Generation of Photon Pairs in Single-Photon Absorption for Probing Inner-Valence Excited and Multiply Excited States of Molecules around their Double Ionization Potentials

We demonstrate that a pair of photons generated following photoexcitation of diatomic molecules is a very sensitive probe for molecular superexcited states in the inner-valence range. The cross sections for the generation of photon pairs as a function of the incident photon energy reveal, for the first time, superexcited states having internal energies even higher than the double ionization energy of the molecule. Interestingly, these superexcited states dissociate into neutral fragments, escaping electronic autoionizations.

Inner-valence excited states and multiply excited states of molecules are molecular superexcited states of the first kind [1], in which electronic states are embedded in electronic continua. The wavefunctions for these highly excited states cannot be described by simple Born–Oppenheimer products due to mixing with the ionization continua [2]. Thus revealing the dynamics of the formation and decay of inner-valence excited states and multiply excited states, i.e. superexcited states in the inner-valence range, is one of the most important and challenging subjects in physics and chemistry.

Superexcited states embedded in the ionization continua can be probed by detecting photons emitted by an excited neutral fragment, as illustrated in the middle panel of Fig. 1, in which cross sections for the emission of fluorescence photons are shown as a function of the incident photon energy. Resonance peaks due to superexcited states of N_2 are clearly visible. On the other hand they can hardly be seen in the conventional photoabsorption spectrum shown in the lower panel of Fig. 1. The key to observing the superexcited states is measuring the cross sections free from ionization.

Recently we have developed an even more powerful method, the (γ, 2γ) method: a pair of fluorescence photons emitted by a pair of neutral fragments produced in the photoexcitation of a molecule is detected in coincidence in order to eliminate the contribution of ionization to a much larger extent than in the method used in the middle panel of Fig. 1. We are able to measure ionization-free cross sections in the photoexcitation of a diatomic molecule as a function of incident photon energy even in the range where dissociative ionization with excitation ($AB + h\nu \rightarrow A^+ + B + e^- + h\nu'$) takes place. The photon pair generation process resonantly occurs at photon energies equal to the energies of the superexcited states in the inner-valence range and thus features originating from them are highlighted, as is shown in the upper panel of Fig. 1. This opens up a new insight into the photoexcitation of molecules in the extreme vacuum ultraviolet range.

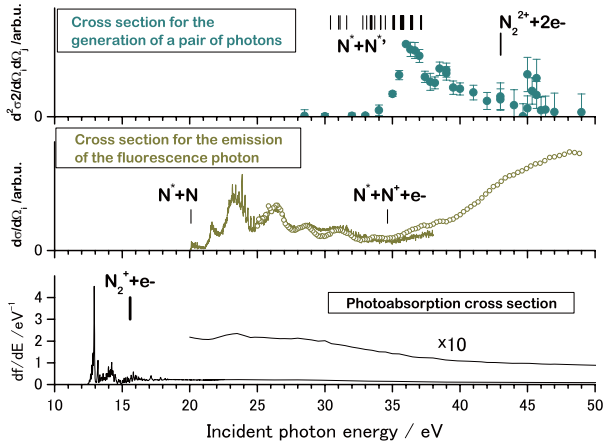

Figure 1
Photoabsorption cross section of N_2 (lower; [7]) and cross sections for the emission of fluorescence photon from an excited N atom (middle; [4]) and for the generation of a pair of photons emitted by a pair of excited N atoms (upper; [4]). The short vertical bars represent the dissociation limits for neutral dissociations and dissociative direct ionization accompanied by the emission of fluorescence photons. The long vertical bars indicate the single and double ionization potentials of N_2.

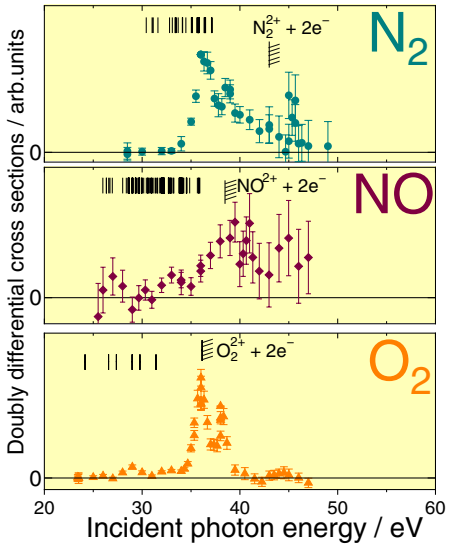

Figure 2
Cross sections for the generation of a pair of photons in the photoexcitation of N_2 (upper; [4]), NO (middle) and O_2 (lower; [5]). The short vertical bars represent dissociation limits for the generation of a photon pair. The vertical bars with hatches indicate the double ionization potentials.

Figure 2 shows the cross sections for the generation of a pair of photons in the photoexcitation of N_2 [4], NO and O_2 [5] differential with respect to solid angles for the emission of photons as a function of the incident photon energy. The cross section curves reveal, for the first time, inner-valence excited and multiply excited states of these molecules in the energy range where ionization from the innermost valence electrons takes place. It is emphasized that these states are the highest neutral excited states ever found in the inner-valence range. Remarkably, even above the double ionization potentials, there exist neutral states dissociating into neutral fragments escaping from electronic autoionization, making a contribution to photon pair generation comparable to those below the double ionization potentials.

For NO and O_2 sharp dips are observed just above the double ionization potentials. The positions of the dips agree well with those of the ground electronic state of O_2^{2+} ($X\ ^1\Sigma_g^+$) and the first excited state of NO^{2+} ($A\ ^2\Pi$) reported by Dawber *et al.* [6]. The dips seem to be attributable to decreases in branching ratios for photon pair generation due to the opening of autoionization channels into doubly charged states or Rydberg excited singly charged states converging to them.

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