K-edge absorption spectra of gaseous hydrides

Alojz Kodre[1,2], Robert Hauko[3], Jana Padežnik Gomilšek[3], Iztok Arčon[4,2] and Giuliana Aquilanti[5]

[1] *University of Ljubljana, Faculty of Mathematics and Physics, Jadranska 21, SI-1000 Ljubljana, Slovenia*
[2] *J. Stefan Institute, Jamova 39, Ljubljana, SI-1000 Ljubljana, Slovenia*
[3] *University of Maribor, Faculty of Mechanical Engineering, Smetanova 17, SI-2000 Maribor, Slovenia*
[4] *University of Nova Gorica, Vipavska 13, SI-5000 Nova Gorica, Slovenia*
[5] *Elettra Syncrotrone Trieste, I-34149 Basovizza, Italy*
alojz.kodre@fmf.uni-lj.si

X-ray absorption spectra in the energy region of absorption edges reveal fine details of the mechanism of inner-shell photoexcitation: in particular in spectra of free atoms or simple molecules, the simplest being gaseous hydrides [1-2]. In a collection of data from consecutive and homologous elements, analyzed by a common procedure, the reaction channels can be identified with better precision and reliability than in analysis of individual spectra.

Absorption spectra of the hydrides of $3p$ elements (PH_3, H_2S in HCl) were measured at the XAFS beamline of the Elettra synchrotron in Trieste: a new type of adjustable absorption cell for measurement of noxious gases at room temperature and at low photon energies was developed for the purpose. For the analysis, data from an earlier experiment on $4p$ hydrides (GeH_4, AsH_3, H_2Se, HBr), and published data of $2p$ hydrides (CH_4, NH_3, H_2O, HF) [3-4] as well as SiH_4 and the noble gases concluding the isoelectronic series (Ne, Ar, Kr) were adopted. The spectra are compared to respective calculated spectra, obtained by atomic HF86, GRASP codes and molecular DFT (Density functional theory) ORCA code [5].

Our analysis of the pre-edge structures showed that the energies and probabilities of single-electron transitions into the lowermost orbitals with the molecular character were strongly affected by the symmetry of the molecule, essentially in the same way in $3p$ and $4p$ homologues, but not in $2p$ homologues with a stronger influence of the core charge. In transitions to higher orbitals with prevailing atomic character the influence of the molecular field is negligible.

The fine structure immediately above the K edge stems from the coexcitation of valence electrons. These coexcitations can be explained as a two-step process: the inner-shell photoeffect followed by the shake-up of a valence electron predominantly to a free atomic orbital. The process is markedly different from coexcitations of more tightly bound electrons [3]. The results of relative shake-up probabilities can be compared to results of emission spectroscopies, the probabilities of double excitation to bound states show a correlation with the dissociation probability of the molecule.

This research was supported by the Slovenian Research Agency (P1-0112). We acknowledge access to the SR facilities of ELETTRA (beamline XAFS, pr. 20150107 and 20115112) and PETRAIII (beamline P65, pr. I-20160044 EC) at DESY, a member of the Helmholtz Association (HGFW).We would like to thank Edmund Welter(PETRA III) and Luca Olivi (ELETTRA) for assistance during the experiment.

[1] A. Kodre, I. Arčon, J. Padežnik Gomilšek, 8.1 Photoexcitation processes in atoms & 3.23 Gases, accepted for publication in International Tables for Crystallography, Volume 1, 2018.
[2] R. Hauko, J. Padežnik Gomilšek, A. Kodre, I. Arčon, G. Aquilanti, Radiat. Phys. Chem. 139, 2017, 66.
[3] R. Prešeren, A. Kodre, I. Arčon, M. Borowski, J. Sinchrotron Rad. 8, 2001, 279.
[4] J. Schirmer *et al*, Phys. Rev. A 47, 1992, 1136.
[5] F. Neese, Wiley Interdiscip. Rev.: Comput. Mol. Sci. 2, 2012, 73.