Relevance of dissociative molecular states for resonant two-center photoionization of heteroatomic dimers

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Abstract

Photoionization of a weakly bound van-der-Waals dimer, composed of two atomic species \( A \) and \( B \), is studied theoretically. Atom \( A \) can be ionized either directly or via an indirect two-center channel, where atom \( B \) is first resonantly photoexcited and, afterwards, transfers the excitation energy via long-range electron–electron correlations radiationlessly to atom \( A \), causing its ionization. By taking the vibrational nuclear motion of the dimer during the process into account, we analyze the contributions to the photoionization cross section from bound and dissociative molecular states in the final \( A^+–B \) system. For the specific example of a LiHe dimer we show (a) that substantial contributions to both ionization mechanisms result from dissociative Li\(^+\) He states and (b) that the two-center pathway strongly dominates over the direct photoionization channel for photon energies close to one of the molecular LiHe resonances.

Keywords: two-center resonant photoionization, dissociative molecular states, interatomic coulombic decay

(Some figures may appear in colour only in the online journal)

1. Introduction

Since the early days of quantum physics, studies on photoionization in atoms and molecules have represented an important means to gain insight into the structure and dynamics of matter on a microscopic scale. In particular, electron–electron correlations play an important role in many photoionization processes—a prominent example being resonant photoionization, where an autoionizing state is created via photoexcitation which subsequently leads to ionization via Auger decay. Corresponding photoionization studies therefore enable to probe fundamental properties of electron–electron correlations, ranging from short to rather large distances on the atomic scale [1].

The mechanism of resonant photoionization can be generalized to systems consisting of two (or more) atoms. In this case, the resonant excitation of one atom leads to a radiationless energy transfer to a neighbor atom, resulting in its ionization. This decay mechanism, which relies on interatomic electron–electron correlations, is a two-center version of the (usually intraatomic) Auger effect and known as interatomic Coulombic decay (ICD) [3–5]. ICD has been experimentally observed in a variety of systems, comprising mainly van-der-Waals molecules [6–8] and clusters [9] made of noble gas atoms. Due to the weak binding forces, the interatomic distances in these systems are widely extended.

Resonant two-center photoionization (2CPI) represents the generalization of resonant photoionization to diatomic systems [10–12]. In this process a system, containing atoms
A and B of different species and initially being in its electronic ground state, is exposed to a resonant electromagnetic field. In a first step, an autoionizing two-center state is formed via resonant photoexcitation of atom B. In a subsequent second step, the latter stabilizes through ICD, causing ionization of the neighboring atom A. Under suitable conditions, 2CPI can largely dominate over the direct (i.e. single-center) photoionization of atom A. The process was experimentally observed in He-Ne dimers [13, 14] and Ne–Ar clusters [15] using synchrotron radiation to induce the 1s-3p transition in He at about 23 eV and the 2p-3s transition in Ne at about 17 eV, respectively. Both experiments found strong enhancements of the photoelectron yield from Ne and Ar, respectively, due to the two-center ionization mechanism that relies on long-range electron correlations.

The theory of 2CPI has originally been developed for diatomic systems whose internuclear distance \( R \) was assumed to be fixed. This ‘atomic’ description of 2CPI is characterized by a single resonance at the transition energy from the ground to the excited state in atom B. At the resonant photon energy \( \omega \), the enhancement of the two-center ionization channel over the direct photoionization of atom A amounts to \( \sigma^{(2)}/\sigma^{(1)} \sim [c/(\omega R)]^6 \) [10, 11], with \( c \) denoting the speed of light. Considering, for example, a diatomic system of Li and He at inter-nuclear distance \( R = 10 \) a.u., a relative enhancement of Li photoionization of \( \sim 10^6 \) is obtained.

Recently, we have extended the theoretical treatment of 2CPI by including the nuclear motion in a weakly bound heteroatomic dimer [16]. Within this molecular description we have shown for the example of LiHe that the nuclear motion causes a splitting of the single ‘atomic’ resonance into a multiple of resonances. They arise from the various vibrational states in the electronically excited intermediate state of LiHe\(^+\), and exhibit a similarly large enhancement as in the ‘atomic’ approach to 2CPI. In this study, solely bound molecular states were taken into account. At about the same time, ICD in a LiHe\(^+\) dimer has been investigated [17, 18] where it was found that the dissociative continuum of final Li\(^+\) + He molecular states largely dominates over the contribution from bound final Li\(^+\) He states.

In the present paper we develop our previous treatment of 2CPI in heteroatomic van-der-Waals dimers [16] further. Compared to [16], the present consideration differs in two main points. First, in addition to bound intermediate and final states of the dimer, we now include also its dissociative final states into the treatment. Second, considering 2CPI in LiHe dimers we employ now more accurate interatomic potentials than in [16]. Each of these two points turns out to have a very significant impact on the final results.

We note that our study differs from the investigation of ICD in LiHe\(^+\) [17, 18] by the fact that the process of 2CPI is more comprehensive than ICD, as it starts from LiHe in the ground state, includes the interaction with the external electromagnetic field (that may either lead to photoexcitation of He or direct photoionization of Li), and contains the channel of ICD just as a part of the two-center pathway leading to 2CPI. This larger scope, for instance, allows us (in contrast to [17, 18]) to examine the dependence of the cross section for 2CPI on the applied field parameters and to determine its strength as compared with the cross section for direct one-center photoionization.

It is worth mentioning that the influence of the nuclear motion on resonant interatomic phenomena has been studied for various processes. Characteristic signatures of the nuclear dynamics have been identified for ICD in He\(_2\) and HeNe dimers [7, 19], including the influence of the vibrational level structure on the angular distributions of emitted electrons [14, 20]. Besides, 2CPI has been studied in slow atomic collisions where the internuclear distance is not fixed either but subject to the relative atomic motion [21].

The paper is organized as follows. Our theoretical approach is presented in section 2. In section 3 we apply this approach to the process of 2CPI in LiHe dimers demonstrating, in particular, how the inclusion of dissociative molecular states influences the one- and two-center photoionization cross sections and that large amplifications of the two-center channel over the one-center channel are obtained for vibrationally highly excited intermediate states of the dimer. Concluding remarks are given in section 4. Atomic units (a.u.) are used throughout, unless explicitly stated otherwise.

2. Theory of resonant two-center photoionization

As in [16], we consider the process of 2CPI in a molecular system consisting of two atoms A and B, which are both initially in their ground states. At each of the atomic centers, we restrict ourselves to one active electron participating in the process. The corresponding effective nuclear charges are denoted by \( Z_A \) and \( Z_B \), respectively. Within the Born-Oppenheimer picture, the electronic and nuclear dynamics are treated separately, so that the electronic transitions are calculated for fixed internuclear distance \( R \). Note that, for the approximations in the following to be applicable, \( R \) has to be sufficiently large (covering at least several Bohr radii)—a condition met by extended van-der-Waals dimers.

2.1. Transition amplitudes and cross sections

The position of the nucleus of atom A is taken as the origin; the coordinates of the nucleus of atom B, the electron associated with A and the electron associated with B are denoted by \( \mathbf{r} \), \( \mathbf{r}' = \mathbf{r} + \mathbf{r} \) and \( Z_B \) respectively, where \( \mathbf{r} \) is the position of the electron of atom B relative to the nucleus \( Z_B \) (see figure 1(a)). The two-center ionization mechanism involves two steps, the photoexcitation of atom B and the subsequent radiationless energy transfer leading to the ionization of A (see figure 1(b)). The transition in atom B will be assumed to be dipole-allowed. For atom A to be ionized in a two-center process involving atom B, the ionization potential \( I_A = |\epsilon_A| \) has to be smaller than the energy difference \( \omega_B = \epsilon_e - \epsilon_x \) of the electronic transition in atom B.

To describe the two-center photoionization process including the nuclear motion, the relevant initial, intermediate and final electronic and vibrational configurations have to be specified. In the Born-Oppenheimer approximation, the
that the direct (one-center) photoionization process shares the same initial and final state with the two-center channel.

The external field is described as a classical electromagnetic wave with linear polarization. By setting the polarization axis along the z-axis and applying the dipole approximation, the vector potential reads:

$$A(t) = A_0 \cos(\omega t) \text{ with } A_0 = \hat{A}_0 e_z.$$  \hfill (1)

It leads to the interaction $\hat{W}_A e^{-i\omega t}$ with the electron in atom A (where it induces direct photoionization) and the interaction $\hat{W}_B e^{-i\omega t}$ with the electron in atom B (which, as a result, is photoexcited). Here we have introduced the abbreviations:

$$\hat{W}_A = \frac{A_0}{2e} \hat{p}, \quad \hat{W}_B = \frac{A_0}{2e} \hat{p} .$$  \hfill (2)

Furthermore, the interatomic coupling required for the two-center energy transfer is mediated by:

$$\hat{V}_{AB}(\mathbf{R}) = \text{r} \cdot \xi - \frac{3}{2} (\mathbf{r} \cdot \mathbf{R})(\xi \cdot \mathbf{R}) .$$  \hfill (3)

This long-range dipole–dipole interaction is valid for large interatomic distances.

Employing time-dependent perturbation theory, the transition amplitudes for two-center and one-center photoionization, respectively, read:

$$S^{(2)} = -2\pi i \sum_{\nu_1} \delta (E_{b,\xi} + E_i - E_{a,\xi} - E_{\nu_1} - \omega) \times \langle \Phi_{b,\xi} | v_{AB}(\mathbf{R}) | \Phi_{a,\xi} \psi_{\nu_1}(R,\nu_1) \rangle,$$

$$\times \langle \Phi_{a,\xi} \psi_{\nu_1}(R,\nu_1) | \Phi_{b,\xi} \psi_{\nu_1}(R,\nu_1) \rangle \epsilon + E_{\nu_1} + \omega - E_{a,\xi} + \frac{i}{2} \Gamma ,$$

$$\hfill (4)$$

$$S^{(1)} = -2\pi i \delta (E_{b,\xi} + E_i - E_{a,\xi} - E_{\nu_1} - \omega) \times \langle \Phi_{b,\xi} | v_{AB}(\mathbf{R}) | \Phi_{a,\xi} \psi_{\nu_1}(R,\nu_1) \rangle,$$

$$\hfill (5)$$

hence, the decay width $\Gamma$ accounts for the instability of the autoionizing state due to the excitation of atom B.

From equations (4) and (5), the photoionization cross sections are obtained:

$$\sigma^{(1,2)} = \frac{1}{2\pi} \int \frac{d^3k}{(2\pi)^3} |S^{(1,2)}|^2 .$$  \hfill (6)

In equation (4), the 2CPI transition amplitude $S^{(2)}$ involves a coherent summation over the vibrational levels of the excited state. Furthermore, both cross sections $\sigma^{(1)}$ and $\sigma^{(2)}$ are summed incoherently over the final nuclear states [23].

2.2. Decay widths

The resonance width $\Gamma$, accounting for the instability of the excited state of atom B, includes the radiative width $\Gamma_{\text{rad}}$ as well as the ICD width $\Gamma_{\text{ICD}}$:

$$\Gamma = \Gamma_{\text{rad}} + \Gamma_{\text{ICD}}.$$  \hfill (7)
While the radiative decay rate:
\[
\Gamma_{\text{rad}} = \frac{4 \omega_0^2}{3e} \left| \langle \chi_a | \chi_e \rangle \right|^2 ,
\]  
(8)
describes the decay of the excited state of atom B via spontaneous emission of a photon, the ICD width \( \Gamma_{\text{ICD}} \) is associated with the radiationless transfer of the transition energy in B to atom A, leading to its ionization. In a system of two atoms at fixed internuclear distance, the ICD width is given by:
\[
\Gamma_{\text{ICD}}(R) = \int \frac{d^3k'}{(2\pi)^3} |\mathcal{V}_{AB}(k', R)|^2 \delta(\epsilon_k + \epsilon_g - \epsilon_e - \epsilon_f) ,
\]  
(9)
where \( \mathcal{V}_{AB}(k', R) = \langle \Phi_{k,g} | \mathcal{V}_{AB}(R) | \Phi_{k,e} \rangle \) denotes the matrix element regarding the electronic transition. Relying on the dipole-dipole interaction (3), the ICD width scales as \( \Gamma_{\text{ICD}}(R) \sim R^{-6} \). (Note, however, that significant deviations from this simple scaling arise at small internuclear distances; see, e.g. [17]).

When the atoms form a molecular state with vibrational quantum number \( \nu_a \), the corresponding ICD width of this state can be obtained approximately by taking an average over the probability density \( |\psi_a(R, \nu_a)|^2 \) of the nuclear wave function:
\[
\Gamma_{\text{ICD}} = \int \Gamma_{\text{ICD}}(R) |\psi_a(R, \nu_a)|^2 dR .
\]  
(10)
This expression, that is intuitively understandable, has also been used in [16]. It can be obtained by noting that, in the first order of perturbation theory, the transition amplitude for ICD including the nuclear motion contains an integration of the form:
\[
\int \langle \psi_f | \mathcal{V}_{AB}(k, R) | \psi_a \rangle e^{-i\Delta E_{1f}t} dt ,
\]  
for a given vibrational state \( \psi_a \). Here, \( \Delta E_{1f} = E_{g,e} + E_{k,g} - E_{k,e} \) denotes the energy difference between the autoionizing and final two-center states. To obtain the corresponding ICD width, this amplitude has to be squared and afterwards summed over the final nuclear states \( \psi_f \). From the resulting expression—when neglecting the weak \( E_f \)-dependence of \( \Delta E_{1f} \) that is mainly determined by the electronic energies—one can isolate a completeness relation of the final nuclear states,
\[
\sum_f |\psi_f \rangle \langle \psi_f | = 1 ,
\]  
(11)and, thus, ends up with the averaged ICD width from equation (10). We note that the sum extends over all discrete bound states and the dissociative continuum.

### 2.3. Bound and dissociative molecular states

The nuclei move in an interatomic potential \( V_f(R) \), that supports a certain number of discrete bound states with vibrational quantum number \( \nu_n \ (n \in \{i,a,f\}) \). In order to describe 2CPI to a large extent analytically, we shall assume that \( V_f(R) \) can be approximated by a Morse potential of the form:
\[
v_{\text{Morse}}(R) = D \left( 1 - e^{-\alpha(R-R_0)} \right)^2 - 1 ,
\]  
(12)
here, \( D \) denotes the depth of the potential, \( R_0 \) the equilibrium distance and \( \alpha \) describes the width of the potential. As a result, the bound vibrational wave functions are given analytically as:
\[
\psi_{\nu_b}(R, \nu_b) = \frac{\alpha b(\nu_b)}{\Gamma(\kappa - \nu_b)} e^{-\kappa/2} z^{\nu_b/2} L_{\nu_b}^{(b)}(z) ,
\]  
(13)with the Gamma function \( \Gamma(x) \), the associated Laguerre polynomials \( L_{\nu_b}^{(b)}(z) \), \( b = \kappa - 2\nu - 1 \), \( z = ke^{-\alpha(R-R_0)} \), \( \kappa = \sqrt{\frac{2 \omega_0 D}{\alpha^2}} \) and the reduced mass \( \mu \) [24]. The corresponding vibrational energy shifts are:
\[
E_{\nu_b}(\nu) = \frac{2D\alpha^2}{\mu} \left[ \left( \nu + \frac{1}{2} \right) - 1 \kappa \left( \nu + \frac{1}{2} \right)^2 \right] .
\]  
(14)

Bound vibrational states arise in the initial, intermediate and final state of the 2CPI process. The transition matrix elements including the vibrational states describe the overlap of the wave functions corresponding to the different electronic configurations.

In addition to our previous consideration [16], we also take dissociative wave functions in the final state into account. They are needed to describe photoionization of a dimer where, as a result of the process, the molecular bond breaks. The dissociative nuclear wave functions in the Morse potential (12) are given by:
\[
\psi_{\nu_d}(R, \nu) = e^{-\nu/2} \left[ A z^{\nu/2} F(-s + i\epsilon, 2i\epsilon + 1; z) 
+ A^* z^{-\nu/2} F(-s - i\epsilon, -2i\epsilon + 1; z) \right] ,
\]  
(15)where \( F \) denotes the confluent hypergeometric function, \( \epsilon = \sqrt{\frac{2\mu E_{\nu_d}}{\alpha}} \), \( 2s = 2a - 1 \), \( z = 2ae^{-\alpha(R-R_0)} \), \( a = \sqrt{\frac{2\mu D}{\alpha^2}} \) and \( A = \Gamma(-2i\epsilon) / \Gamma(-s - i\epsilon) \) [25]. In our computational scheme we apply dissociative wave functions that have been normalized within a box of length \( \ell = 600 \) a.u. Subsequently, a discrete spectrum of energies is obtained when demanding \( \psi_{\nu_d}(R, \nu) = 0 \) at \( R = \ell \). Here, energies up to \( E_{\nu_d} \approx 0.7 \) eV are considered.

As a consequence, the one-center and two-center photoionization cross sections (6) are computed by summing incoherently over the bound and dissociative final molecular states. The two-center pathway involves, besides, a coherent summation over the vibrational bound states of the intermediate state in the transition amplitude (4). Regarding the electronic states, the same wave functions as in [16] are applied.

### 3. Results and discussion

We now apply our theoretical approach to calculate the one-center and two-center photoionization cross sections in a...
The $^7$Li$^4$He dimer, including the effects of the nuclear motion. This dimer is a particularly interesting molecule of extreme quantum nature, forming in its ground state a very weakly bound quantum halo system whose mean internuclear separation lies far beyond the outer classical turning point of the interatomic potential \cite{26,27}. The fact that this molecule is so extremely extended (having a mean internuclear distance of about 53 a.u. in the ground state \cite{26,27}) renders our theoretical approach presented in section 2 particularly suitable.

The cross sections are calculated as function of the photon energy of the external electromagnetic field. The considered energy interval covers the transition energies to all vibrational levels of the electronically excited intermediate LiHe$^+$(1s2p$_0$) state. The internuclear axis is taken along the polarization direction of the field.

Regarding the interatomic potentials $V_a(R)$, we use the same potential curve for the initial state as in \cite{16}, which supports exactly one bound vibrational level. However, for the intermediate state LiHe$^+$(1s2p$_0$), the new potential curve from \cite{18} is employed, yielding 20 bound vibrational levels. Finally, the data from \cite{28} is considered for the final state, where eight bound vibrational levels are included. The potential curves are fitted to Morse potentials of the form \eqref{12} and the nuclear wave functions are obtained from equations \eqref{13} and \eqref{15}. The fitted parameters are compiled in table 1.

Figure 2 depicts the ratio of two-center to one-center photoionization cross sections when only the bound vibrational levels of the final molecular state are considered. A series of peaks results, located at photon energies that are resonant to a transition energy between the intermediate and the electronically excited LiHe$^+$ molecule. Each vibrational level $\nu_a$ gives rise to a peak.

For vibrationally highly excited intermediate states, very large amplifications of the photoionization yield due to the two-center pathway result. The enhancement over the direct one-center photoionization reaches values up to $\approx 10^9$. This level of enhancement is similar to those found in our recent study \cite{16} (see figure 5 therein) and also in the original study of 2CPI where molecular effects were not included \cite{10}.

However, while a comparably strong amplification was found in \cite{16} for the lower excitations, as well, this has changed drastically in our present calculations. It is mainly caused by the different interatomic potential curve applied for the intermediate state whose minimum is located at substantially smaller internuclear distances than in \cite{16}. Therefore, transitions to lower lying vibrational states $\nu_a$ are suppressed by small Franck-Condon factors, characterizing the overlap of the nuclear wave functions. As a result, for photon energies that resonantly populate vibrational states with small quantum numbers $\nu_a$ in LiHe$^+$, the strong enhancement found in \cite{16} has disappeared: the 2CPI cross section $\sigma^{(2)}$ only slightly exceeds the cross section $\sigma^{(1)}$ for direct photoionization of Li, as figure 2 shows.

Conversely, vibrationally highly excited intermediate states possess large overlaps with the initial, largely extended vibrational wave function, leading to very considerable enhancements up to $\approx 10^9$ of the photoionization yield. This is apparent when comparing the Franck-Condon factors, describing the transition from the initial to the intermediate state, $F_{ia}(\nu_a = 0) \approx 0.0015$, and $F_{ia}(\nu_a = 19) \approx 0.82$. Thus, the application of the improved interatomic potential curve has revealed that the impact of the molecular transition dynamics during 2CPI in LiHe strongly distinguishes between low and high lying vibrational states in the electronically excited LiHe$^+$ dimer. We furthermore note that the decay widths are increased as compared to \cite{16}, which is also mostly due to the shifted minimum position of the potential curve of the intermediate state.

The inclusion of dissociative final states leads to additional contributions to the cross section. For resonant photon energies $\omega$, the two-center photoionization cross sections are depicted in figure 3, along with the individual contributions from the bound and dissociative final states, respectively.

It turns out that the dissociative final states contribute strongly to the 2CPI cross section. The corresponding growth of the cross section due to their inclusion increases when increasing the vibrational level of the intermediate state. Considering the resonance peaks, the amplification of the 2CPI cross section by the inclusion of dissociative final states yields relative contributions to the total cross section between less than 1% (for $\nu_a = 0$) to almost 80% (for $\nu_a = 19$).

Figure 4 illustrates the photon energy dependence of the 2CPI cross section between the two resonant energies corresponding to the intermediate vibrational levels $\nu_a = 18$ and $\nu_a = 19$. The partial contributions from bound and dissociative final states are shown by dashed and dotted lines, respectively. Again, the particularly significant contribution from the dissociative final states to the 2CPI cross section in this range of photon energies is apparent. As in \cite{16}, the decay widths decreases when increasing $\nu_a$. For the two resonance peaks, $\Gamma \approx 1.5 \times 10^{-5}$ eV for $\nu_a = 18$ and $\Gamma \approx 2.5 \times 10^{-6}$ eV for $\nu_a = 19$. These are small compared to the width $\Gamma \approx 2.4 \times 10^{-4}$ eV of the first peak $\nu_a = 0$.

\begin{table}[h]
\centering
\caption{Fitted Morse parameters (in atomic units) for the potential curves of initial, intermediate and final electronic configurations.}
\begin{tabular}{|c|c|c|}
\hline
 & Initial & Intermediate & Final \\
\hline
$D$ & $5.7 \times 10^{-6}$ & $1.4 \times 10^{-2}$ & $2.9 \times 10^{-3}$ \\
$R_{eq}$ & 11.9 & 6.5 & 3.6 \\
$\alpha$ & 0.43 & 0.58 & 0.70 \\
\hline
\end{tabular}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2}
\caption{Ratio of the photoionization cross sections in LiHe when considering all bound vibrational levels of the final state.}
\end{figure}
This interatomic decay process constitutes the second step in its decay to the excited LiHe* 1s2p state. Similar oscillations have been predicted for ICD of lithium, depending on the energy cross section at fixed resonant photon energy shows an oscillatory behavior depending on the energy $E_{\text{dis}}$ of the dissociative state. The individual contributions are depicted regarding the bound (blue triangles), and the dissociative states (dotted).

To complete this section we note that our treatment does not include dissociation channels in the intermediate states. This is justified for the range of photon energies considered here which are too small to resonantly populate the dissociative energy levels, rendering 2CPI via these intermediate states not efficient. Moreover, even if higher photon energies were applied, enabling a resonance coupling to these dissociative states, we do not expect that 2CPI in LiHe would proceed as efficiently as through the bound vibrational states of LiHe*. Because of rather long time scales typical for ICD in this system, the nuclei after dissociation would considerably separate from each other, leading to suppression of the interatomic energy transfer required for ICD.

4. Conclusion

Resonant two-center photoionization in weakly bound diatomic systems has been studied, including the nuclear motion and considering LiHe dimers as example. We focused on the relevance of dissociative final states, this way extending our previous study [16] of 2CPI where solely bound molecular states were taken into account. To this end, we have analyzed the 2CPI cross section as a function of the photon energy of the resonant electromagnetic field that induces the process.

In comparison with a purely 'atomic' treatment assuming fixed nuclei, the inclusion of nuclear motion leads to a splitting of the 2CPI cross section into a vibrational multiplet of peaks that are located at the resonant transition energies to the intermediate molecular states. The contribution from dissociative channels to these peaks was generally found to be relevant and particularly large when 2CPI proceeds through vibrationally highly excited intermediate states that allow for substantial overlap with the initial nuclear wave function in the LiHe ground state. For the highest vibrational levels, the contributions from dissociative states even strongly dominate over those final states where the molecule remains bound. This main result on 2CPI of LiHe is in accordance with recent findings for ICD of the excited LiHe* (1s2p) state [17].

The inclusion of dissociative final states enhances both the two-center and the direct (one-center) photoionization of Li in the dimer. However, the relevant range of dissociative energies is much more extended for 2CPI (reaching up to $\approx 0.6 \text{ eV}$) than for the direct process. Moreover, 2CPI was shown to strongly dominate over direct photoionization, when high vibrational levels of the intermediate state are populated. The magnitude of enhancement can reach $\sigma^{(2)}/\sigma^{(1)} \approx 10^6$, in agreement with earlier predictions [10, 16].

We point out that a corresponding experiment on 2CPI in LiHe might become feasible in the near future, since ICD in helium droplets doped with lithium and rubidium atoms has recently been observed [29]. Under these circumstances, however, ICD was found to mainly proceed from the 1s2s 1S state in helium and to compete with a charge-exchange decay channel akin to Penning ionization.
Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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