]). Such studies of spin polarization, which exists due to the influence of the spin—orbit interaction on the ground, ionic or continuum states, give information on details of the photoionization process (partial cross sections for transitions into different energy-degenerate sub-continua [3]) which cannot be obtained by other experimental methods.

First studies with molecules [4] did not yield any polarization of photoelectrons because the fine structure splittings of the spin—orbit interaction have probably not been resolved. The present paper reports on the first spin polarization values measured in the photoionization of molecules. $CO_2$ and $N_2O$ have been selected because of the existence of an orbitally degenerate state at the ionization threshold showing a spin—orbit splitting [5—7] that could be resolved in the experiment.

These molecules have their ionization threshold in the VUV where conventional methods for producing circularly polarized radiation break down. Such polarization experiments can, however, be performed with the radiation emitted by a synchrotron into directions above and below the synchrotron plane, since this radiation contains a large fraction of circular polarization.

A schematic diagram of the apparatus built at the 2 5 GeV synchrotron in Bonn is shown in fig. 1. A 10 m normal-incidence monochromator with a plane holographic grating (4960 lines/mm) and a concave mirror which produces an image of the electron beam in the exit slit has been built. The radiation coming from the electron beam is cut off in vertical direction by an aperture which is movable up and down for selecting radiation of left or right circular polarization. The size of the electron beam determines the resolution of the monochromator the bandwidth of the radiation coming through the 1 5 mm exit slit has been measured to be 0 05 nm using a second VUV monochromator for calibration. The polarized radiation passes through the molecular beam and is analyzed by the arrangement shown in fig. 1. The degree of circular polarization [8] of the radiation emitted into an angular range from 1 to 3.5 mrad vertical with respect to the synchrotron plane has been determined to be 0.83 ± 0.03 in the wavelength range between 89 and 97 nm

The photoelectrons produced are extracted by an electric field independently of their direction of emission,
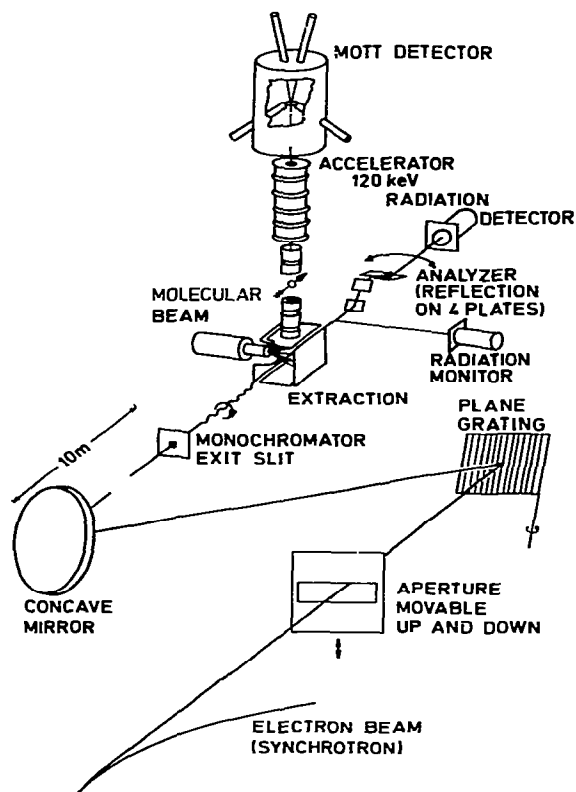
Fig 1. Schematic diagram of the apparatus.

focused by electron optical components and accelerated to 120 keV for spin polarization analysis in a Mott detector [3]. The first polarization values of photoelectrons obtained from Xe atoms using this apparatus as well as more details of the experimental arrangement are published elsewhere [9].

The main disadvantage of this photoionization procedure is given by the fact that all electrons produced are extracted by an electric field of about 30 V/cm. Because the target (section of radiation and molecular beam) has a size of about 5 mm, all photoelectrons have an energy spread of about 15 eV. Therefore the use of a differential electron spectrometer in order to resolve spin—orbit fine structure splittings (20 meV) would be nonsensical. For an angle and kinetic energy resolved analysis of the spin polarization (as performed in ref. [10] using unpolarized radiation) the intensity of the circularly polarized synchrotron radiation ($10^9$ photons/s) is two orders of magnitude too low.

The spin polarization and the intensity of the photoelectrons measured are thus average values corresponding to all molecular orbitals reached by the photon energy. The measurements on $CO_2$ and $N_2O$ have been performed directly at the ionization threshold in order to separate optically the fine structure splitting of the ion ($^2\Pi_{3/2g}$, $^2\Pi_{1/2g}$).

In the upper and the lower part of fig. 2 the experimental results of the photoelectron intensity (circles) and spin polarization (horizontal error bar: bandwidth of the radiation used, vertical error bar: single statistical error of the spin polarization analysis) are shown for $CO_2$. Because the position of the zero point of our wavelength scale is only known within an uncertainty of about 1 nm, whereas the difference of two wavelengths has the accuracy of 0.01 nm, our scale has been calibrated by comparison of our photoelectron intensity with the total ion current measured in ref. [5] (dotted line in the upper part of fig. 2). The differential photoelectron spectrum measured in
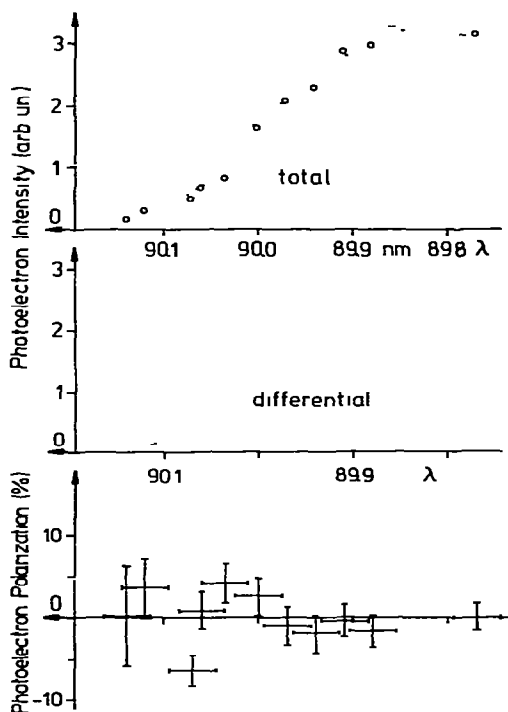
Fig 2. Photoionization of $CO_2$ at the threshold Upper part measured photoelectron intensity (circles. this work. dotted line. ref [5]) Middle part differential photoelectron spectrum given by ref [5]. Lower part measured spin polarization of photoelectrons.
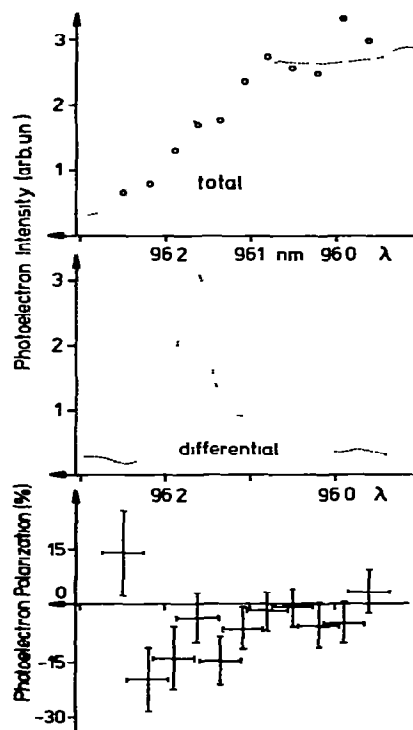
Fig 3 Photoionization of $N_2O$ at the threshold Upper part measured photoelectron intensity (circles, this work; dotted line, ref. [11]) Middle part differential photoelectron spectrum given by ref [7]. Lower part measured spin polarization of photoelectrons

ref [5] is drawn in the middle of fig 2 in order to show the spin—orbit fine structure splitting of the $CO_2^+$ ion At the foot of the $^2\Pi_{3/2g}$ peak the spin polarization has been measured to be $-6.6 \pm 2.0\%$.

Fig. 3 shows the results obtained on $N_2O$ The photoelectron intensity measured is compared with the results of ref [11] (upper part), while in the middle the differential photoelectron spectrum measured in ref. [7] is shown The spin polarization (lower part) shows also negative values at the foot of the $^2\Pi_{3/2}$ peak, but the polarization peak at $N_2O$ seems to be higher and broader than in the case of $CO_2$.

For a theoretical discussion of the process investigated, we shall adopt a one-particle approximation and consider only dipole transitions We assume that the Born—Oppenheimer approximation can be used for calculating all transition matrix elements, and that either Hund's case (a) or (b) is applicable We therefore may classify states according to $\Lambda$ and $\Sigma$, the projection of orbital and spin angular momentum on the molecular axis. We neglect vibrations of the molecule, because the (0,0,0) transition is the lowest one observed [5,7] Any influence of the reported hot band occurring in the spectrum of $N_2O$ has not been taken into account, thus neglecting the influence of a vibrational angular momentum, which could arise from an excitation of a vibrational quantum of the bending vibration.

The highest occupied molecular orbital for $CO_2$ and $N_2O$ is of $\pi_g$-type, filled with 4 electrons, thus giving rise to a $^1\Sigma_g$ ground state. Since we have no center of inversion in $N_2O$, the quantum number g is only approximate in this case. If we couple spin and orbital angular momentum, the resulting molecular orbitals may be labelled by irreducible representations of the $D_{\infty h}$ or $C_{\infty v}$ double group In order to discuss both cases simultaneously, we subsequently drop the indices g and u, keeping in mind that the selection rule g—u holds rigorously for dipole transitions in the case of $CO_2$.

Classifying with respect to the molecular double group, we have spin orbitals of $e_{1/2}$ and $e_{3/2}$ type, both doubly occupied and separated by the fine structure splitting of the lowest state of the ion, which has been resolved in our experiment, that means, that all transitions at threshold start from the $e_{3/2}$ molecular orbital and yield a $\Pi_{3/2}$ ion state. We may determine the irreducible representation of the wavefunction of the outgoing electron by group theoretical techniques [12], looking for all molecular orbitals that can be reached from an $e_{3/2}$ orbital by a dipole transition and may couple to a $\Pi_{3/2}$ ion core. Firstly we study the case that the direction of the incoming circularly polarized $\sigma^+$ light is collinear with the molecular axis. In fig. 4, the allowed transitions are shown by full arrows. The components of the irreducible representation $e_j$ are denoted by $e \pm j$. Secondly, in order to take into account the random orientation of the molecular axis in the experiment, we define two coordinate systems, a laboratory system $(\vartheta, \varphi)$ and a molecular-fixed $(\vartheta', \varphi')$ system. The molecular system with the internuclear axis as polar axis is obtained from the laboratory system ($z$ axis is the direction of photon spin) by three successive rotations with Euler angles $(\alpha, \beta, \gamma)$. Spherical harmonics written in the laboratory system may be expressed in the other frame by applying the rotation matrix [13],

$$Y_{l,m}(\vartheta, \varphi) = \sum_{m'} D^{l*}_{m,m'}(\alpha, \beta, \gamma) Y_{l,m'}(\vartheta', \varphi').$$ (1)

To calculate the polarization of the emitted photoelectrons in the direction of the incident light beam, we firstly transform the dipole operator defined in the laboratory frame to the molecular system. Then we calculate the components of the spin polarization vector and integrate over $(\vartheta', \varphi')$, because all photoelectrons produced have been extracted by an electric field independently of their direction of emission. Finally, we take the projection of the polarization on the $z$ axis, and integrate it over the Euler angles in order to determine the total polarization for an ensemble of randomly oriented molecules, in the approximation that molecular rotation is slow [14].

By the use of (1), the dipole operator for right-handed circularly polarized light is transformed to the molecular frame

$$D = r \sin \vartheta \, e^{i\varphi} = -(\tfrac{8}{3}\pi)^{1/2} r Y_{1,1}(\vartheta, \varphi) = k Y_{1,1}(\vartheta, \varphi),$$

$$D' = k e^{i\alpha} [\tfrac{1}{2}(1 + \cos\beta) e^{i\gamma} Y_{1,1} - 2^{-1/2} \sin\beta \, Y_{1,0} + \tfrac{1}{2}(1 - \cos\beta) e^{-i\gamma} Y_{1,-1}].$$

Starting from the $e - 3/2$ orbital, we now have two more allowed transitions, corresponding to the newly introduced terms $Y_{1,0}$ and $Y_{1,-1}$ in the dipole operator. They are shown in fig. 4 by dotted and dashed arrows, respectively. The $e - 5/2$, $e - 3/2$ and $e - 1/2$ continuum orbital are reached. Neglecting the possibility of spin flips, the matrix elements for these transitions are

$$A_{-1/2}(\alpha, \beta, \gamma) = \langle F_\sigma(r, \vartheta') \!\downarrow | e^{i\alpha} \tfrac{1}{2}(1 + \cos\beta) e^{i\gamma} k Y_{1,1} | F(r, \vartheta') e^{-i\varphi} \!\downarrow \rangle = \tfrac{1}{2} e^{i\alpha}(1 + \cos\beta) e^{i\gamma} B_\sigma,$$

$$A_{-3/2}(\alpha, \beta, \gamma) = \langle F_\pi(r, \vartheta') e^{-i\varphi'} \!\downarrow | -2^{-1/2} e^{i\alpha} \sin\beta \, k Y_{1,0} | F(r, \vartheta') e^{-i\varphi'} \!\downarrow \rangle = -2^{-1/2} e^{i\alpha} \sin\beta \, B_\pi,$$ (2)

$$A_{-5/2}(\alpha, \beta, \gamma) = \langle F_\delta(r, \vartheta') e^{-2i\varphi'} \!\downarrow | e^{i\alpha} \tfrac{1}{2}(1 - \cos\beta) e^{-i\gamma} k Y_{1,-1} | F(r, \vartheta') e^{-i\varphi'} \!\downarrow \rangle = \tfrac{1}{2} e^{i\alpha}(1 - \cos\beta) e^{-i\gamma} B_\delta,$$
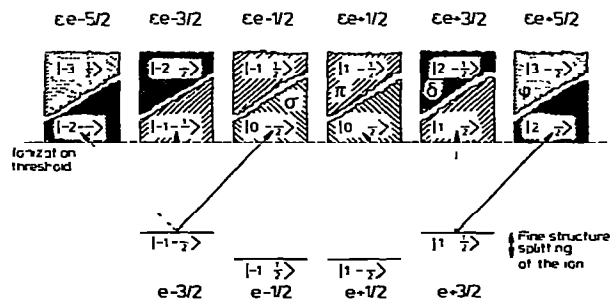


Fig. 4. Continuum orbitals reached from the highest occupied molecular orbitals of $CO_2$ and $N_2O$. $e \pm j$ denote the irreducible representations for the ground state molecular orbitals, $\epsilon e \pm j$ of the continuum orbitals. The kets give the $\Lambda$, $\Sigma$ quantum numbers. Full arrows: transitions with circularly polarized $\sigma^+$ light; dashed arrows: transitions with circularly polarized $\sigma^-$ light; dotted arrows: transitions with linearly polarized $\pi$ light, neglecting spin flip transitions.

where $F_\Lambda(r, \vartheta')e^{-i\Lambda\varphi'}\downarrow$ denote the continuum wavefunction, $|\Lambda, -1/2\rangle$, and $F(r, \vartheta')e^{-i\varphi'}\downarrow$ the wavefunction of the $|-1, -1/2\rangle$ ground state orbital $B_\Lambda$ is the dipole matrix element for a transition between the two states expressed in the molecular frame.

The total wavefunction of the electrons having made the transition from the $e - 3/2$ orbitals is given by the coherent superposition

$$A_{-1/2}|\epsilon, 0, -1/2\rangle + A_{-3/2}|\epsilon, -1, -1/2\rangle + A_{-5/2}|\epsilon, -2, -1/2\rangle .\tag{3}$$

The matrix elements for the transitions from the initial state $e + 3/2$ are calculated in a similar way. Using the density-matrix formalism [2] and adding the density matrices which are related to the transitions from both ground state orbitals, we can evaluate the polarization vector by using the relations

$$P_{z'} = \text{tr}\,\rho\,\sigma_{z'}/\text{tr}\,\rho , \qquad P_{x'} = \text{tr}\,\rho\,\sigma_{x'}/\text{tr}\,\rho , \qquad P_{y'} = \text{tr}\,\rho\,\sigma_{y'}/\text{tr}\,\rho .\tag{4}$$

We find

$$\rho_{11} = \tfrac{1}{4}(1 - \cos\beta)^2 B_\sigma^2 + \tfrac{1}{4}(1 + \cos\beta)^2 B_\delta^2 + \tfrac{1}{2}\sin^2\beta B_\pi^2 ,$$

$$\rho_{22} = \tfrac{1}{4}(1 + \cos\beta)^2 B_\sigma^2 + \tfrac{1}{4}(1 - \cos\beta)^2 B_\delta^2 + \tfrac{1}{2}\sin^2\beta B_\pi^2 ,\tag{5}$$

$$\rho_{12} = \rho_{21} = 0$$

All interference terms vanish with the integration over $(\vartheta', \varphi')$ due to the orthogonality of the $\varphi'$-dependent parts of the wavefunctions

The polarization is then given by

$$P_{x'} = P_{y'} = 0 .$$

$$P_{z'} = \frac{\rho_{11} - \rho_{22}}{\rho_{11} + \rho_{22}} = \frac{(B_\delta^2 - B_\sigma^2)\cos\beta}{\tfrac{1}{2}(B_\sigma^2 + B_\delta^2)(1 + \cos^2\beta) + \sin^2\beta B_\pi^2} .\tag{6}$$

The polarization in the laboratory frame is obtained by multiplying by $\cos\beta$ (which is equivalent to a transform of the polarization vector with $D_{00}^1$) and integrating the numerator and the denominator separately over $(8\pi^2)^{-1}\sin\beta\,d\alpha\,d\beta\,d\gamma$

$$P_z = \tfrac{1}{2}(B_\delta^2 - B_\sigma^2)/(B_\sigma^2 + B_\delta^2 + B_\pi^2)\tag{7}$$

The cross sections for photoionization into the different partial continua have been estimated by a discrete basis-set calculation Spin–orbit coupling corrections have not been included. Starting from a self-consistent-field wavefunction for $CO_2$, a single excitation CI calculation has been done [15], leading to a discrete pseudospectrum of energies and oscillator strengths, from which a continuous oscillator strength distribution has been constructed. Details of the method are published elsewhere [16].

The photoionization cross sections for $CO_2$ at the Koopmans' theorem ionisation potential of 14.7 eV have been calculated to be 1 5 Mb. 1 Mb and 0 1 Mb for ionization to a $\sigma$, $\pi$ or $\delta$ continuum state, respectively, yielding a spin polarization of $-27\%$, calculated with (7) This value shows the same sign and order as the measured polarization of $-7\%$.

Spin flips, which occur due to spin–orbit coupling in the continuum or due to a deviation from Hund's case (a), may be taken into account in a straightforward way, using wavefunctions which are linear combinations of pure $|\Lambda, \Sigma\rangle$ states and going through the same formalism It turns out, that the spin polarization is decreased by a depolarization factor that depends on the mixing coefficients of the wavefunction.

Use of symmetric top wavefunctions gives additional information, because of the possibility of resolving the contributions of various rotational levels and of the three transitions with $\Delta J = 0, \pm 1$, $J$ being the total angular momen-

tum. A summation over all possible transitions yields, however, an expression equal to (7). The formulas for a detailed analysis have been derived, but their presentation is beyond the scope of this paper.

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