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Fluorescence cascades evoked by resonant interatomic Coulombic decay of inner-valence excited neon clusters

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ABSTRACT

Resonant interatomic Coulombic decay (RICD) in inner-valence excited neon clusters is observed by a combination of vacuum-ultraviolet (VUV) and UV/visible fluorescence spectroscopy. These ultrafast interatomic electronic processes efficiently quench radiation emission from *inner-valence* excited clusters. After RICD took place, *outer-valence* excited clusters relax further by emission of fluorescence. The direct correspondence of the structures observed in the VUV and UV/visible fluorescence signals implies that the final states of the spectator RICD decay by a cascade of radiative decays: First, by the Rydberg-to-Rydberg transitions in the UV/visible spectral range, and then, by the Rydberg-to-valence transition in the VUV range. Our study demonstrates a possibility of detecting interatomic electronic processes by UV/visible fluorescence spectroscopy.

1. Introduction

When weakly-bound systems, such as van-der-Waals or hydrogen-bounded clusters, interact with exciting-radiation, an efficient energy transfer between two neighboring species in a cluster may occur by an ultrafast interatomic electronic process. Since its discovery [1], interatomic and intermolecular Coulombic decay (ICD) and related processes have been subjects of comprehensive experimental and theoretical investigations [2–5]. An important consequence of ICD is that the energy transferred to a neighbor is used to eject typically a low kinetic energy electron (the ICD electron). These electrons are proven to be genotoxic and may induce irreparable damage in living tissues [6]. It has also been shown experimentally [7–10] and theoretically [11–13], that an ICD process can be triggered by a resonant excitation of nobel gas dimers and clusters, a process termed RICD.

In all those experimental studies, ICD was probed in ultra-high vacuum by analyzing the charged particles via electron and/or ion spectroscopy. Such charged particles, however, may not be used to prove ICD processes in dense media, like, e.g., in large clusters or biological matter, due to their very short mean free path. The orders of magnitude larger mean free path of photons opens a door to investigate interatomic processes inside dense media. Recently [14], we have demonstrated that interatomic processes can also be studied by means of undispersed fluorescence spectroscopy. We found that RICD following the inner-valence excitation of neon clusters opens a particular fluorescence relaxation pathway. Resonant features observed in the time-resolved VUV fluorescence signal from clusters were found to be in one-to-one correspondence with those in the low-energy electron yield, which was measured simultaneously, providing thereby an unambiguous proof of ICD.

In the present work, by employing a similar technique we demonstrate that ICD can also be studied by detecting photons emitted in the UV/visible fluorescence range. In order to validate this detection technique, we combined it here with the detection of VUV photons, which has already been proven to be a probe for ICD [14]. However, as will become evident below, UV/visible fluorescence spectroscopy can be a separate tool to study interatomic processes, as suggested in the study of radiative relaxation of inner-shell excited argon clusters [15]. Simultaneous detection of the VUV and UV/visible fluorescence, realized here, allowed us to uncover a detailed relaxation route of the inner-valence excited clusters. The paper is organized as follows. The presently studied

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process and details of the experiment are described in Section 2. The experimental results are analyzed and discussed in Section 3. We conclude with a brief summary.

2. Experiment

The present experiment was carried out with the prototypical neon clusters. The process under consideration (schematically illustrated in Fig. 1) and the used experimental setup are very similar to those from our previous study of neon clusters [14]. At first (Fig. 1a), the resonant photon excites an inner-valence electron of a Ne atom into the *np*-Rydberg state. In an isolated atom, this excitation is followed by ultrafast autoionization, which usually dominates over radiative decay and thus suppresses any emission of fluorescence. Only for very high principle quantum numbers *n*, radiative decay can compete with autoionization [16]. Because of the presence of neighbors in the cluster, the inner-valence excited state can alternatively relax by the ICD process, in which the excess energy is transferred to a neighboring atom to release a slow ICD electron from it (Fig. 1b). As demonstrated theoretically [12] and verified experimentally [8] for Ne dimers, the efficiency of the spectator RICD for the 4*p*-excitation becomes comparable to, and for the 5*p*-excitation even dominant over, the autoionization. This efficiency grows with cluster size [17,18].

After the spectator RICD took place, the originally excited atom still possesses a part of the excess energy, which is deposited in the Rydberg *np*-electron and can only be released by the emission of a photon. Because the radiative decay rate grows significantly with the energy of the emitted photon, i.e., $\Gamma_r \sim \omega_{fi}^3$, one can expect that the Rydberg-to-valence $np \rightarrow 2p$ transition will dominate over the Rydberg-to-Rydberg $np \rightarrow 3s$ one (note that the former transition is forbidden only in systems with central symmetry). One thus would expect predominant fluorescence emission in the VUV range [14]. Here, we demonstrate that the Rydberg *np*-electron relaxes by the fluorescence cascade (Fig. 1c). In spite of the above argumentation, the still excited Ne atom releases first a UV/visible fluorescence photon by the Rydberg-to-Rydberg transitions, and subsequently a VUV photon by the Rydberg-to-valence transition.

Experiments were performed at the synchrotron radiation facility SOLEIL (Paris) at the PLEIADES beamline in its multibunch operation mode. A slit-width of 300 µm of the plane grating monochromator (PGM) was chosen to obtain a bandwidth of the exciting photons of about 12 meV at 44 eV. The neon cluster jet is produced by supersonic expansion through a 30 µm diameter nozzle separating the high pressure gas inlet from the vacuum in the expansion chamber and cooled by a liquid helium flow cryostat. For these measurements, the nozzle was cooled down to 75 K, which, following Hagena's formulae [19], leads to mean cluster sizes of about $\langle N \rangle \sim 30$. After passing through a 1.5 mm diameter skimmer (BEAM DYNAMICS, INC.), the jet is transferred into the interaction chamber, where it is crossed with the linearly polarized photon beam of the monochromatized synchrotron radiation.

The UV/visible and VUV photons released in the second and third steps of the cascade (Fig. 1c) were simultaneously detected by the well-established set-up for photon-induced fluorescence-spectroscopy [20] (PIFS). It has already been successfully utilized to investigate autoionization [21–25] and Auger decay [26–30] in molecules.

Briefly, an open-face stack of three micro-channel plates (MCP) was used to detect energetic ions and VUV photons with wavelength below 120 nm. The stack is mounted in a differentially pumped chamber, separated from the interaction chamber by an aperture. The front of the MCPs is always set to −2600 V. Applying additionally −150 V to a mesh in front of the stack, both energetic ions produced by Coulomb explosion (with kinetic energies of some eV [3]) and VUV photons are simultaneously detected. The former contribution to the recorded signal is typically by a factor of 10 larger than the later. In order to differentiate this total signal, the photon yield was acquired separately by setting the mesh voltage to +200 V, which repels all ions. The yield of energetic ions can thus be obtained by subtracting the photon yield from the total signal, both normalized to the acquisition time, as the photon flux was constant in top-up operation of the synchrotron.

The UV/visible fluorescence was collected using a MCP detector with bialkali photocathode and fused silica window, which covers the wavelength range from 300 to 630 nm. The exciting-photon energy was varied in steps of 20 meV in the wide range of 46.8–48.7 eV (in steps of 10 meV in the narrow range of 46.9–47.7 eV) and calibrated against the 2s-ionization threshold of neon atoms at 48.48 eV. In a separate measurement performed at an exciting-photon energy of 47.09 eV, the VUV signal was dispersed by a 1-m-normal-incidence monochromator equipped with a gold-coated 1200 l/mm grating, achieving a resolution of about $\Delta\lambda \sim 2$ nm. The dispersed fluorescence was detected with a position sensitive open-face MCP detector as used in previous investigations [14].

3. Results and discussion

The presently measured total yields of the ions and of the VUV fluorescence are compared in Fig. 2. In the shown exciting-photon energy range, the former exhibits three distinct resonant features and a broad ionization threshold [18] (see Fig. 2a). Those resonant structures were also observed in the spectrum of the low kinetic

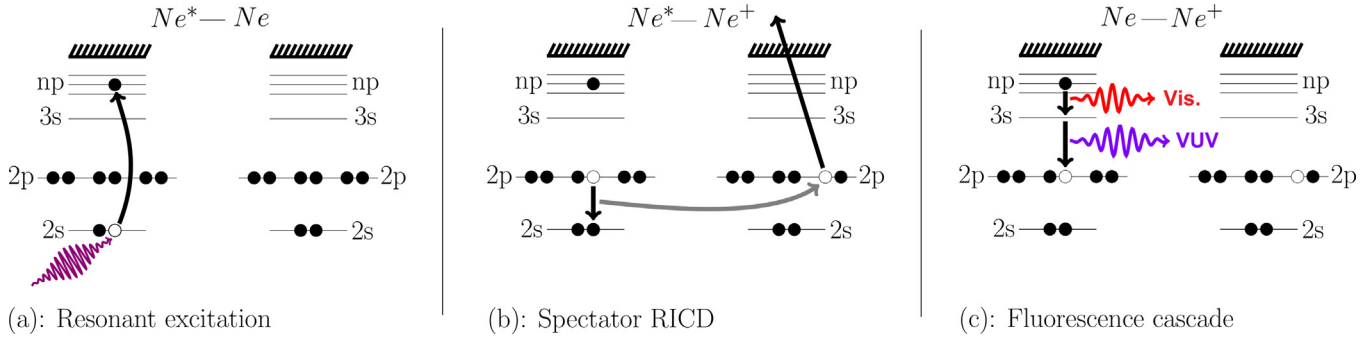

Fig. 1. The presently studied relaxation mechanism of inner-valence excited neon clusters, exemplified by dimers. Panel (a): the inner-valence 2s-electron of one Ne atom is resonantly promoted to an *np*-Rydberg state by the absorption of an exciting-photon. Panel (b): the thus created 2s-hole is filled by an outer-valence 2p-electron from the same excited atom, and the released energy is transferred to ionize a 2p-electron of the neighboring Ne atom resulting in an ejection of a low kinetic energy ICD electron. Panel (c): after RICD, the excited Ne atom relaxes by a cascade of radiative decays, which consists of a $np \rightarrow 3s$ transition emitting a UV/visible photon and a subsequent $3s \rightarrow 2p$ transition releasing a VUV photon.