Real-time Evolution of the Valence Orbitals in a Dissociating Molecule as Revealed by Femtosecond Photoelectron Spectroscopy

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Abstract. We follow in real time the evolution of the valence orbitals of Br_2 molecules as the bonds break during dissociation with femtosecond vacuum-ultraviolet (VUV) photoelectron spectroscopy and with simulations of the nuclear and electron dynamics.

Introduction

How does a chemical bond break? The obvious answer to this question is given by laser femtochemistry [1], a combination of femtosecond (fs) laser technology and laser spectroscopy that allows for tracking in real time the nuclear dynamics during chemical reactions such as molecular dissociations. However, it is the valence electrons that form the bonds and their evolution during dissociation remains elusive when probing the nuclear dynamics. So how does a chemical bond actually break?

Photoelectron spectroscopy is one of the most direct ways of characterizing chemical bonding in molecules: With sufficiently high photon energy all valence states can be probed and their orbital energies and populations are reflected in the measured photoelectron binding energies and intensities.

We used time-resolved photoelectron spectroscopy based on a pump-probe scheme to watch in real time a chemical bond break. We followed the evolution of all valence orbitals during the ultrafast (<100 fs) dissociation of Br_2 molecules in the gas phase all the way from the photo-excited molecules to the free atoms. This allowed for unprecedented insight into how and on what time scale valence electrons rearrange when a covalent bond breaks [2].

Experimental Methods

We used a fs laser-pump and VUV-probe scheme with VUV pulses from high-order harmonic generation (HHG). Br_2 molecules are excited by absorption of one laser-pump photon (wavelength 400 nm) to the $^1\Pi_u$ dissociative state (population of the antibonding $8\sigma_u$ orbital at the equilibrium inter-nuclear distance of 2.3 Å). The molecules are ionized after a well-defined fs time delay by a VUV-probe pulse (15th harmonic of the fundamental, photon energy 23.5 eV, pulse duration 120 fs, generation medium Xe, approximate flux 10^9-10^{10} photons/s at 1kHz repetition rate in a focus smaller than 100x100 μm^2). Photoelectron energies are analyzed with a time of flight spectrometer. Dissociation from the $^1\Pi_u$ state results in two ground-state Br atoms.

Nugent-Glandorf and Strasser et al. have demonstrated the feasibility of this experiment in pioneering investigations [3, 4] but the greatly improved temporal

resolution (135±5 fs) and sensitivity in our experiment combined with a theoretical description allows for unprecedented insight into the evolution of the electronic structure during Br_2 dissociation. For in-depth analysis we also calculated the electronic structure of an ensemble of dissociating Br_2 molecules. Classical molecular dynamics simulations provided distributions of nuclear distances versus time delay and binding energies and photoelectron intensities were calculated in fs steps from the excited molecule to the free atom.

Results and Discussion

Measured and calculated valence-electron binding energies are depicted in Figure 1 (left).
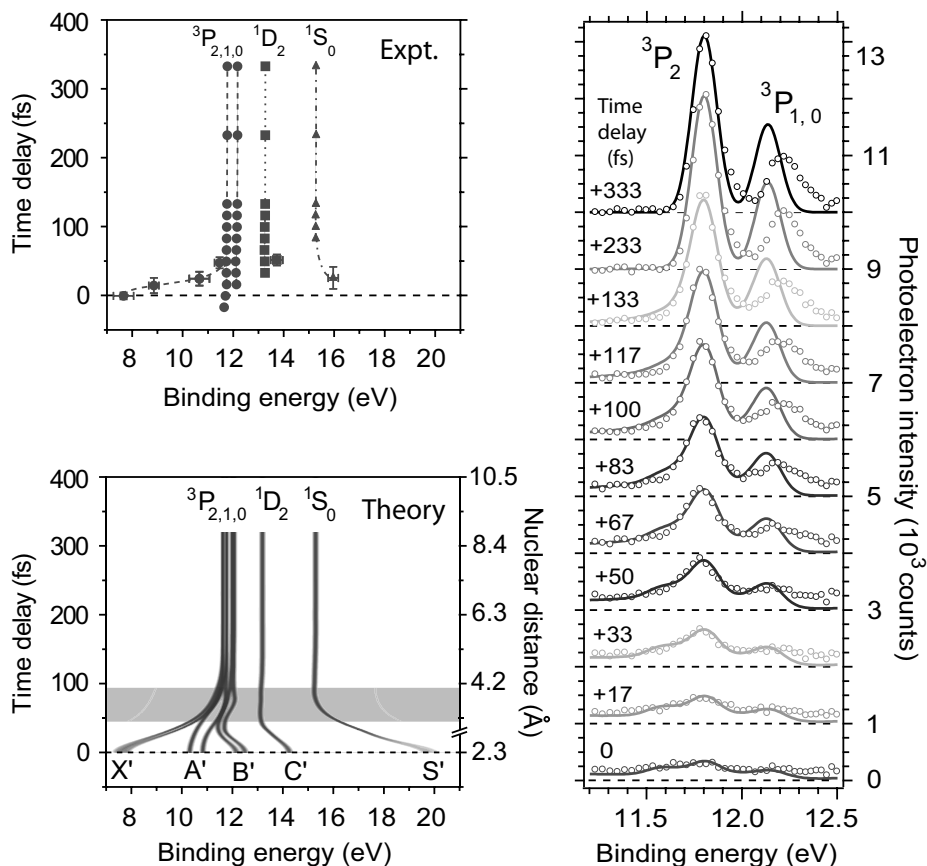

Fig. 1. Measured (left, top) and calculated (left, bottom) valence orbital energies as a function of pump-probe delay time and inter-nuclear distance. Right: Measured (circles) and calculated (solid lines) evolution of part of the valence band photoelectron spectrum.

Clearly, states start shifting immediately after excitation and by up to 4 eV while some essentially remain at constant energy. States are mixing and merging after approximately 50 fs when the atoms already travel at constant speed (~2.1 Å/ 100 fs)

and until less than 100 fs (nuclear distance close to 4 Å) when the electronic structure of the free atoms is essentially established. Those states corresponding to σ orbitals show the largest shifts because they arise from atomic orbitals oriented along the bond whose overlap changes most with changing bond length. Horizontal cuts in Figure 1 (left) correspond to photoelectron spectra at the respective delay time (Figure 1 right) and vertical cuts reflect the population dynamics of states with the respective binding energy (not shown here).

The evolution of the photoelectron spectrum close to 12 eV (Figure 1 right) from a broad distribution to the well-defined peaks of the free atoms demonstrates how we can spectroscopically distinguish the valence states of the excited molecule (0 fs delay) and of the free atoms (+333 fs delay).

These observations motivate an electronic-structure based definition of a transition period lasting from 50 fs (~3 Å) to less than 100 fs after excitation (~4 Å) during which valence electrons rearrange to form the orbitals of the free atoms. Our methodology, the analysis of the data and the calculations will be presented in detail in a forthcoming publication [2]. Our approach can be contrasted with laser femtochemistry with a particular emphasis on the sensitivity of the different approaches to different effects (electronic versus nuclear dynamics) [2].

Conclusions

We mapped in real time the evolution of the valence electronic structure of a diatomic molecule as the covalent bond breaks. Orbital energies and population dynamics of the valence states of Br_2 molecules during dissociation were followed with femtosecond photoelectron spectroscopy and simulations of the nuclear and electron dynamics. Our results allow for an unprecedented insight into how a chemical bond breaks.

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