

## LETTER TO THE EDITOR

# Spin-polarised photoelectrons produced from CH<sub>3</sub>Br molecules by unpolarised and circularly polarised VUV radiation

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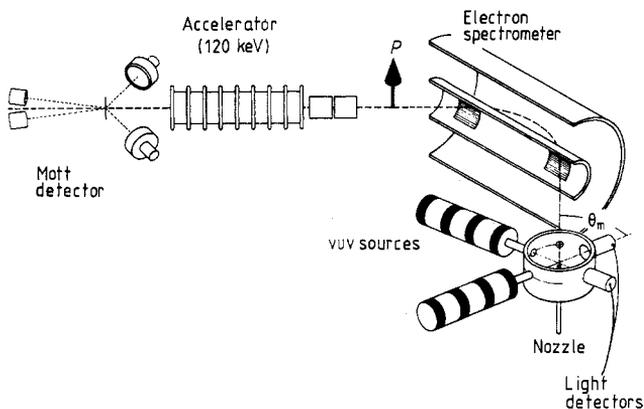
**Abstract.** It has been experimentally verified for CH<sub>3</sub>Br that spin-polarised photoelectrons can be ejected from unoriented molecules if the radiation is circularly polarised or even unpolarised. The polarisation values and the experimental data of the asymmetry parameter  $\beta$  are discussed by use of Cherepkov's formulae.

One of the topics of atomic photoionisation is that photoelectrons ejected from unpolarised atoms can be spin polarised, if the VUV radiation is circularly polarised or even unpolarised (for a review see Heinzmann 1980). Such studies of spin polarisation which arises from the influence of the spin-orbit interaction on the ground, ionic or continuum states give information on the details of the photoionisation process which cannot be obtained by other experimental methods. Measurements of the spin polarisation and studies of the photoionisation cross section as well as of the angular distribution of photoelectrons complement each other to yield information about photoionisation of atoms that can, in principle, be complete.

This letter reports the first experimental results for spin polarisation of photoelectrons ejected by unpolarised light from molecules. These measurements as well as studies of spin polarisation of photoelectrons produced by circularly polarised radiation and of the asymmetry parameter  $\beta$  of the angular distribution, also reported, have been performed with CH<sub>3</sub>Br. Using the equations of the general formalism for the angular distribution of photoelectrons with defined spin orientation derived for unoriented molecules by Cherepkov (1981) a short discussion is given as to which of the different experimental results complement each other.

Experiments of the spin polarisation of photoelectrons ejected by unpolarised light from unpolarised targets are hampered by the fact that the photoionisation process has to be studied resolved to the ejection angle  $\theta$ , to the photon energy, to the photoelectron energy and to the spin (Heinzmann *et al* 1979). They combine the intensity problems of photoelectron spin analysis with the difficulties of angular and energy distribution studies. A schematic diagram of the apparatus used is shown in figure 1.

The VUV radiation emerging from capillary discharge tubes yielding very intense rare-gas resonance lines (Heinzmann and Schönhense 1980) crosses the atomic beam in a region free of electric and magnetic fields. The photoelectrons produced pass through an electron spectrometer (CMA) and are accelerated to an energy of 120 keV for

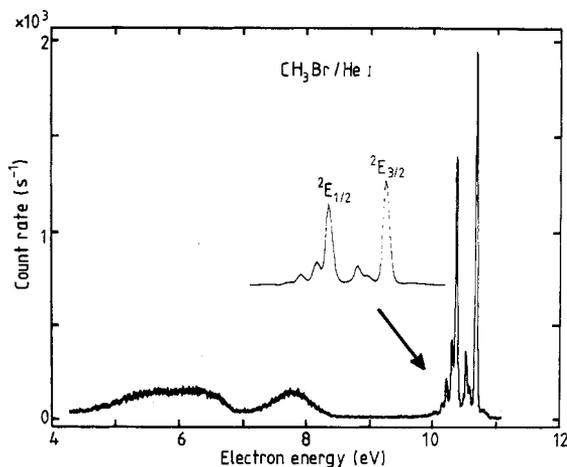


**Figure 1.** Schematic diagram of the apparatus for the measurement of  $\xi$ .

analysis of spin polarisation determined by the left-right asymmetry of the electron intensity scattered through  $120^\circ$  by the gold foil of the Mott detector (Kessler 1976). The spin polarisation  $P(\theta)$  is described by a parameter  $\xi$  (Heinzmann *et al* 1979, Cherepov 1981) which can be directly obtained from  $P$ , if the photoionisation experiment is performed at the magic angle  $\theta_m = 54^\circ 44'$  ( $\xi = 1.061P(\theta_m)$ ).

Figure 2 gives the energy spectrum of the photoelectrons from  $\text{CH}_3\text{Br}$  produced by He I radiation (58.43 nm). This spectrum which agrees with the recent results of Ragle *et al* (1970) and Karlsson *et al* (1977) shows a pronounced fine-structure splitting (320 meV) due to spin-orbit interaction corresponding to the ionic ground state  $^2E_{3/2}$  and the excited ionic state  $^2E_{1/2}(0-0)$ .

The spin polarisation parameter  $\xi$  obtained in the experiment using VUV radiation of three different wavelengths (Ar I, Ne I, He I) are given in table 1. In accordance with the corresponding results in atomic photoionisation (Heinzmann 1980), the polarisation of photoelectrons associated with the ionic fine-structure states  $^2E_{3/2}$  and  $^2E_{1/2}$



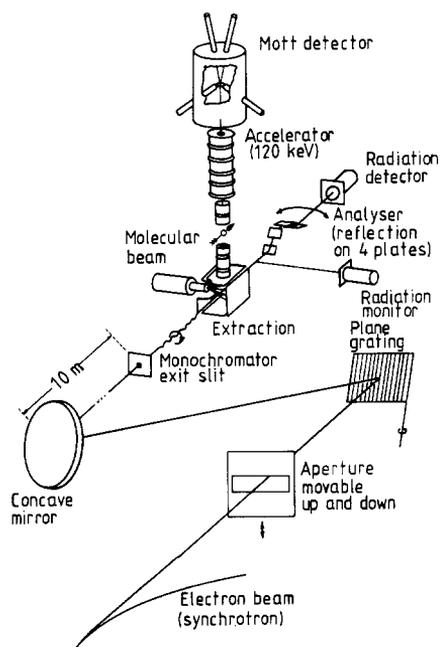
**Figure 2.** Photoelectron spectrum of  $\text{CH}_3\text{Br}$  excited with He I radiation.

**Table 1.** Experimental results for  $\xi$  and  $\beta$ .

Ionic state	Wavelength (nm)	Kinetic energy (eV)	$\xi$	$\beta$
$^2E_{3/2}$	104.82	1.28	$-0.05 \pm 0.01$	—
$^2E_{3/2}$	73.59	6.31	$-0.12 \pm 0.01$	—
$^2E_{1/2}$	73.59	5.99	$0.11 \pm 0.01$	—
$^2E_{3/2}$	58.43	10.68	$-0.11 \pm 0.01$	$1.3 \pm 0.1$
$^2E_{1/2}$	58.43	10.36	$0.08 \pm 0.01$	$1.3 \pm 0.1$

(0-0)<sup>†</sup> differs in sign, which shows the necessity of resolving the fine structure by use of the electron spectrometer. Table 1 also gives the values of the asymmetry parameter  $\beta$  obtained (for He I only) using an apparatus quite similar to that one shown in figure 1, in connection with a rotatable plane polariser (Schönhense 1980). Opposite to the spin polarisation of photoelectrons this  $\beta$  parameter has been measured within the error bars to be the same for electrons leaving the ions in the  $^2E_{3/2}$  or the  $^2E_{1/2}$  fine-structure state.

Experimental studies of the polarisation of photoelectrons produced by circularly polarised VUV radiation have been performed by use of the synchrotron radiation in Bonn. The synchrotron emission is linearly polarised in the plane of the synchrotron, but above and below the plane it is largely circularly polarised. A schematic diagram of the apparatus is shown in figure 3.

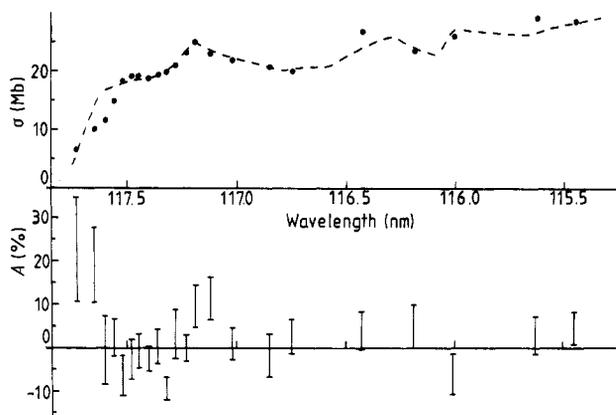
**Figure 3.** Schematic diagram of the apparatus for the measurement of  $A$ .

<sup>†</sup> All unresolved contributions due to vibronic modes different from 0-0 have been estimated to be negligibly small within our error bars.

A 10 m normal incidence monochromator with a plane grating and a concave mirror yields monochromatised radiation of a bandwidth of 0.05 nm. The radiation coming from the electron beam is cut off in the vertical direction by an aperture, which is movable up and down for selecting radiation of left- and right-handed circular polarisation. After passing through the atomic beam the circular polarisation of the radiation was analysed polarimetrically to be  $83 \pm 3\%$  for the wavelength range of interest (Heinzmann *et al* 1980a).

The photoelectrons produced were extracted by an electric field regardless of their direction of emission and accelerated to 120 keV for spin polarisation analysis in a Mott detector. Because of the electric field across the atomic beam all photoelectrons extracted have an energy spread of about 15 eV. Thus an electron spectrometer could not be used. Therefore, the ionic fine-structure splitting due to the spin-orbit interaction had to be resolved optically performing the experiment only close to the photoionisation threshold, where the ion is definitely in the ground state  $^2E_{3/2}$  only.

Using this apparatus, the polarisation of photoelectrons from  $\text{CO}_2$  and  $\text{N}_2\text{O}$  has been recently measured by Heinzmann *et al* (1980b). The experimental results on  $\text{CH}_3\text{Br}$  are given in figure 4. The wavelength dependence of the photoelectron intensity measured (points in the upper part of figure 4) is in very good agreement with the photoionisation cross section measured by Person and Nicole (1971) including the resonance structure at 117.2, 116.5 and 116.0 nm (induced very probably by autoionisation processes (Person and Nicole 1971, Baig *et al* 1981)).



**Figure 4.** Photoionisation of  $\text{CH}_3\text{Br}$ . Upper part: photoelectron intensities (points, this work) and cross section (broken curve by Person and Nicole (1971)); lower part: spin polarisation  $A$  measured.

The spin polarisation values  $A$  obtained are shown in the lower part of figure 4. The error bars represent the single statistical error of the spin polarisation analysis including the experimental uncertainty of the light polarisation; horizontal error bars of 0.05 nm, not shown in figure 4, are given by the bandwidth of the radiation used. Especially at the wavelengths of the autoionisation resonances the spin polarisation data also seem to show resonance structure (between 117.3 and 117.1 nm there is a sign change of the polarisation from  $-10\%$  to  $+10\%$ ). It is worth noting that the whole energy range shown in figure 4 corresponds to the ionic ground state  $^2E_{3/2}$  only. The second ionisation threshold (excited ionic state  $^2E_{1/2}$ ) is at 114.2 nm.

Although the formulae describing the spin polarisations and the asymmetry parameter  $\beta$  of photoelectrons in Cherepkov's letter (1981) have been derived for diatomic molecules only, they may also be used for a rough interpretation of the photoionisation data of  $\text{CH}_3\text{Br}$  (Felps *et al* 1976).

Under the assumption that the phaseshifts of the continuum wavefunctions  $\delta_{l,m_l}$  do not depend on the projection  $m_l$  of the orbital angular momentum  $l$  of the photoelectrons onto the molecular axis and under the further assumption that transitions into continuum states with  $l \geq 3$  can be neglected, Cherepkov's (1981) formulae (7)–(14) yield for the special case of the photoion in the  ${}^2E_{3/2}$  state:

$$A = \frac{1}{2}B^{-1}(D_{22}^2 - D_{00}^2 - D_{10}^2 - D_{20}^2) \quad (9')$$

$$\xi = -\frac{1}{4}B^{-1}\sqrt{\frac{3}{5}}D_{00}(D_{21} + 2\sqrt{2}D_{22}) \sin(\delta_d - \delta_s) \quad (11')$$

$$\beta = \frac{2}{7}B^{-1}[D_{21}^2 + D_{22}^2 - D_{20}^2 + \sqrt{3}D_{20}(2\sqrt{2}D_{22} - D_{21}) + 3\sqrt{2}D_{21}D_{22} - \frac{7}{5}(D_{10}^2 + D_{11}^2 + 3D_{10}D_{11}) + 7\sqrt{\frac{3}{5}}D_{00}(D_{21} + \sqrt{2}D_{22}) \cos(\delta_d - \delta_s)] \quad (8')$$

where

$$B = D_{00}^2 + D_{10}^2 + D_{11}^2 + D_{20}^2 + D_{21}^2 + D_{22}^2 \quad (12')$$

and the matrix elements  $D_{lm_l}$  and the phases  $\delta_l$  coincide with those defined by equations (13) and (14) of Cherepkov's letter.

While the spin polarisation  $A$  of the photoelectrons produced by circularly polarised radiation is a linear combination of partial cross sections (squares of matrix elements), the parameter  $\xi$  describing the polarisation of photoelectrons obtained using unpolarised light is determined by an interference term only. This is in complete accordance with the corresponding photoionisation process in atoms (Cherepkov 1974). It can easily be deduced from the formulae shown above that  $|A| \leq 0.5$  and  $|\xi| \leq \frac{3}{8}\sqrt{\frac{3}{5}} = 0.29$ .

From these upper limits of  $A$  and  $\xi$  one can see that polarisation effects in molecular photoionisation are generally a factor of about two smaller than in atomic physics. This is due to the fact that for the photoionisation of randomly oriented molecules the integration of the spin polarisation over all Euler angles yields a depolarisation factor of two (Heinzmann *et al* 1980b). Opposite to the polarisation parameters, the asymmetry parameter  $\beta$  defined by equation (8') can reach the full range of values between  $-1$  and  $+2$  as in the case of atomic photoionisation.

Using the experimental value  $\xi = -0.11$  (see table 1) and equation (11') in connection with the upper limit of 0.29 mentioned above one obtains  $|\sin(\delta_d - \delta_s)| > 0.38$ . On the other side the measured  $\beta$  value of 1.3 at the same energy can only be explained according to equation (8') if  $|\cos(\delta_d - \delta_s)| > 0.5$ . Both together yield  $0.12 < (\delta_d - \delta_s)/\pi < 0.33$ .

It is worth noting that the Coulomb phaseshift  $\sigma_d - \sigma_s$  for the corresponding kinetic energy 10.68 eV of photoelectrons is  $0.56\pi$ . This means that the phases of the continuum wavefunctions of photoelectrons from  $\text{CH}_3\text{Br}$  are strongly shifted with respect to the Coulomb phaseshifts.

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