Angle- and spin-resolved photoelectron spectroscopy of the $p\pi$ outer valence shell of HBr molecules

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Abstract. Using circularly polarized synchrotron radiation, the photoionization of HBr molecules was studied by angle- and spin-resolved photoelectron spectroscopy in the photon energy range from 11.7 eV to 21 eV. For photoelectrons corresponding to the final ionic states $\text{HBr}^+ \ X^2\Pi_{3/2}(v = 0)$ and $\ X^2\Pi_{1/2} (v = 0)$, the energy dependence of the dynamical photoionization parameters was measured and compared with ab initio calculations for $\text{HBr}^+$ by Raseev et al. and RRPA calculations for Kr$^+$ by Huang et al.. This comparison indicates that, for energies above the electronic autoionization region, photoemission from the outer valence orbital exhibits distinct atomic behavior. By combining the experimental data for the cross section $\sigma$ and the spin polarization parameter $\Delta$, sums of partial cross section contributions to $\sigma$ were determined and analyzed to obtain specific information on the outgoing partial electron waves. Furthermore, the validity of the so-called non-relativistic relationships for the dynamical photoionization parameters was tested as a function of equal photon and kinetic photoelectron energy, respectively.

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1 Introduction

The $p\pi$ outer valence shell of the heavier hydrogen halides is characterized by a well-defined lone-pair orbital localized at the halogen atom. Consequently, it may be expected that the photoemission from this orbital shows some or perhaps even substantial atomic characteristics, which should be reflected in the dynamics of the outgoing partial electron waves. HBr belongs to this class of molecules and krypton represents the appropriate atomic system for comparison, since it is the corresponding isoelectronic united atom limit. For a very detailed analysis of the photoionization dynamics, spin-resolved photoelectron spectroscopy is a highly suitable technique. Therefore we have undertaken spin-resolved studies on HBr molecules in order to probe the extent to which the photoionization process may be described by atomic-like properties and how this affects the dynamical parameters characterizing the emitted photoelectron waves. Furthermore, we have analyzed the influence of spin-orbit coupling on the spin polarization parameters.

The first molecular angle-integrated spin polarization measurements of photoelectrons using circularly polarized synchrotron radiation were performed in 1980 on CO$_2$ and N$_2$O [1]. Later on, similar studies of the spin polarization parameter $\Delta$ were carried out for the spin-orbit autoionization region for CH$_3$Br molecules [2, 3]. Furthermore, the parameter $\zeta$ was measured for I$_2$, Br$_2$, CH$_3$Br and CH$_3$I using resonance radiation from an unpolarized light source [4]. More recently, spin- and angle-resolved experimental results were presented for HI molecules for all five dynamical parameters, namely the partial cross section $\sigma$, the spin polarization parameters $\Delta$, $\zeta$, $\alpha$ and the $\beta$ parameter of the angular distribution [5]; in addition, partial cross section contributions were obtained from experimental results of $\Delta$ and $\sigma$ for outgoing partial waves [6]. The general non-relativistic theory of Cherepkov [7] was applied in the first MQDT calculations for $\Delta$ and $\xi$ in the $^2\Pi$ spin-orbit autoionization region of the ionic ground state of HI [8] and for all dynamical parameters of inner and outer shell photoionization of the hydrogen halides HBr and HI [9] derived in the frozen-core static-exchange approximation. The influence of molecular electronic autoionization and predissociation processes on the photoionization was theoretically studied for the parameters $\Delta$, $\beta$ and $\sigma$ of HBr$^+$ [10] using a unified MQDT treatment. Experimental results of the spin polarization and the partial cross section [10, 11] were recently compared with this calculation in the resonance region between 12.7 eV and 14.7 eV. Rotationally resolved studies of photoelectron spin polarization were

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carried out using frequency converted laser radiation for HI [12, 13] and HCl [14].

In this paper we present the completion of our investigation with circularly polarized synchrotron radiation on HBr with the experimental results for the partial cross sections \( \sigma \), the asymmetry parameters \( \beta \), all three spin polarization parameters \( A, \xi, \alpha \) and partial cross sections \( a \), the asymmetry parameters \( \phi \), all three spin polarization parameters \( A, \xi, \alpha \) determined from \( \phi \) and \( \alpha \) for the \( X^{2}I_{3/2}(v = 0) \) and \( X^{2}P_{1/2}(v = 0) \) final ionic states of HBr for photon energies from the threshold at 11.67 eV up to \( E_{\text{Photon}} = 21 \text{ eV} \). The effects of the spin-orbit coupling on the spin polarization parameters obtained for the two \( \chi^{2}I_{3/2}(v = 0) \) and \( \chi^{2}P_{1/2}(v = 0) \) final ionic states are investigated by direct comparison. The experimental data of HBr + are compared with molecular ab initio calculations by Raseev et al. [9] and with results for the \( X^{2}I_{3/2}(v = 0) \) and \( X^{2}P_{1/2}(v = 0) \) final ionic states of HI [5, 6]. Similarities observed for the outer p-subshell photoionization process in the atomic and molecular cases are described for the rare gases Kr [15, 16], Xe [16, 17] and the hydrogen halides HBr, HI.

2 Experimental

The photoelectron spin polarization and intensity measurements were carried out at the storage ring BESSY using circularly polarized synchrotron radiation at the 6.5 m NIM [18] with an apparatus described previously [17]. Briefly, an effusive beam of HBr molecules (purity 98%) was crossed at right angles by the focussed monochromatic light. For the spin polarization measurements the bandwidths of the synchrotron radiation were \( \Delta E_{\text{FWHM}} = 0.4 \text{ nm} \) or 0.5 nm; the intensity measurements were obtained with a bandwidth of \( \Delta E_{\text{FWHM}} = 0.17 \text{ nm} \). The uncertainty in the accuracy of the photon energy scale was \( \Delta E = 0.05 \text{ nm} \). The degree of circular photon polarization determined with a four-mirror analyzer was 92% \( \pm 3\% \). The photoelectrons emitted at the reaction angle \( \Theta \) (angular resolution \( \Delta \Theta_{\text{FWHM}} = 5^\circ \)) were analyzed by a rotating simulated hemispherical spectrometer [19] using an energy resolution of \( \Delta E_{\text{FWHM}} = 120 \text{ meV} \) for the spin polarization measurements and of \( \Delta E_{\text{FWHM}} = 75 \text{ meV} \) for the intensity measurements. Subsequently, the photoelectrons were accelerated to 100 keV and the electron spin was analyzed with a Mott-detector (Sherman function \( S = -0.23 \pm 0.02 \)). The spin polarization components \( A(\Theta) \) (component parallel to the photon momentum) and \( P_{\perp}(\Theta) \) (component perpendicular to the reaction plane defined by the momenta of the photon and photoelectron) are described by the energy dependent parameters \( A, \alpha, \xi \) and \( \beta \) according to the equations [17]:

\[
P_{\perp}(\Theta) = \frac{2 \cdot \xi \cdot \cos \Theta \cdot \sin \Theta}{1 - \beta/2 \cdot P_{2}(\cos \Theta)}
\]

(1)

\[
A(\Theta) = \gamma \frac{A - \alpha \cdot P_{2}(\cos \Theta)}{1 - \beta/2 \cdot P_{2}(\cos \Theta)}.
\]

(2)

Here, \( P_{2}(\cos \Theta) \) is the second Legendre polynomial and \( \gamma \) denotes the light helicity. (Lefebvre-Brion and coworkers use the notation \( P_{\perp}, \xi \) and \( \gamma \) for the spin polarization parameters \( A \) and \( \xi \) are determined either at the magic angle of \( \Theta_{m} = 54.74^\circ \) \( (P_{2}(\cos \Theta_{m}) = 0) \) or they result from a least-squares fit of the \( A(\Theta) \)- and \( P_{\perp}(\Theta) \)-angular distributions (Fig. 2) like the parameters \( \alpha \) and \( \beta \) describing the asymmetry of the angular distribution of the spin polarization and the intensity, respectively. Most of the \( \beta \) parameters presented in this paper were determined not only from the angular distributions for \( A(\Theta) \) (three fit parameters) but also simultaneously from those for \( P_{\perp}(\Theta) \) (two fit parameters). In comparison to previous results where \( \beta \) was obtained only from the \( A(\Theta) \)-distribution [5, 17], this simultaneous fit leads to an improved accuracy of \( \beta \) values determined from angle-resolved spin polarization measurements. The effects of instrumental asymmetries on the spin polarization measurements were eliminated by using alternately left- and right-handed circularly polarized light for the determination of the \( A(\Theta) \)-values and by rotating successively the electron spectrometer from \( + \Theta \) to \( - \Theta \) for the recording of the \( P_{\perp}(\Theta) \)-dependence [20]. Due to this elimination of instrumental asymmetries, the experimental results of \( P_{\perp}(\Theta) \) are plotted only for \( \Theta \). Spin polarization measurements were performed at different HBr stagnation pressures for a range of base pressures \( (3.0 \cdot 10^{-4} \text{Pa} \rightarrow 4.0 \cdot 10^{-2} \text{Pa}) \) inside the experimental chamber to examine the influence of the residual target gas on the spin polarization of the photoelectrons. No pressure dependence of the polarization values was observed and all further measurements were carried out with base pressures of less than 0.02 Pa.

The photoelectron spectra were recorded at the magic angle \( \Theta_{m} = 54.74^\circ \) with the electron spectrometer using a channeltron as detector. The data obtained were normalized by correcting for changes in the target gas pressure, for the wavelength dependence of the photon flux behind the monochromator exit slit as measured with a calibrated GaAsP-photodiode, and for the transmission characteristics of the electron spectrometer. The latter was determined by recording the energy dependence of the photoelectron intensity of the \( \text{Xe}^{+2}P_{3/2} \) and \( \text{Xe}^{+2}P_{1/2} \) final ionic states for which the photoionization cross sections are well-known [21] (constant-ionic-state measurements of \( \text{Xe} \), as discussed in detail elsewhere [5]). Characteristic background signals arising from unpolarized photoelectrons with low kinetic energy produced by photoemission from solid surfaces inside the chamber were subtracted from the spectra. The influence of photoelectrons corresponding to the HBr + \( 2\Pi_{3/2}(v = 1) \) first vibrationally excited state on the experimental intensity and spin polarization data of the \( 2\Pi_{1/2}(v = 0) \) state was taken into account in the error estimations on the condition that the intensity contributions of the two \( 2\Pi_{1/2}(v = 0) \) spin-orbit components should have equal magnitude either at same photon energies (within the electronic autoionization region) or at same electron kinetic energies (above the \( A^{2}S^{+} \) ionization threshold). Constant-ionic-state measurements for the two \( 2\Pi_{1/2}(v = 0) \) spin-orbit final ionic states of \( \text{DBr}^{+} \) (which has a different vibrational spacing but the same electronic structure as compared to \( \text{HBr}^{+} \)) exhibit equal magnitude of the intensities at equal photon energies for the electronic autoionization region [22]. This suggests that this should also be the case for \( \text{HBr}^{+} \). Therefore, the