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Photo- and Auger-Electron Recoil Induced Dynamics of Interatomic Coulombic Decay

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At photon energies near the Ne K edge it is shown that for $1s$ ionization the Auger electron, and for $2s$ ionization the fast photoelectron, launch vibrational wave packets in a Ne dimer. These wave packets then decay by emission of a slow electron via interatomic Coulombic decay (ICD). The measured and computed ICD electron spectra are shown to be significantly modified by the recoil induced nuclear motion.

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For molecular ionization, excitation, and electronic decay the Born-Oppenheimer and Franck-Condon approximations are successfully invoked to describe most of the observed phenomena. Two assumptions are usually made: First, the nuclei are considered frozen in coordinate space during the electronic transition, and second, the momentum coupling between electrons and nuclei is neglected. This is obvious in the often used Franck-Condon approximation to electronic transitions of a molecule where the electronic dipole matrix element is evaluated at the equilibrium distance of the ground state and the resulting vibrational spectrum is due to overlaps of the vibrational levels of the ground and final electronic states of the transition. Domcke and Cederbaum [1] showed theoretically that relaxing the Franck-Condon approximation for photoionization gives rise to momentum coupling between electrons and nuclei which can lead to an observable "recoil effect." For high energetic photoelectrons the recoil momentum imparted differently onto the nuclei may result in non-Franck-Condon vibronic excitations. This effect has only recently been confirmed experimentally not only in molecules [2,3] but also in solid states [4]. In addition, the recoil effect can also lead to an observable phase shift of the photoelectron [5].

It is pointed out here that recoil effects are not only relevant for photoionization, but also for Auger decay, and are particularly relevant for subsequent decay processes following either photoionization or Auger decay. Specifically, in the present letter we demonstrate that interatomic Coulombic decay (ICD) in the Ne dimer is significantly modified by the recoil momentum of a fast electron emitted along the internuclear axis. ICD, first introduced in [6], is a decay where the transfer of relaxation energy from one site of a weakly bound complex can lead to the emission of a low energy electron from a neighboring site. ICD, resulting in a doubly charged state of the dimer, takes place in Ne_2 after its $2s$ ionization

$$\begin{aligned} \mathrm{Ne}/\mathrm{Ne} + \hbar\omega &\rightarrow \mathrm{Ne}^+(2s^{-1})/\mathrm{Ne} + e_P^- \\ &\rightarrow \mathrm{Ne}^+(2p^{-1}) + \mathrm{Ne}^+(2p^{-1}) + e_P^- + e_{\mathrm{ICD}}^-, \end{aligned} \tag{1}$$

and has recently been studied, both experimentally [7–10] and theoretically [11–13]. In addition, ICD after Auger decay of the $1s$ vacancy, resulting in a triply charged state of the Ne dimer

$$\begin{aligned} \mathrm{Ne}/\mathrm{Ne} + \hbar\omega &\rightarrow \mathrm{Ne}^+(1s^{-1})/\mathrm{Ne} + e_P^- \\ &\rightarrow \mathrm{Ne}^{2+}(2s^{-1}2p^{-11}P)/\mathrm{Ne} + e_P^- + e_A^- \\ &\rightarrow \mathrm{Ne}^{2+}(2p^{-21}D) + \mathrm{Ne}^+(2p^{-1}) \\ &\quad + e_P^- + e_A^- + e_{\mathrm{ICD}}^-, \end{aligned} \tag{2}$$

has also been observed experimentally [14–16] and interpreted theoretically [17–19]. For both reactions (1) and (2), ICD takes place on a time scale comparable to the nuclear motion of the Ne atoms (the time for the electronic decay of ~100 fs is comparable to the typical time for the nuclear dynamics, which is ~300 fs). As a consequence, as clearly demonstrated in [13,19], the nuclear dynamics considerably influence the ICD spectrum providing a good agreement between theory and experiment. Since the potential energy surfaces of these singly or doubly charged dimers

are very shallow we expect that the recoil momentum of a fast electron imparted onto the nuclear dynamics will lead to an observable modification of the ICD spectra for both reactions (1) and (2).

The present experiment has been performed at BL UE56/1 SGM at BESSY using the COLTRIMS technique [20–22]. It is similar to that reported in [16]. In order to produce fast photo- and Auger electrons we used a photon energy of $\hbar\omega = 880.2$ eV, which is 10 eV above the $1s$ ionization threshold of Ne_2. This corresponds to a $2s$ photoelectron energy of $E_P = 831.7$ eV in reaction (1) and to a $1s$ photoelectron energy of $E_P = 10$ eV and an Auger-electron energy of $E_A = 772$ eV in reaction (2). The corresponding recoil energy, as given by the mass ratio of the electron and the Neon atom, is about 22 meV.

The coincident detection of both fragment ions and the ICD electron allows us to identify the initial ICD state and, hence, to identify reactions (1) and (2). Determining the directions of the high energy photo- or Auger electron with respect to the direction of fragmentation of Ne_2 is essential to study the recoil effect, since the induced nuclear motion depends strongly on this direction. The momentum vector of the fast photoelectron in reaction (1) was obtained from the measured momenta of the two ions and the ICD electron using momentum conservation. In reaction (2), both photo- and Auger electrons are emitted from the same site where the initially created core hole was localized, thus, imparting their respective recoil momenta onto the same atom which finally becomes the Ne^{2+} fragment. The latter localization was verified by showing the broken symmetry of the photoelectron angular distribution [14,15]. Although the sum recoil momentum is relevant for the recoil effect and directly measured in our experiment as indicated above, we refer in the following for simplicity to the recoil momentum of the Auger electron only. For a recoil momentum parallel to the bond, the fragmentation direction coincides, due to the fast Auger decay and the fast dissociation, with the dimer axis at the instant of photoabsorption. If the recoil momentum is perpendicular to the bond, it causes a rotation of the dimer before dissociation. This rotation of the internuclear axis due to the recoil effect is estimated for present parameters to be maximally 9° per 100 fs.

Figure 1 comprises the results of the present experiment. The normal ICD electron spectra measured for reaction (1) at different directions between the fast photoelectron and the dimer axis are shown in the upper panel. For the perpendicular recoil momentum the data are integrated over the photoelectron emission angle θ_P in between 66°–114° (dots). Since both detected ions have the same charge (Ne^+), the two cases where the photoelectron is emitted along the dimer axis compressing or stretching its bond cannot be distinguished. Therefore, we show the experimental spectrum integrated over the photoelectron emission 0°–53° and 127°–180° (triangles). The ICD

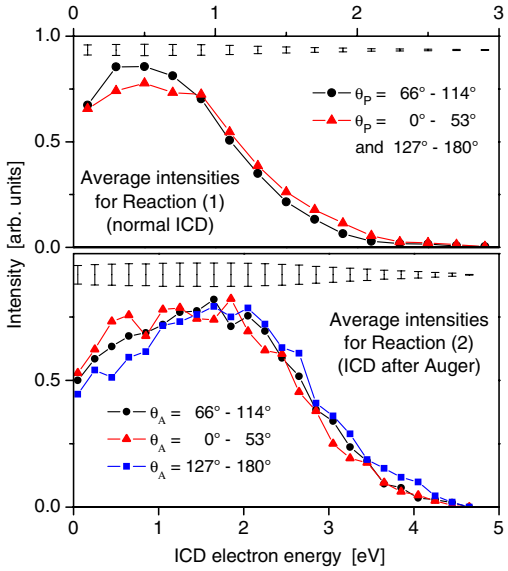

FIG. 1 (color online). Intensities of the ICD electrons measured in coincidence with the photoelectrons emitted at different directions after $2s$ ionization of Ne_2 (top) and with the Auger electrons after $1s$ ionization of Ne_2 (bottom). All spectra are normalized to the same integral. Typical errors are shown on top by bars.

spectra observed for reaction (2) at different directions of the fast Auger electron are shown in the lower panel of Fig. 1. For the perpendicular recoil momentum (dots) we again show the experimental spectrum integrated over θ_A in between 66°–114°. Knowing that the site of the Ne^{2+} fragment received the recoil momentum together with the measured direction of the momentum allows us to experimentally distinguish the compression from the stretching of the bond. If we define θ_A with respect to the direction of the detection of the Ne^{2+} fragment, the compressing mode will correspond to $\theta_A = 0°$ and the stretching mode—to $\theta_A = 180°$. The experimental ICD spectra integrated over θ_A in between 0°–53° (compressing mode) and in between 127°–180° (stretching mode) are also shown in the lower panel of Fig. 1 by triangles and squares, respectively. One can see that the ICD spectra measured for different directions of the fast electron are noticeably different, and the difference is larger than typical errors shown by bars on the top of each panel.

In order to interpret the present experiment we applied the time-dependent theory of wave packet propagation for ICD as in [12,13,19]. We utilized the same potential energy curves (PECs) and ICD rates as in [13,19,23] which allowed us to interpret the experimental ICD spectra measured without recoil effect [7]. In order to take the recoil of nuclei by a fast electron into account we proceed along the same lines as suggested in [1]. For simplicity we assume that the fast electron with momentum $\mathbf{k}_e$ was emitted from the left atom of the dimer located at $\mathbf{R}_L$. After instantaneous emission of a fast electron the intermediate wave

packet created on the ICD initial PEC will get an additional phase $e^{-i\mathbf{k}_e\cdot\mathbf{R}_L}$. By separating the vibrational motion of the dimer described by coordinate $\mathbf{R}$ from the motion of its center of gravity described by $\mathbf{R}_S$ the above phase factorizes as $e^{-i\mathbf{k}_e\cdot\mathbf{R}_S}e^{-i\mathbf{k}_e\cdot(\mathbf{R}/2)}$. Apart from the phase factor $e^{-i\mathbf{k}_e\cdot\mathbf{R}_S}$ describing the center of gravity motion, the initial condition for the intermediate wave packet $|\Psi_d(t)\rangle$ which propagates on the PEC of the state decaying by ICD reads

$$|\Psi_d(t=0)\rangle = |v_0\rangle e^{-i(\mathbf{k}_e/2)\cdot\mathbf{R}} = |v_0\rangle e^{-i(\mathbf{k}_e/2)R\cos\theta_{P/A}}, \quad (3)$$

where $|v_0\rangle$ is the wave function of the zero vibration level of the Ne_2 ground state.

Time evolutions of the wave packet $|\Psi_d(t)\rangle$ propagating on the PEC of the $Ne^{2+}(2s^{-1}2p^{-1}{}^1P)Ne$ state decaying by ICD (initial ICD state) computed for different recoil modes in reaction (2) are shown in Fig. 2. The maximal value of the recoil momentum transferred to the vibrational motion, $\frac{k_e}{2}\cos\theta_A = \pm 3.77$ a.u., which corresponds to the Auger electron emitted along the dimer axis $\theta_A = 0°/180°$ with an energy $E_{k_e} = 772$ eV, was used in the calculations. For $\theta_A = 90°$, the wave packet is created at the right turning point of the PEC of the initial ICD state and starts to propagate inwards without initial velocity (middle panels). It reaches the left turning point after about 100 fs and makes a complete oscillation cycle after about 350 fs. In the case of a compressing mode (left panels), the wave packet starts to propagate inwards with an initial velocity provided by the recoil and reaches the left turning point much earlier. In the stretching mode (right panels), the wave packet starts to propagate outwards with an initial velocity opposite to that in the compressing mode. It turns back after about 100 fs and reaches the left turning point much later.

The ICD spectra computed accounting for the recoil of the nuclei are depicted for both reactions in Fig. 3. In order to facilitate comparison between theory and experiment we averaged the computed spectra over the emission directions of the fast photo- or Auger electron. Since recoil induced rotations of the internuclear axis cause additional uncertainties of maximum 9° in the determination of the angles $\theta_{P/A}$ during the typical lifetime for the ICD of about 100 fs, we depict computed spectra averaged in the intervals 0°–60°, 60°–120°, and 120°–180°. Thus, on average, for the first and last intervals only about 83% of the maximal recoil effect for compressing and stretching modes are accounted for in the depicted spectra (dashed lines), and about 25% of the recoil are included for the middle interval (solid lines).

Figure 3 demonstrates the enormous influence of the nuclear dynamics launched by the recoil momentum on the computed ICD spectra. As discussed above, in the compressing mode the dimer spends more time at smaller internuclear distances. This results in a preferable emission of the low energy ICD electrons (compare red dashed and solid lines on the lower panel of Fig. 3), since the energy difference between the potential curves of the initial and the final ICD transition states and with this the kinetic energy of the ICD electron decreases with smaller internuclear distances. In the stretching mode the dimer spends more time at larger internuclear distances and high energy ICD electrons are preferably emitted (compare blue dashed and solid lines on the same figure). In reaction (1) these modes are indistinguishable due to the identical Ne^+ fragments, and the recoil leads, as expected, to a broadening of

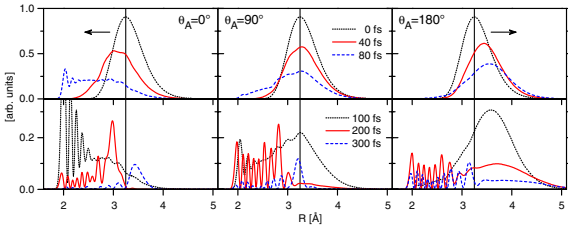

FIG. 2 (color online). Modulus squared of the wave packet propagating on the PEC of the state $Ne^{2+}(2s^{-1}2p^{-1}{}^1P)Ne$ decaying by ICD computed at different times. The excitation of the compressing mode (left panels), vibrational recoil free mode (middle panels), and stretching mode (right panels) are shown. The maximal value of the recoil momentum transferred to the nuclear vibrational motion, $|k_e|/2 = 3.77$ a.u., which corresponds to the Auger-electron energy $E_{k_e} = 772$ eV, was used in the calculations. Note that due to ICD the norm of the wave packet decreases in time.

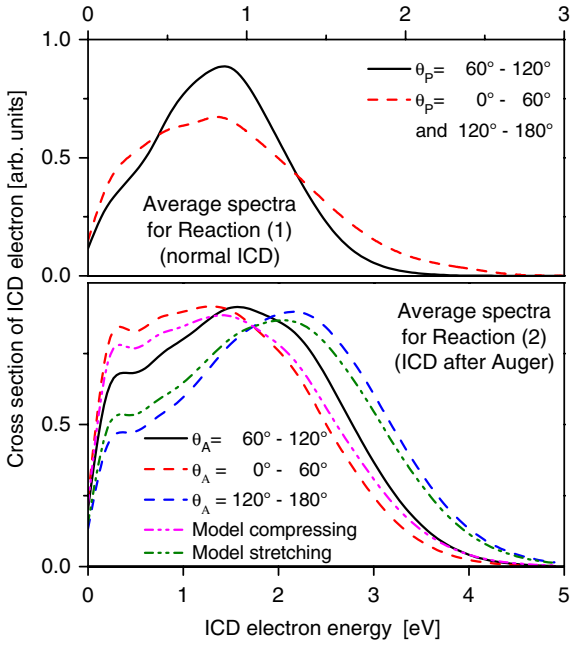

FIG. 3 (color online). Computed spectra for normal ICD of Ne_2 (top) and ICD after Auger decay (bottom). The spectra were averaged over the directions of the recoil momentum (see legend). Model spectra simulating the additional presence of ETMD (see text) for stretching and compressing modes are also shown on the lower panel. All spectra are normalized to the same integral.

the distribution (compare dashed and solid lines on the upper panel of Fig. 3).

By comparing Figs. 1 and 3, one can see that the presently measured effect is much weaker than theory shows, but that the qualitative agreement supports the recoil interpretation. As shown in [16], the ICD transition between the $Ne^{2+}(2s^{-1}2p^{-1}{}^1P)/Ne$ and $Ne^{2+}(2p^{-2}{}^1D) + Ne^{+}(2p^{-1})$ states for reaction (2) overlaps with the electron transfer mediated decay (ETMD, [24]) transition between the $Ne^{2+}(2s^{-2})/Ne$ and $Ne^{2+}(2p^{-2}{}^3P) + Ne^{+}(2s^{-1})$ states. Since we detect only electrons with an initial kinetic energy up to 12 eV within a solid angle of emission of 4π the statistics as well as the resolution in the high energy region of the auger electrons was not enough to separate these two channels out of the kinetic energy of the Auger electron. Hence the ETMD transition is also included in the experimental spectrum. The ratio of the ICD to ETMD transitions estimated from the present experiment is 83% to 17%. In contrast to ICD, in ETMD the Auger electron is emitted from the site which becomes the Ne^{+} fragment leading, therefore, to the opposite recoil effect. The model spectra estimated for compressing and stretching modes assuming the same nuclear dynamics for the ETMD and the above ICD to ETMD ratio are shown for reaction (2) in the lower panel of Fig. 3 by dash-dotted-dotted lines. One can see that accounting for the presence of ETMD improves the agreement between the presently measured and computed electron spectra for reaction (2). As shown in [13,19], partial spectra computed for different initial and final ICD states are notably different. The remaining discrepancy between presently computed and measured spectra can be connected with the fact that equal partial ICD rates were used in the present calculations.

In conclusion, we have demonstrated a breakdown of the Franck-Condon approximation for decay processes following the emission of a fast electron by studying ICD of Ne dimers both experimentally and theoretically. The ICD spectra measured for the ICD of the $Ne_2^{+}(2s^{-1})$ states and the ICD after Auger decay of the $Ne_2^{+}(1s^{-1})$ states unambiguously demonstrate significant modifications of the nuclear dynamics accompanying ICD by the recoil momentum imparted on the nuclei by fast photo- and Auger electrons. Our calculations illustrate an enormous effect of the recoil of the nuclei on the computed wave packets and ICD spectra supporting the present measurements. ICD processes following the emission of a fast electron provide a time averaged image of the nuclear wave packet, which has received the initial momentum, and hence allocate a sensitive tool to study the recoil effect.

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