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Double ionization of the hydrogen chloride molecule: Influence of the target orientation on multiple differential cross sections

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ABSTRACT

We report in this work multiple differential cross sections for the double ionization of isolated hydrogen chloride molecules impacted by electrons. The calculations are performed within the first Born approximation by considering a target molecular state described by means of a single-center molecular wave function. In the initial state, the incident electron is described by a plane wave, while in the final state Coulomb wave functions are used for modeling the interaction between the two ejected electrons and the residual target ion, the scattered electron being described by a plane wave. Additionally, a Gamow factor is introduced to take into account the Coulomb repulsion between the two outgoing particles. The contributions to the various differential cross sections of the four outermost orbitals of the hydrogen chloride molecule, namely, 4σ, 5σ, $2\pi_x$, and $2\pi_y$, are then reported for specific target orientations and by considering only the case of two electrons ejected from the same molecular orbital. The obtained results point out the effect of the target orientation on both the $(e, 3e)$ and the $(e, 3-1e)$ collisions and clearly evidence the signature of the well-known double ionization mechanisms, namely, the shake-off and the two-step 1 processes for all the cases investigated.

1. Introduction

It is well known that electron-induced collisions on atoms or molecules play an important role in many scientific fields like physics, chemistry, biology and even medicine where there is nowadays a high demand for accurate data in particular for describing the interactions induced by charged particles in biological medium (medical imaging, radiotherapy treatment planning, nuclear medicine, *etc.*). In this context, experimental data as well as theoretical models have extensively been reported in the literature for both electron- and positron-induced collisions in water, the latter being commonly used as surrogate of the living matter [1–7].

Double ionization of HX-type diatomic molecules is known for leading to dication species rather stable in solution and then extremely chemically reactive [8]. Thus, in the gas phase, dications have been observed in several high-energy systems like plasmas [9], ionized gases, excimer lasers [10], interstellar clouds [11], *etc.* In this context, the hydrogen chloride (HCl) molecule is very interesting since isoelectronic with the rare-gas element argon, whose atomic spectrum has extensively been studied [12] and whose size permits *ab initio* calculations of the Auger transition energies. Moreover, the HCl molecule is involved in many industrial domains: production of hydrochloric acid, pharmaceutical and chemical transformations (hydro-chlorination of rubber, production of vinyl and alkyl chlorides), and semiconductor industry (etching of the semiconductor crystals and purification of the silicon).

Under these conditions, numerous theoretical [13,14] and experimental [15–19] works were performed to determine the different energy states of the HCl^{2+} dication. Additionally, many experimental studies focused on electron-induced collisions on HCl were reported. Let us cite the first electron scattering measurements reported by Brüche [20] using a Ramsauer type apparatus for impact energies between 4 eV and 30 eV. More recently, Rohr and Linder [21,22] have used the crossed-beam technique to measure differential cross sections for vibrational excitation in e-HCl collisions from threshold (0.357 eV) up to 8 eV. Similarly, Knot et al. [23] reported differential cross sections for electron impact vibrational excitation in the primary energy range 0.15–6 eV for angles ranging from 15° to 135°. Vibrational doubly differential cross sections were also measured by Shafer and Allen [24] in a larger angular range (15–180°) from threshold up to 3 eV. Besides, Radle et al. [25] have reported elastic cross sections indirectly obtained from

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measurements of differential cross sections performed with a high-resolution crossed-beam electron spectrometer in the energy range 0.5–10 eV while Hamada and Sueoka [26] measured total cross sections of electron collision with HCl using a linear transmission type time-of-flight apparatus from low to intermediate impact energies 0.8–400 eV.

On the theoretical front, numerous investigations were focused on vibrational and rotational excitations induced by electron impact [27–35]. Many authors also reported theoretical total cross sections for electron scattering over different energy regimes [35–37]. Let us cite the variational *R*-matrix calculations performed by Pfingst et al. [35] as well as the free-parameter approach based on the spherical complex optical potential (SCOP) model reported by Jain and Baluja [36] to calculate total cross sections for e-HCl collisions in the energy range 10–5000 eV. Very recently, total cross sections have been reported by Vinodkumar et al. [37] over a wide energy range, namely, from 0.1 eV to 2 keV by using the *R*-matrix method coupled with the Quantemol-*N* software in the sub-ionization region and with the SCOP model for high impact energies. However, despite its importance in the different above-cited fields, to the best of our knowledge, the hydrogen chloride has never been studied in the double ionization context. Under these conditions, the current work, in which the dependence of the multiple differential cross sections with respect to the hydrogen chloride molecule orientation is detailed orbital by orbital, appears as a pioneer one since to the best of our knowledge, neither experimental nor theoretical results are up to now available in the literature.

Similarly to our previous works [5–7], the target molecule is here described by means of a single-center molecular wave function whose radial and angular parts are expressed by Slater-type functions [38] and real solid harmonics [39], respectively. In the following, we briefly outline the theoretical model used for describing the double ionization of oriented hydrogen chloride molecules and report five-fold, four-fold, triply and doubly differential cross sections for the four outermost orbitals of the hydrogen chloride molecule. Conclusions about the influence of the target molecule orientation on the double-ionization process are finally summarized.

Atomic units (a.u.) are used throughout unless indicated otherwise.

Table 1
Experimental values of binding energies for the various final states of the double-ionized HCl molecule reported in the current work. These values are taken from Refs. [18,19].

Molecular final state	Binding energies (eV)
$(2\pi_x)^{-2}$	37.7 [18]
$(2\pi_y)^{-2}$	38.8 [18]
$(5\sigma)^{-2}$	45.0 [18]
$(4\sigma)^{-2}$	67.1 [19]

The fundamental bound state of the HCl target molecule is here described by means of the single-center molecular wave functions reported by Moccia [40]. They are all centered at a common origin, namely, the heaviest atom (chlorine). The 18 bound electrons of the hydrogen chloride molecule in the fundamental state configuration $^1\Sigma^+$ are then distributed among nine molecular wave functions corresponding to the nine molecular orbitals denoted 1σ, 2σ, 3σ, $1\pi_x$, $1\pi_y$, 4σ, 5σ, $2\pi_x$, and $2\pi_y$. Under these conditions, the hydrogen chloride target can be described by means of N_{orb} ($N_{orb} = 9$) molecular functions expressed by

$$\upsilon_j(\boldsymbol{r}) = \sum_{k=1}^{N_{at}(j)} a_{jk}\Phi_{n_{jk}l_{jk}m_{jk}}^{\xi_{jk}}(\boldsymbol{r}), \qquad (2)$$

where $N_{at}(j)$ refers to the number of the different atomic functions used in the development of the jth molecular orbital (with j varying from 1 to N_{orb}), while a_{jk} denotes the weight of each real atomic component $\Phi_{n_{jk}l_{jk}m_{jk}}^{\xi_{jk}}(\boldsymbol{r})$ expressed as (see Moccia [40] for more details)

$$\Phi_{n_{jk}l_{jk}m_{jk}}^{\xi_{jk}}(\boldsymbol{r}) = R_{n_{jk}}^{\xi_{jk}}(r)S_{l_{jk}}^{m_{jk}}(\hat{r}) \qquad (3)$$

where $\hat{r}$ refers to the solid angle of the position vector $\boldsymbol{r}$ and $R_{n_{jk}}^{\xi_{jk}}(r)$ the radial part, expressed by Slater-type functions [38],

$$R_{n_{jk}}^{\xi_{jk}}(r) = \frac{(2\xi_{jk})^{n_{jk}+1/2}}{\sqrt{(2n_{jk})!}}r^{n_{jk}-1}e^{-\xi_{jk}r} \qquad (4)$$

and $S_{l_{jk}}^{m_{jk}}(\hat{r})$ the angular part expressed by means of real solid harmonics [39] and given by

$$\begin{cases} S_{l_{jk}}^{m_{jk}}(\hat{r}) = \left(\dfrac{m_{jk}}{2\left|m_{jk}\right|}\right)^{\frac{1}{2}}\left\{Y_{l_{jk}}^{-\left|m_{jk}\right|}(\hat{r}) + (-1)^{m_{jk}}\left(\dfrac{m_{jk}}{\left|m_{jk}\right|}\right)^{\frac{1}{2}}Y_{l_{jk}}^{-\left|m_{jk}\right|}(\hat{r})\right\} \quad \text{if} \quad m_{jk} \neq 0 \\ S_{l_{jk}}^{m_{jk}}(\hat{r}) = Y_{l_{jk}}^{0}(\hat{r}) \quad \text{if} \quad m_{jk} = 0 \end{cases} \qquad (5)$$

2. Calculation method

The double ionization process of the hydrogen chloride target by electronic impact – assumed as a pure electronic transition – may be schematized by

$$e_i^- + \mathrm{HCl} \rightarrow e_s^- + e_1^- + e_2^- + \mathrm{HCl}^{2+}, \qquad (1)$$

where the incident, the scattered and the two ejected electrons are denoted e_i^-, e_s^-, e_1^- and e_2^-, respectively. The corresponding momenta $\boldsymbol{k}_i$, $\boldsymbol{k}_s$, $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$ are linked to the kinetic energies *via* the relations $k_i = \sqrt{2E_i}$, $k_1 = \sqrt{2E_1}$, $k_2 = \sqrt{2E_2}$ and $k_s = \sqrt{2(E_i - E_1 - E_2 - I^{2+})}$, I^{2+} being the energy needed to extract two electrons from a given target molecular orbital (see Table 1 where we have reported the values used in the current work, taken from Refs. [18,19]). Let us remind that we only here consider the case of two outgoing electrons ejected from the same molecular orbital.

For more details, we refer the reader to Moccia [40] where all the coefficients (a_{jk}, ξ_{jk}) and quantum numbers n_{jk}, l_{jk}, m_{jk} are reported.

In the framework of the first Born approximation, the fivefold differential double ionization cross section for each molecular subshell is given by

$$\frac{d^5\sigma_j}{d\Omega_1 d\Omega_2 d\Omega_s dE_1 dE_2} = (2\pi)^4\frac{k_1k_2k_s}{k_i}\left|T_j\right|^2, \qquad (6)$$

where $d\Omega_s$, $d\Omega_1$ and $d\Omega_2$ represent the solid angles of the scattered and the two ejected electrons, respectively, while dE_1 and dE_2 refer to the energy transfer intervals of the ejected electrons. Let us remind that the index j refers to one of the four outermost final states of the doubly ionized hydrogen chloride molecule considered here, namely, those corresponding to the ejection of two electrons from the same molecular orbital $2\pi_x$, $2\pi_y$, 5σ and 4σ. In addition, the hydrogen chloride molecule target being randomly oriented in the space while the above-cited wave functions refer to a particular molecular orientation given by the Euler angles (α, β, γ), so

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