

K-edge absorption spectra of isoelectronic gaseous hydrides: a combination of atomic and molecular channels

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The fine detail in the x-ray absorption spectra in the energy region of absorption edges provides the insight into the mechanism of inner-shell photoexcitation: in particular in spectra of free atoms or simple molecules, the simplest being gaseous hydrides [1-2].

Measured *K* edge absorption spectra of hydrides of *3p* (PH₃, H₂S in HCl) and *4p* (GeH₄, AsH₃, H₂Se, HBr) elements, and published data of *2p* hydrides (CH₄, NH₃, H₂O, HF) as well as SiH₄ [3-6] and the noble gases at the end of the isoelectronic series (Ne, Ar, Kr) are compared to the respective calculated spectra, obtained by atomic HF86, GRASP codes [7] and molecular DFT (Density functional theory) ORCA code [8]. For a clearer view of intraatomic processes, the weak and simple structural (XAFS) signal of the molecule is removed from the spectra.

Among the spectral features below the continuum limit, those with the lowest energy belong to the transition of the core electron to the lowermost free orbitals with the molecular character. They are, as a rule, wider than the transitions to the higher orbitals with prevailing atomic character. The theoretical description with DFT code without specific adaptations is sufficient for a qualitative picture of the pre-edge structure. The fine structure immediately above the *K* edge stems from the coexcitation of valence electrons. We have proved that the 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. This process is markedly different from coexcitations of more tightly bound electrons [9].

In the collection of consecutive and homologous data, analyzed by a common procedure, the reaction channels can be identified with better precision and reliability than in analysis of individual spectra. Our analysis showed that the energies and probabilities of single-electron transitions into the molecular orbitals are 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 atomic orbitals the influence of the molecular field is negligible.

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