THE PHOTOABSORPTION AND PHOTOIONIZATION OF BROMINE REVISITED.

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During the last few years we proceeded with the investigation of the ionization and dissociation dynamics of bromine derivatives of ethylene [1]. Photoabsorption spectroscopy (PAS), photoionization mass spectrometry (PIMS) and photoelectron spectroscopy (PES and TPES) were applied. The disubstituted derivatives 1,1-$C_2H_2Br_2$ and cis- and trans-1,2-$C_2H_2Br_2$ are suspected to be more sensitive to photodissociation than their corresponding difluorinated and dichlorinated compounds. Atomic Br or molecular Br_2 could thus contaminate the spectra. This has been observed, e.g., in the PAS of CH_3Br [2].

To be able to ensure the purity of the spectra of the above mentioned brominated derivatives, the molecular Br_2 has been reinvestigated by PAS and PIMS in the 5-15 eV photon energy range.

The PAS of Br_2 has been reported by Venkateswarlu [3] between 8.183eV and 10.538 eV using a 10m concave grating spectrograph. PIMS has been applied to Br_2 by Dibeler et al. [4,5] between 10 eV and 13 eV photon energy. These authors studied the Br^+ fragment ion formation between 10 eV and 12.5 eV. Only the ion-pair formation Br^+/Br^- takes place in this range. More recently, Yencha et al. [6] published a synchrotron radiation work on Br_2. The ion-pair process is reported between 10.332 eV and 10.875 eV and discussed in detail. These authors also measured the TPES of Br_2 at high resolution [7].

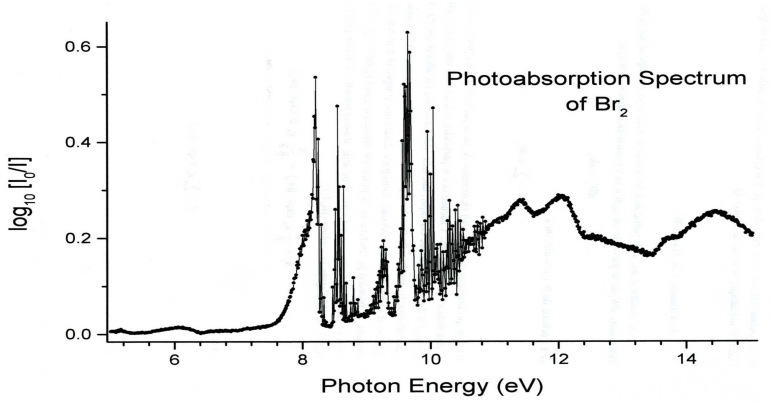

Fig. 1: Photoabsorption Spectrum of Br_2 in the 5.0 eV to 15.0 eV photon energy range.

We investigated the PAS and the PIMS of Br_2 by using the BESSY synchrotron radiation dispersed by a 3m-NIM monochromator. For recording the PAS, slits were set at 40µm whereas for the PIMS work, 200 µm slits were used. Fig.1 shows the PAS spec-trum as observed

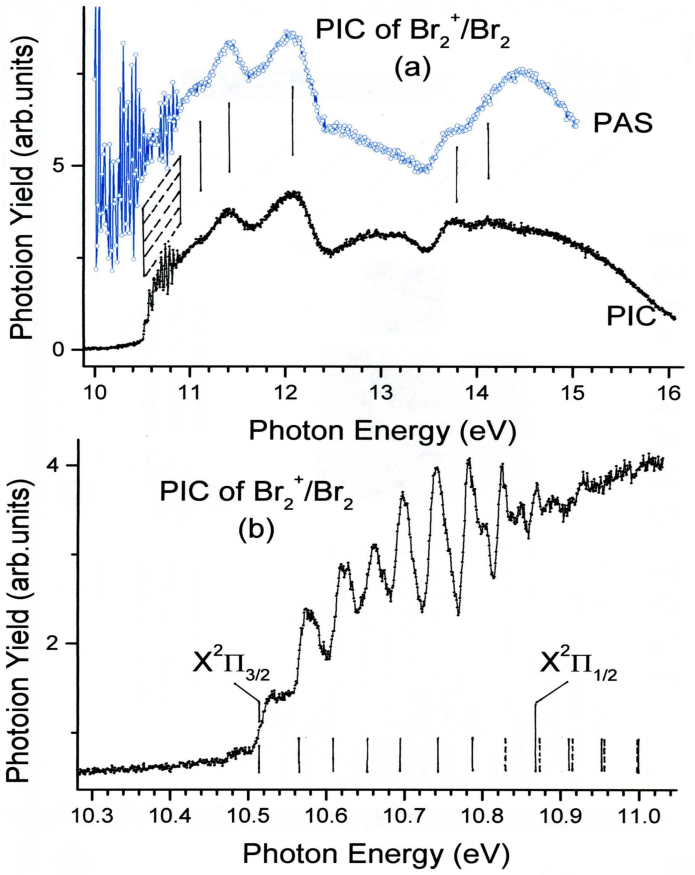

Fig. 2: Photoionization efficiency curve of Br_2^+/Br_2.

in the 5-15 eV photon energy range.

At low photon energy two broad bands are spread from 5.8 eV to 6.4 eV and 7.0 eV to 8.0 eV. The former is weak and structureless whereas the latter shows one or more vibrational progressions. This region has been measured carefully with 0.5 meV energy increments. About 50 vibrational levels are observed. Their analysis is in progress.

The medium (8.0-10.8 eV) photon energy range is characterized by numerous very sharp and strong to weak peaks. These are analyzed in terms of Rydberg series. The 8.2-10.5 eV region has already been analyzed in great detail by Venkateswarlu [3].

At high energy (10.5-15.0 eV) several weak sharp as well as weak broad features are observed. Fig. 2(a) clearly shows the close correlation between the structures observed in the PAS and the photoionization (PIC) as indicated by vertical bars. The dashed region corresponds to the dense fine structure measured in the threshold region.

Fig. 2(b) shows the ionization threshold region of Br_2 on an expanded energy scale. Vertical bars are positioned at critical energies corresponding to the two adiabatic ionization energies $X^2\Pi_{3/2}$-$^2\Pi_{1/2}$ and to the vibrational progression observed in Br_2^+ determined by TPES [7]. Direct ionization as well as vibrational autoionization is involved. The lowest adiabatic ionization energy has been measured at 10.517 eV in excellent agreement with ZEKE-PFI-measurements [8].

The efficiency of Br^+ production from Br_2 has been measured between 10eV and 15 eV photon energy. At high photon energy, i.e., above 14.0 eV the Br^+ ion current steeply increases reaching a maximum near 14.8 eV. Critical energies are measured at 13.98 eV, 14.1 eV, 14.26 eV, 15.51 eV and 15.62 eV and should correspond to the dissociative ionization Br_2 into $Br+Br^+$.

Below 14 eV the ionization efficiency shows fairly strong resonance shaped features corresponding to the production of an ion-pair Br^+/Br^- through the reaction

$$Br_2 + h\nu \rightarrow Br^+ + Br^- (^1S_0) \quad (1)$$

where Br^+ is produced in its ground configuration $4p^4$ giving rise to $^3P_2$, $^3P_1$, $^3P_0$, $^1D_2$ and $^1S_0$ electronic states. The corresponding thermochemical onsets of reactions (1) are displayed in Fig. 3(a). Furthermore, a fairly extended fine structure is observed upwards from the successive thresholds. The first band is shown on an expanded energy scale in Fig. 3(b) as recorded with a MgF_2 filter having a cutoff at 10.8 eV. A vibrational progression is observed with a characteristic wavenumber of 322±24 cm^{-1} in very good agreement with earlier observations [6]. The resolution obtained in the present work allows us to highlight several "doublets" in this band corresponding to a second progression with the same wavenumber of 322 cm^{-1} but blue-shifted by 12 meV (96 cm^{-1}). Further analysis and assignment are in progress.

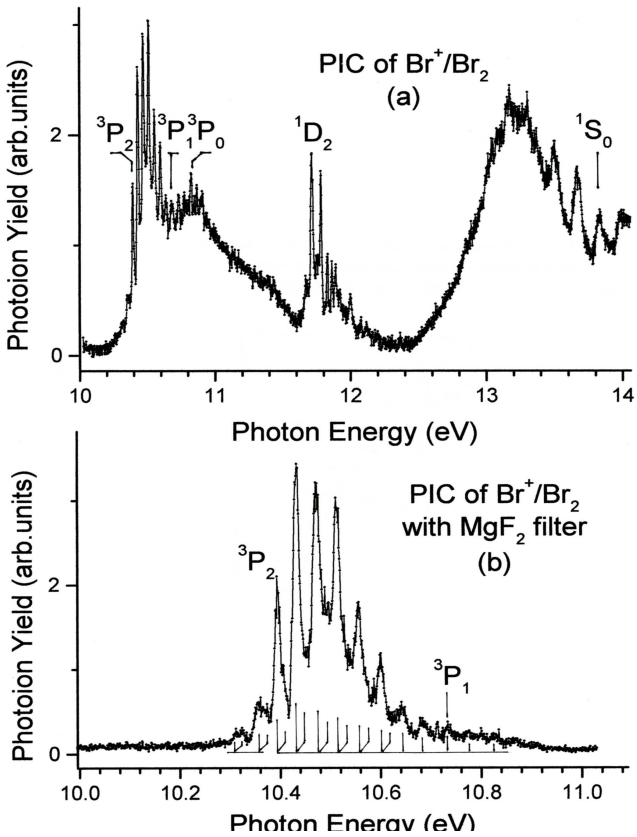

Fig. 3: The PIC of Br^+/Br_2 between 10-14 eV.

Acknowledgments.

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References.

[1]. R. Locht, B. Leyh, H.W. Jochims, H. Baumgärtel, BESSY Annual Report (2005) 56.
[2]. R. Locht, B. Leyh, H.W. Jochims, H. Baumgärtel, Chem. Phys. 317 (2005) 73.
[3]. P. Venkateswarlu, Can.J.Phys. 47 (1969) 2525.
[4]. J.D. Morrison, H. Hurzeler, M.G. Inghram, J.Chem.Phys. 33 (1960) 821.
[5]. V.H. Dibeler, J. Walker, K.E. McCulloh, H.M. Rosenstock, J.Chem.Phys. 53 (1970) 4715; ibid. Intern.J.Mass Spectrom.Ion.Phys. 7 (1971) 209.
[6]. A.J. Yencha, D.K. Kela, R.J. Donovan, A. Hopkirk, A. Kvaran, Chem.Phys.Letters 165 (1990) 283.
[7]. A.J. Yencha, A. Hopkirk, A. Hiraya, R.J. Donovan, J.G. Goode, R.R.J. Maier, G.C. King, A. Kvaran, J. Phys.Chem. 99 (1995) 7231.
[8]. T. Ridley, D.A. Beattie, M.C.R. Cockett, K.P. Lawley, R.J. Donovan, PCCP 4 (2002) 1398.