THE VUV PHOTOABSORPTION SPECTROSCOPY AND PHOTOIONIZATION OF HALOGENATED ETHYLENES: BROMO-DERIVATIVES.

R. Locht[1], B. Leyh[1], H.W. Jochims[2], H. Baumgärtel[2].
[1] Molecular Dynamics Laboratory, Department of Chemistry, Institute of Chemistry, University of Liège, Sart-Tilman par B-4000 Liège 1, Belgium.
[2]Institut für Physikalische und Theoretische Chemie, Freie Universität Berlin, Takustrasse 3, D-14195 Berlin, Germany.

For several years we investigate halogenated derivatives of methane and ethylene with focusing on the dynamics of highly excited states of their cations. For this purpose photoabsorption (PAS), photoelectron spectroscopies (PES, TPES and CIS), photoionization mass spectrometry (PIMS) and fragment ion translational energy (TES) spectroscopy are applied. Discharges in rare gases and synchrotron radiation are used as light sources. The VUV-PAS, PIMS, PES and TPES study of CH_3X (X=F, Cl, Br) [1,2,3] and C_2H_3X (X=Cl, Br) [4,5] have been reported.

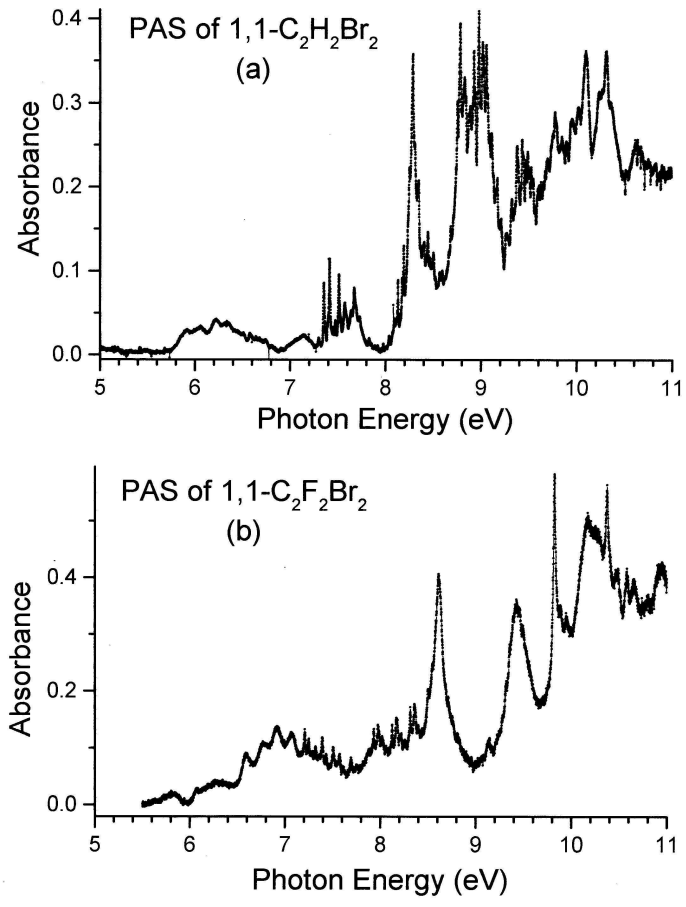

Fig. 1: VUV absorption spectrum of 1,1-$C_2H_2Br_2$ compared with that of 1,1-$C_2F_2Br_2$.

Almost all disubstituted derivatives of ethylene corresponding to $C_2H_2X_2$, where X=F and/or Cl, have been extensively investigated by Kaufel [6] using synchrotron PIMS. Almost all fragment ions have been recorded and thermochemcal data have been deduced.

In the frame of the present ongoing project, the PAS, PES, TPES and CIS spectra have been reported earlier for 1,1-$C_2H_2F_2$ and the three isomers of $C_2H_2Cl_2$ [7]. However, data about the disubstituted bromoethylenes are very scarce. To the best of our knowledge only the VUV-PAS of trans-1,2-$C_2H_2Br_2$ [8] is available in the literature. PES spectra have been reported by Wittel and Bock [9]. PIMS work on cis- and trans-

$C_2H_2Br_2$ has been published by Momigny [10].

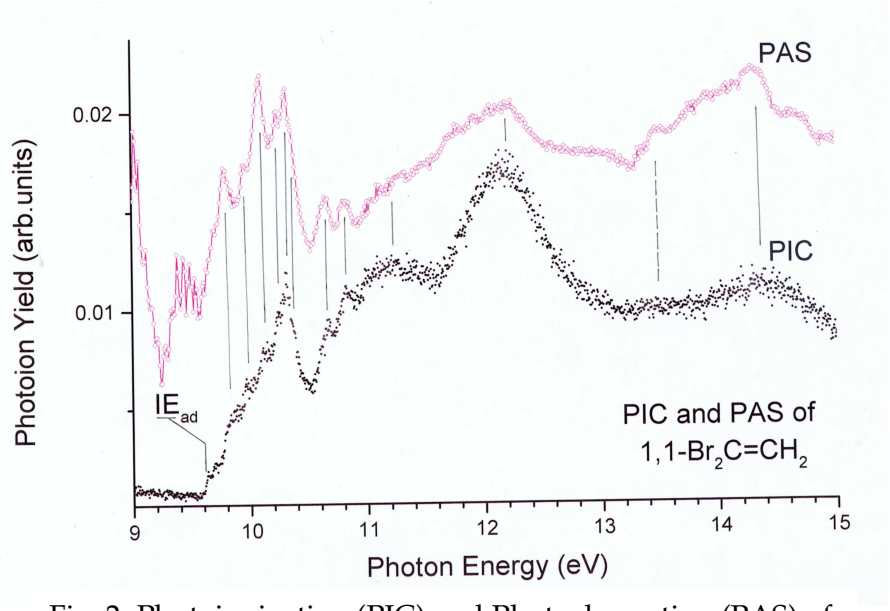

Fig. 2: Photoionization (PIC) and Photoabsorption (PAS) of 1,1-$C_2H_2Br_2$ between 9-15 eV photon energy.

The photoabsorption spectrum of 1,1-$C_2H_2Br_2$ has been recorded on the 3m-NIM beamline between 5 eV and 15 eV photon energy. The result is shown in Fig. 1(a) for the 5-11 eV photon energy range. Above the usual π→π* valence transition, the Rydberg transitions start up from 7.2 eV. The detailed analysis of this part of the spectrum is in progress. Interesting is the comparison with the corresponding difluorinated compound 1,1-$C_2F_2Br_2$ as displayed in Fig. 1(b) and recorded under the same conditions. Both spectra clearly show similarities but (i) the π→π* transition is stronger and blue-shifted and (ii) several peaks, e.g., at 8.2 eV, 8.8 eV and near 10 eV in $C_2H_2Br_2$ are blue shifted in $C_2F_2Br_2$. This has very likely to be ascribed to the expected perfluoro-effect. It is also highly interesting to compare the PAS of these two latter compounds to those characterizing 1,1-$C_2H_2X_2$ and 1,1-$C_2F_2X_2$ (with X= F and/or Cl). These VUV spectra have been measured earlier [11].

The photoionization mass spectrum of 1,1-$C_2H_2Br_2$ recorded at 20 eV photon energy essentially shows three ions, i.e., $C_2H_2Br_2^+$, $C_2H_2Br^+$ and $C_2H_2^+$. Fig. 2 displays the photoionization efficiency curve (PIC) of $C_2H_2Br_2^+$ between 9.0-15.0 eV photon energy. The PAS of 1,1-$C_2H_2Br_2$ as measured in the high photon energy range is also displayed in Fig. 2. Vertical bars highlight the close correlation between the features observed in the PIC of the molecular ion and the PAS of the neutral molecule. IE_{ad} indicates the position of the adiabatic ionization energy IE_{ad}(1,1-$C_2H_2Br_2$)= 9.612±0.010 eV. This value is lower than the PES value of 9.63 eV reported by Wittel and Bock [9]. However, these authors do not mention the error limits on their reported measurements. At higher photon energies the vibrational structure is visible but more and more embedded in the autoionization structure.

Acknowledgments.

The authors are indebted to the FNRS and the EU (Contract n°RII3-2004-506008) for financial support.

References.

[1]. R. Locht, B. Leyh, A. Hoxha, D. Dehareng, H.W. Jochims, H. Baumgärtel, Chem. Phys. 257 (2000) 283; R. Locht, J. Momigny, E. Rühl, H. Baumgärtel, Chem.Phys. 117 (1987) 305.
[2]. R. Locht, B. Leyh, A. Hoxha, H.W. Jochims, H. Baumgärtel, Chem. Phys. 272 (2001) 259; R. Locht, B. Leyh, A. Hoxha, D. Dehareng, K. Hottmann, H.W. Jochims, H. Baumgärtel, Chem.Phys. 272 (2001) 293.
[3]. R. Locht, B. Leyh, H.W. Jochims, H. Baumgärtel, Chem.Phys. 317 (2005) 73; R. Locht, B. Leyh, D. Dehareng, K. Hottmann, H.W. Jochims,, H. Baumgärtel, 323 (2006) 458.
[4]. R. Locht, B. Leyh K. Hottmann, H. Baumgärtel, Chem.Phys. 220 (1997) 207.
[5]. A. Hoxha, R. Locht, B. Leyh, D. Dehareng, K. Hottmann, H.W. Jochims, H. Baumgärtel, 260 (2000) 237; ibid. Chem.Phys. 256 (2000) 239.
[6]. R. Kaufel, Ph.D. Dissertation, FU Berlin (1985).
[7]. R. Locht, B. Leyh, H.W. Jochims, H. Baumgärtel, BESSY Jahresbericht (1996) 156; B. Leyh, R. Locht, K. Hottmann, H. Baumgärtel, BESSY Jahresbericht (1995) 163.
[8]. K. Wittel, W.S. Felps,, L. Klasinc, S.P. Glynn, J.Chem.Phys. 65 (1976) 3698.
[9]. K. Wittel, H. Bock, Chem.Ber. 107 (1974) 317.
[10]. J. Momigny, Bull.Classe Sci.Acad.Roy.Belg. 46 (1960) 686.
[11]. R. Locht, B. Leyh, H.W. Jochims, H. Baumgärtel, BESSY Jahresbericht (2005) 56.