

Observation of Core-Hole Localization in the Ne₂ Dimer

Here we report that the neon 1s photoelectron angular distributions (PADs) from Ne dimers relative to the dissociation directions of the fragment ion pairs strongly depend on the decay channels following photoionization leading to Ne⁺ + Ne²⁺ and Ne⁺ + Ne⁺ ion pairs. For the Ne⁺ + Ne²⁺ channel with fast interatomic Coulombic decay (ICD) of the Auger final states, non-inversion-symmetric patterns in the molecular frame PADs (MF-PADs) were observed, showing direct evidence for core-hole localization of the symmetric system. For the Ne⁺ + Ne⁺ channel with slow radiative decay of the Auger final states, dipolar patterns in the laboratory frame PADs (LF-PADs) were observed, clearly showing that the radiative process is slow enough to allow dicationic dimers to rotate many times before fragmentation.

Core-hole localization in symmetrical systems is a fundamental problem of X-ray spectroscopy and concerns some basic aspects of quantum theory. It is considered that the core hole created by X-ray absorption is localized even in symmetric molecules. In particular, symmetry restrictions in the orbital picture are not related to core-hole delocalization [1]. In such symmetry-adapted representations, the question arises as to whether or not the core hole should be considered localized on one specific atom in symmetrical systems. One can argue that a simple answer to the question does not exist due to the fact that the selection of the appropriate physical representation depends on the measurement

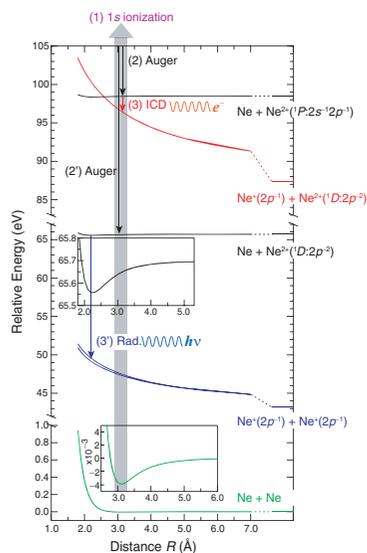


Figure 1
Calculated potential energy curves for the singly, doubly, and triply ionized states of Ne₂, which are relevant to the Ne⁺ + Ne²⁺ and Ne⁺ + Ne⁺ dissociation channels. The vertical axis represents the energy relative to two Ne atoms.

scheme [2]. We have recently demonstrated [3], at the undulator BL-2C, that the core-orbital photoionization process in Ne dimers (Ne₂) provides us with an ideal showcase to resolve this elusive fundamental problem.

The decay process of core-ionized Ne₂ can be described by a two-step model as indicated with the calculated potential energy curves in Fig. 1. In the first step the Auger decay following the photoemission occurs at the initial core-hole site leading to [Ne–Ne²⁺], and in the second step a charge separation into two sites takes place during successive decays. Following the absorption of a photon by Ne₂, the set of momentum vectors of the Ne 1s photoelectron and all fragments from a free Ne₂ can be measured in coincidence by using imaging and timing techniques. Figure 2 shows the plotted intensities of Ne 1s photoelectrons (produced by process (1) of Fig. 1) with respect to the dissociation axis of the fragment ions. When the Auger final states decay via ICD [4] in the second step to produce a Ne⁺ + Ne²⁺ ion pair ((2) → (3) in Fig. 1), the whole process from the photoemission to the dissociation into Ne⁺ + Ne²⁺ proceeds on a time scale which is much shorter than that of a rotational period. Therefore, the dissociation direction of Ne⁺ + Ne²⁺ can be considered as the direction of the dimer axis at the instant of the Ne 1s photoemission. Because of the localized nature of the atomic Auger decay, one can presume that the initial core-hole memory was carried by the Ne²⁺ fragment ion. As can be seen in Fig. 2(a), broken inversion symmetry of the PADs is seen clearly for the Ne⁺ + Ne²⁺ channel. We can thus conclude that the coincident PADs for the Ne⁺ + Ne²⁺ channel result in MF-PADs which show non-inversion-symmetric patterns due to symmetry lowering of the core ionized [Ne–Ne⁺]. It should be noted here that the degree of core-hole localization is not directly related to the degree of the lack of inversion symmetry in the MF-PADs. The MF-PAD for the polarization geometry perpendicular to the dissociation axis in Fig. 2(a) shows a nearly inversion-symmetric pattern, due to the weaker influence of the scattered wave in the geometry.

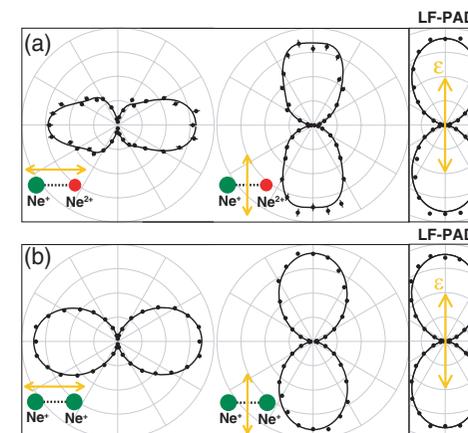


Figure 2
Polar plots of the Ne 1s PADs from Ne₂ in coincidence with (a) Ne⁺ + Ne²⁺ and (b) Ne⁺ + Ne⁺ fragments at 10 eV photoelectron energy. The polarization vector (ϵ) of the incident light and the dissociation direction of the ion pairs are indicated. The LF-PADs obtained by integrating the PADs over all the emitting directions of the corresponding ion pairs, are shown on the right. Filled circles: experimental data; thick curves: fits to the data.

In the two-step model for the Ne⁺ + Ne⁺ channel, on the other hand, a possible second step of the fragmentation pathway from the Auger final state [Ne + Ne²⁺(¹D: 2p⁻³)] is radiative decay, as shown with (2') → (3') in Fig. 1. During the lifetime (~ns) of the radiative decay leading to symmetric charge separation, the dicationic dimer can rotate many times, since the rotational period is about 100 ps. Therefore, the memory of the molecular axis at the instant of photoionization is completely lost in the Ne⁺ + Ne⁺ ion pair. As shown in Fig. 2(b), the PADs for the Ne⁺ + Ne⁺ channel depend only on the polarization vector, and they are almost identical to the laboratory frame PADs (LF-PADs) which were obtained by integrating the PADs over all the back-to-back directions of the ion pairs. Thus, the Ne⁺ + Ne²⁺ channel retains the memory of both the dimer orientation and the initial core-hole lo-

calization, while both are lost in the Ne⁺ + Ne⁺ channel.

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