LETTER TO THE EDITOR

Determination of partial photoionisation cross sections of methyl bromide in the first autoionisation range by use of spin polarisation photoelectron spectroscopy

F Schäfers†, M A Baig‡ and U Heinzmann†

† Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-1000 Berlin 33, West Germany
‡ Physikalisches Institut der Universität Bonn, Nussallee 12, D-5300 Bonn 1, West Germany

Abstract. Using recent experimental data on photoelectron spin polarisation combined with the high-resolution spectrum of methyl bromide, which has also been recently reported, the partial photoionisation cross sections for the ionisation of CH_3Br from the 4π ground-state orbital into the energy degenerate continua $\varepsilon\sigma$, $\varepsilon\pi$ and $\varepsilon\delta$ have been determined separately. Quantitative results, obtained for the autoionising resonances between 116 and 118 nm, are reported and discussed.

Experimental work in recent years has shown that spin polarisation of photoelectrons is a rule rather than an exception for most atomic and molecular systems (for a review see Heinzmann 1980a). One way to obtain polarised photoelectrons is the Fano effect, a spin polarisation transfer from the ionising light (circularly polarised radiation) to the photoelectrons, produced even if they are extracted by an electric field regardless of their direction of emission. These studies were hampered by the fact that most atoms and molecules have their ionisation threshold in the VUV where conventional methods for producing circularly polarised radiation break down. Nevertheless, it was possible to perform such experiments using synchrotron radiation from the 2.5 GeV Bonn electron accelerator where the light emitted above and below the synchrotron plane has been found to be largely circularly polarised (Heinzmann *et al* 1982).

In molecular photoionisation, such measurements have been performed with CO_2 and N_2O (Heinzmann *et al* 1980) and recently with CH_3Br (Heinzmann *et al* 1981). Very new spin polarisation results of photoelectrons emitted from iodine and bromine molecules by unpolarised VUV radiation have just been reported (Schönhense *et al* 1982). The first spin polarisation calculations were performed for CO_2 by Hess (Heinzmann *et al* 1980). For diatomic molecules, a general theoretical treatment of photoelectron spin orientation was carried out by Cherepkov (1981a, b). In these theoretical papers it was verified that the existence of a spin polarisation as well as the spin density matrix formalism expressing the spin polarisation as a function of dipole matrix elements and the phaseshift differences are both quite similar to the case of atomic photoionisation.

In atomic photoionisation spin polarisation data and the results of photoelectron intensity spectroscopy complement each other. One thus obtains a complete set of quantum mechanical data about the photoionisation process studied, i.e. bound–free dipole matrix elements and phaseshift differences of the continuum wavefunctions (Heinzmann 1980b). Recently a high-resolution absorption spectrum of CH_3Br was reported in the wavelength range 1100–1250 Å (Baig *et al* 1982). Thus the partial photoionisation cross sections (squares of dipole matrix elements) could be determined separately for the first time for molecular photoionisation by combining this intensity spectrum with the spin polarisation data. It is the purpose of this letter to report this for CH_3Br; since the phaseshift difference of the continuum wavefunctions were also obtained recently (Heinzmann *et al* 1981), this is a further important step towards a 'complete' molecular photoionisation experiment.

The high-resolution spectrum of methyl bromide in the wavelength range 110 to 125 nm has been studied (Baig *et al* 1982) by using the 0.5 GeV Bonn synchrotron radiation as a background source. A description of the apparatus and the experimental techniques employed in obtaining the spectra is given elsewhere (Connerade *et al* 1980, Baig *et al* 1981). In brief, they were recorded in the first order of a 3 m normal incidence vacuum spectrograph equipped with a 5000 lines/mm holographic grating yielding a resolution of ±0.0005 nm. The main advantage of this spectroscopic technique is that the optical resolution is two orders of magnitude higher than the radiation bandwidth obtainable in spin polarisation photoelectron spectroscopy. Therefore, this is the best method of identification for absorption resonances. The disadvantage is the inaccurate determination of an absorption background lying under a resonant absorption structure or, in other words, the difficulty of finding the absolute position of the zero line in the densitometer trace of a spectrograph plate. Furthermore, absorption spectroscopy is more suited to the determination of Rydberg series limits than to that of continuum thresholds because, in molecular photoionisation, these can be different from each other in contrast to the atomic case.

On the other hand the spin polarisation technique has other advantages and disadvantages which really complement those of optical absorption spectroscopy. Experimental studies of the polarisation of photoelectrons produced by circularly polarised synchrotron radiation in Bonn used a 10 m normal incidence monochromator for radiation emitted out of the plane of the synchrotron. Up to 10^{10} photons/s have been obtained with a bandwidth of 0.08 nm and a degree of circular polarisation of about 80% (Heinzmann *et al* 1982). The photoelectrons produced at the molecular beam 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. The details of the experimental arrangement are described elsewhere (Heinzmann 1980b, Schäfers *et al* 1982). The main disadvantage of any spin polarisation analysis is that one looses an intensity factor of about 10^3 in the spin detector. Therefore, all spin polarisation values have uncertainties of a few per cent due to statistical errors in the electron counting technique. An advantage of spin polarisation measurements is that, by definition, they give absolute data. Furthermore, the disadvantage that one does not get a very high wavelength resolution for resonance structures in practice, is partly offset by the fact that structures in spin polarisation resonances are always much broader than in the corresponding cross section resonances as discussed in the literature (Heinzmann and Kessler 1978, Cherepkov 1980).

The technique of spin polarisation spectroscopy within autoionising resonances is a tool to identify the nature of the resonant autoionising states and to determine their

angular momentum quantum numbers. This has been demonstrated for the first time in the atomic photoionisation in Tl (Heinzmann *et al* 1975, 1976) and is illustrated here for CH_3Br.
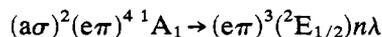
The photoionisation process studied is due to the excitation of the 4π lone-pair electron localised on a bromine site to the continuum

$$(a\sigma)^2(e\pi)^4\,^1A_1 \to (e\pi)^3(^2E_{3/2})\varepsilon\lambda$$
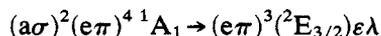
with

$$\lambda = 0, 1, 2 \qquad (\sigma, \pi, \delta)$$

or via autoionisation

$$(a\sigma)^2(e\pi)^4\,^1A_1 \to (e\pi)^3(^2E_{1/2})n\lambda$$

into the continuum. Between the first two ionisation thresholds $^2E_{3/2}$ (0, 0) and $^2E_{1/2}$ (0, 0), there is a pronounced autoionisation resonance region as known from the atomic photoionisation (see, for example, Heinzmann 1980b). In CH_3Br Baig *et al* (1982) have recently resolved these autoionisation resonances and performed an MQDT analysis.

We have convoluted this high-resolution spectrum with a monochromator transmission profile corresponding to the 0.08 nm bandwidth used in the spin polarisation spectroscopy work. The resulting shape of the resonance profiles in connection with the absolute cross section of Person and Nicole (1971) enables one to determine the absolute total photoionisation cross section in the autoionisation range shown in figure 1 as the uppermost curve. It is worth noting that the shape of the pronounced
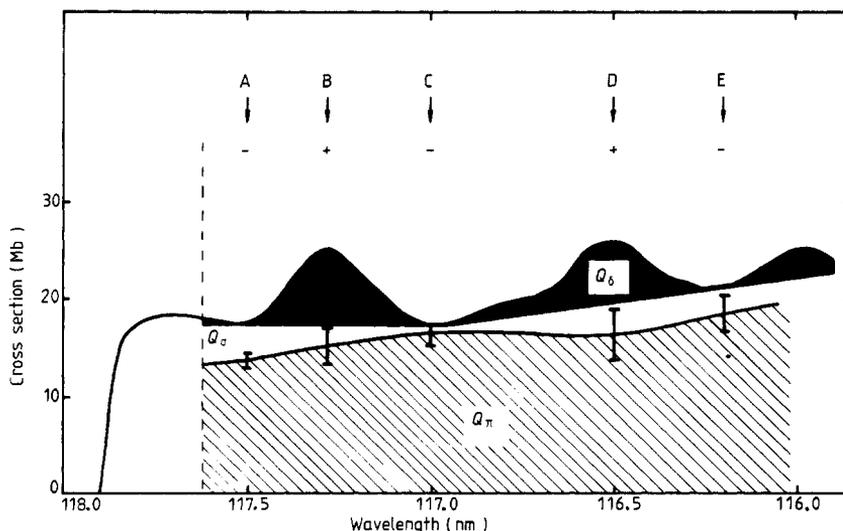

Figure 1. Partial photoionisation cross sections Q_π (dashed), Q_σ (white) and Q_δ (black) as functions of the wavelength in the first autoionisation range of CH_3Br. The vertical broken line indicates the position of the first photoionisation threshold (Baig *et al* 1982). The signs $-$ and $+$ show the signs of the spin polarisation values measured for photoelectrons emitted at the wavelengths A–E where the total cross section has its minima and maxima. The error bars due to the uncertainty in spin polarisation data indicate the uncertainty for Q_σ and Q_π.

resonance structure with minima and maxima indicated by the positions A–E in figure 1 is in quantitative agreement with the corresponding photoelectron intensity structures (Heinzmann *et al* 1981). One first consequence is, however, that the wavelengths corresponding to the photoelectron values have to be shifted by about 0.1 nm to longer wavelengths due to the comparison with the new highly resolved resonance data of Baig *et al* (1982). It is not surprising that figure 1 does not show the microstructure within the resonance profiles shown originally because of the convolution procedure mentioned above.

The signs of the spin polarisation results measured for photoionisation of CH_3Br using right-handed circularly polarised radiation at the minima and the maxima (positions A–E) are also shown in figure 1. It is typical that all minima are connected with photoelectrons of negative spin polarisation where photon spin and electron spin are antiparallel whereas in the maxima it is the opposite. This can be explained by the corresponding polarisation formula (Heinzmann *et al* 1980)

$$P = \tfrac{1}{2} \frac{P_\sigma Q_\sigma + P_\pi Q_\pi + P_\delta Q_\delta}{Q_\sigma + Q_\pi + Q_\delta} \tag{1}$$

where P_σ, P_π and P_δ are the spin polarisation values of the electrons in the partial continua $\varepsilon\sigma$, $\varepsilon\pi$ and $\varepsilon\delta$, respectively, and Q_σ, Q_π and Q_δ are the corresponding partial cross sections for the transitions into the energy degenerate partial continuum orbitals. Equation (1) describes the polarisations of three final states superimposed incoherently (they are orthogonal to each other) after weighting them with the partial cross sections. The factor $\tfrac{1}{2}$ comes from the fact that the photoionisation process is studied at randomly oriented molecules due to integration of $P(\Theta)$ over all Euler angles (Heinzmann *et al* 1980).

On the assumption that the influence of the spin–orbit interaction on the continuum wavefunctions is negligible, which is a good approximation for CH_3Br, CO_2 or N_2O but not for molecules with heavier atoms such as CH_3I (Dagata *et al* 1981) or I_2 (Schönhense *et al* 1982) one obtains (Heinzmann *et al* 1980):

$$P_\sigma = -1 \qquad P_\pi = 0 \qquad P_\delta = +1. \tag{2}$$

From equations (1) and (2) one has

$$P = \tfrac{1}{2} \frac{Q_\delta - Q_\sigma}{Q_\delta + Q_\sigma + Q_\pi}. \tag{3}$$

In a conventional photoionisation or absorption experiment one measures the total cross section $Q = Q_\sigma + Q_\pi + Q_\delta$ since one cannot distinguish between transitions into different continua. A measurement of the polarisation yields, however, information on the individual channels, as one can immediately see from equation (3). If, for example, with $Q_\pi = 0$, Q_σ or Q_δ dominates, the polarisation P tends to -0.5 or $+0.5$, respectively. It is worth noting that Q_π brings only a depolarisation effect in the denominator of equation (3) because of $P_\pi = 0$. The positive values of the spin polarisation at the resonance maxima B and D and the negative polarisation values at the minima A, C and E, where destructive interference between autoionising and continuum states takes place, show that the autoionisation resonances have δ character.

Quantitatively, using the absolute new cross section results (figure 1) and the spin polarisation data one obtains the partial photoionisation cross sections Q_π, Q_σ and

Q_δ separately at the five positions A–E. This is shown in table 1 and figure 1, including errors bars due to the uncertainty of the polarisation values. It has been assumed that Q_σ and Q_π do not show a pronounced structure opposite to Q_δ between the five positions A–E, if the resolution is not much better than the 0.08 nm used. Therefore figure 1 shows dashed and white areas for Q_π and Q_σ, respectively, additional to the black area for the Q_δ partial cross section.

Table 1. Experimental values of the spin polarisation of photoelectrons and of the partial and total photoionisation cross sections for CH_3Br at the wavelengths A–E where the total cross section has its minima and maxima.

Position	Wavelength (nm)	Polarisation (%)	Q_σ (Mb)	Q_π (Mb)	$Q_\sigma + Q_\pi$ (Mb)	Q_δ (Mb)	Q_δ^0 (Mb)	$Q_\sigma + Q_\pi + Q_\delta$ (Mb)
A	117.5	-10 ± 2	3.4 ± 0.8	13.6 ∓ 0.8	17.0	0		17.0
B	117.3	$+12 \pm 5$	2.0 ± 2.0	15.3 ∓ 2.0	17.3	8.0	0.2	25.3
C	117.0	-2 ± 5	0.7 ± 1.8	17.0 ∓ 1.8	17.7	0		17.7
D	116.5	$+5 \pm 5$	3.5 ± 2.5	16.3 ∓ 2.5	19.8	6.1	0.16	25.9
E	116.2	-6 ± 5	2.5 ± 2.0	18.6 ∓ 2.0	21.1	0		21.1

Assuming the first two autoionisation resonances to be isolated the shape of the resonance structure measured by Baig *et al* (1982) can be fitted as a Fano-type resonance with the following resonance parameters: resonance wavelengths 117.31 and 116.58 nm, resonance widths $\Gamma = 0.25$ and 0.21 nm and q values 6.2 and 6.0, respectively. In the maxima of the resonance cross section one obtains

$$Q_\delta = Q_\delta^0 (1 + q^2) \tag{4}$$

where Q_δ^0 is the undisturbed partial photoionisation cross section if there is no coupling between continuum and autoionising states. Using equation (4), the q values obtained and the results of Q_δ given in table 1 one obtains

$$Q_\delta^0 = 0.2 \text{ Mb} \qquad \text{for position B}$$

and

$$Q_\delta^0 = 0.16 \text{ Mb} \qquad \text{for position D.}$$

These values are also listed in table 1 in a separate column.

One surprising result shown in figure 1 is that Q_π is larger than Q_σ. For comparison a single-excitation CI calculation starting from self-consistent-field wavefunctions for CO_2 (Buenker and Peyerimhoff 1974) yields 1.5, 1 and 0.1 Mb respectively as partial cross sections for ionisation to σ, π or δ continuum states at the Koopman's theorem ionisation potential of 14.7 eV (Heinzmann *et al* 1980). *Ab initio* calculations, especially for CH_3Br, would be necessary to describe these relations between Q_σ, Q_π and Q_δ or between the corresponding dipole matrix elements.

There is another open question from the experimental point of view. Baig *et al* (1982) have found a series limit in photoabsorption at 117.623 nm, shown in figure 1 as a vertical broken line, and have also interpreted it as a photoionisation threshold. On the other hand there is no doubt that photoelectrons have also been obtained between 117.6 and 117.9 nm indicated by the cross section curve in figure 1 beyond the series limit shown. This may be due to an excited molecular state producing so called 'hot' electrons.

To resolve this discrepancy and decide what type of state is involved at the photoionisation threshold of CH_3Br between 117.6 and 117.9 nm, the new technique of spin polarisation threshold electron spectroscopy (Heckenkamp *et al* 1983) could probably be applied. Further work with the new German dedicated storage ring for synchrotron radiation, BESSY, where two orders of magnitude more intensity of circularly polarised synchrotron radiation are available will enable us to continue spin-resolved photoelectron spectroscopy which will also be emission angle resolved. The results of this letter show that halogen compounds are very interesting examples in the search for a complete quantum mechanical parameter set to describe the molecular photoionisation process studied.

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