

Article

Ionization of Coronene by Proton Impact in the Continuum Distorted Wave–Eikonal Initial State Approximation: Influence of Molecular Orbital Densities

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Abstract

Single-electron emission from the coronene ($C_{24}H_{12}$) molecule induced by the impact of 100 keV H^+ projectiles is investigated using the continuum distorted wave–eikonal initial state approximation within a semi-classical impact-parameter framework. Multi-center orbitals in the initial channel are derived using the Gaussian quantum chemistry software package, while wave functions of the emitted electron in the exit channel are evaluated using a spherically averaged static potential of the molecular core. The evaluated total ionization cross sections and probabilities are compared and discussed with results obtained from a simplified description of the molecule in which the molecular geometry is ignored. The ionization cross sections of the molecular orbitals generally increase monotonically with decreasing binding energy; however, several deviations from this overall trend are observed. Both the overall trend and the deviations are interpreted in terms of information-theoretical quantities.

Keywords: molecular collisions; ionization; energy-differential cross sections; continuum distorted wave methods

1. Introduction

In recent years, there has been increasing interest in the interaction between energetic ions and complex molecular targets. This interest stems not only from the desire to understand fundamental processes but also from the fact that the knowledge gained in this field can be applied in many areas, including radiation therapy, plasma research, astrophysics, and ion-beam technology [1–5]. In collisions involving fast heavy ions with energies in the MeV range, ionization plays a dominant role compared to other processes, such as electron capture. A thorough understanding of ionization processes induced by charged particle impact can provide valuable insight into the energy transfer processes that occur during collisions, the mechanisms of molecular fragmentation, and the electronic structure of molecules, etc. Nowadays, in addition to the study of biologically important DNA/RNA base molecules [2], there is also increasing interest in the interactions between large carbon-based molecules and charged ions [6–8]. The collision dynamics of large molecules may differ significantly from those of atoms and smaller molecules because collective effects can also influence these processes [9].

Polycyclic aromatic hydrocarbons (PAHs) constitute an important class of carbonaceous molecules characterized by delocalized π -electron systems and high chemical stability [6,8]. These molecules are believed to be abundant in the interstellar medium and are thought to contribute significantly to the unidentified infrared emission bands observed



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in numerous astrophysical environments [10]. The charge-state distribution and fragmentation of PAHs are strongly influenced by interactions with cosmic rays and energetic ions, making the investigation of ionization cross sections essential for modeling their evolution and survival under irradiation. Among PAHs, coronene ($C_{24}H_{12}$) is frequently considered a benchmark system because of its highly symmetric structure and relatively large number of valence electrons. Its electronic properties have made it a preferred target in both experimental and theoretical studies addressing photoionization, electron-impact ionization, and ion-induced processes [11–13]. Nevertheless, despite considerable progress in the study of ion collisions with large molecules, reliable ionization cross sections for ion impacts on coronene remain limited, particularly over a broad range of projectile energies.

Over the past few decades, there has been widespread interest in the application of information-theoretic concepts in theoretical chemistry. Concepts originating from information theory have emerged as powerful complementary tools for analyzing electronic systems [14–18]. The connection between information theory and molecular electronic structure arises from the interpretation of electron density as a probability distribution. Quantities such as Shannon entropy [19], Fisher information [20], Onicescu information energy [21], and related information-theoretic measures provide a novel perspective on the spatial organization, localization, and complexity of electron distributions [22,23]. Shannon entropy quantifies the global delocalization or uncertainty of the electronic distribution, whereas Fisher information characterizes its local structure and sensitivity to spatial variations. Onicescu information energy provides a more sensitive measure of localization than Shannon entropy. The coronene molecule has enough electrons to make it worthwhile to analyze its ionization properties from an information-theoretic perspective.

From a dynamical perspective, the description of ionization in ion–molecule collisions involving many-electron targets represents a significant challenge. Several perturbative and non-perturbative approaches have been developed for this purpose [5,24–27], among which the continuum distorted wave–eikonal initial state (CDW-EIS) model has proven to be particularly successful for intermediate- and high-energy collisions [28,29]. The CDW-EIS formalism accounts for the distortion of the active-electron wavefunctions by both the projectile and target Coulomb fields and has been extensively applied to atomic and molecular ionization processes, yielding good agreement with available experimental data for a wide variety of systems [30–33].

In the present work, we investigate the ionization of coronene molecules induced by energetic proton impact within the framework of the CDW-EIS model [33,34]. The molecular electronic structure is described using an independent-electron approach, and quantities characterizing ionization transitions are evaluated for each molecular orbital. The total and differential ionization cross sections are calculated for collisions of 100 keV protons. The obtained results provide theoretical benchmarks for proton–PAH collisions and contribute to a better understanding of radiation-induced processes in large aromatic molecules relevant to both laboratory and astrophysical environments.

Atomic units are used unless otherwise is stated.

2. Theoretical Framework

$C_{24}H_{12}$ is a highly symmetrical, planar polycyclic aromatic hydrocarbon molecule that belongs to the D_{6h} point group in terms of symmetry. Its molecular orbitals (MOs) belong to the one- and two-dimensional irreducible representations (IRs) of the point group. The one-dimensional IRs are denoted by A_n and B_n , and the two-dimensional IRs by E_n , where n varies between 1 and 2 and x represents either g (gerade) and u (ungerade). The molecular orbitals constructed as linear combinations of atomic orbitals (LCAO) were determined using the Hartree–Fock scheme (LCAO-HF). The numerical calculations of the

ground-state multi-center MO wave functions were performed using the GAUSSIAN 16 program package [35] with the 6-311G(d,p) atomic basis set. The single-center expansion (SCE) method [36] provides a very efficient tool to expand the multi-center wavefunctions and the molecular core potential over a single-center which fits to the structure of the molecule (center of mass of the molecule (CMO) in the present case). That is a given $\phi_i(\mathbf{x}')$ multi-center bound MO can be expressed in terms of spherical harmonics $Y_l^m(\hat{\mathbf{x}}')$, (note $\mathbf{x}'$ refers to the frame fixed to the molecule). However, given that a molecule has point group symmetry (D_{6h} for $C_{24}H_{12}$), the use of the symmetry-adapted angular function $X_{hl}^{p,\mu}(\theta', \varphi')$ proves to be very useful for eliminating non-contributing terms in the series expansion, where p and μ label one of the relevant irreducible representations and one of its components, respectively [36]. The index h labels a specific basis at a given angular momentum l for the p th irreducible representations considered. The symmetry-adapted angular function can be derived from the spherical harmonics using a symmetry-dependent transformation matrix, [36]

$$X_{hl}^{p,\mu}(\hat{\mathbf{x}}') = \sum_m b_{hlm}^{p,\mu} Y_l^m(\hat{\mathbf{x}}'), \quad (1)$$

and so $\phi_i(\mathbf{x}')$ is expressed as

$$\phi_i(\mathbf{x}') = \sum_{h,l_i} u_{h,l_i}(\mathbf{x}') X_{h,l_i}^{p,\mu}(\hat{\mathbf{x}}'), \quad (2)$$

where the coefficients are obtained as

$$u_{h,l_i}(\mathbf{x}') = \int d\hat{\mathbf{x}}' [X_{h,l_i}^{p,\mu}(\hat{\mathbf{x}}')]^* \phi_i(\mathbf{x}'). \quad (3)$$

Distorted wave models developed for the ionization of atomic targets [29] using single-center wave functions provided by the SCE method can easily be adapted to the calculation of molecular scattering quantities. We will use the well-known CDW-EIS method to describe collision dynamics and evaluate the scattering quantities [29,37,38]. Assuming that the projectile with charge Z_P travels along a straight-line trajectory $\mathbf{R}(t) = \mathbf{b} + \mathbf{v}t$, where $\mathbf{b}$ is the impact parameter and $\mathbf{v}$ is the constant velocity, the transition amplitude in *prior* form for the ejection of an electron with momentum $\mathbf{k}_e$ from the i th MO, can be expressed as

$$\mathcal{A}_{i\mathbf{k}_e}^-(\mathbf{b}, \omega_E) = -i \int_{-\infty}^{\infty} dt \langle \xi_{\mathbf{k}_e}^{-CDW}(\mathbf{x}, t) | [\hat{h} - i(\partial/\partial t)_r] \xi_{i,\omega_E}^{+E}(\mathbf{x}, t) \rangle, \quad (4)$$

where the initial and final distorted states are given by

$$\xi_{i,\omega_E}^{+E}(\mathbf{x}) = \phi_i(\mathbf{x}, t) L_{\mathbf{v}}^{+E}(\mathbf{s}) \quad \xi_i^{-CDW} = \phi_{\mathbf{k}_e}(\mathbf{x}, t) L_{\mathbf{p}}^{-CDW}(\mathbf{s}) \quad (5)$$

with

$$L_{\mathbf{v}}^{+E}(\mathbf{s}) = \exp[-i \frac{Z_P}{v} \ln(v \cdot \mathbf{s} + \mathbf{v} \cdot \mathbf{s})], \quad (6)$$

and

$$L_{\mathbf{p}}^{-CDW}(\mathbf{s}) = N^* \left(\frac{Z_P}{p} \right) {}_1F_1 \left(-i \frac{Z_P}{p}; 1; -ips - i\mathbf{p} \cdot \mathbf{s} \right), \quad (7)$$

where

$$N(v) = e^{\pi p/2} \Gamma(1 - iv), \quad (8)$$

$\mathbf{s}$ is the electronic coordinate with respect to the projectile nucleus, $\mathbf{p} = \mathbf{k}_e - \mathbf{v}$ and ${}_1F_1$ is Kummer's (confluent hypergeometric) function. The transition amplitude of Equation (4) is expressed in the laboratory frame, while the above ground-state molecular orbitals are represented in a reference frame fixed to the molecule. The transformation of the wave

function (2) to the laboratory frame $\phi_i(\mathbf{x}') \rightarrow \phi_i(\mathbf{x})$ is performed using the Euler angles $\omega_E \equiv (\alpha, \beta, \gamma)$ by applying the transformation properties of symmetry-adapted spherical harmonics: $X_{lh}^{p\mu}(\hat{\mathbf{x}}) = \sum_{m'} \bar{b}_{lm'}^{p\mu} D_{m'v}^l(\omega_E) Y_{lm'}(\hat{\mathbf{x}}')$, where $\bar{b}$ denotes the appropriate expansion coefficient and D_{mv}^l is the rotation matrix [36,39,40]. This is why $\mathcal{A}_{i\mathbf{k}_e}^-$ depends on ω_E . The Hamiltonian $\hat{h}$ is usually assumed to be of the form

$$\begin{aligned}\hat{h} &= \hat{h}_0 - \frac{Z_P}{|\mathbf{x} - \mathbf{R}(t)|} \\ &= -\frac{1}{2}\Delta_{\mathbf{r}} + V_T(x) - \frac{Z_P}{|\mathbf{x} - \mathbf{R}(t)|},\end{aligned}\quad (9)$$

with $\mathbf{r} = \frac{1}{2}(\mathbf{s} + \mathbf{x})$. In the present treatment, V_T , which is the frozen potential of the target core describes only the static screening of the target.

Numerical details on the evaluation of ionization probabilities for ejection of one electron with energy $E_e (= \frac{1}{2}\mathbf{k}_e^2)$ into the solid angle Ω_e ,

$$\frac{d^3 P_i(b)}{dE_e d\Omega_e} = \frac{1}{2\pi} \int d\omega_E \int_0^{2\pi} d\varphi_b |\mathcal{A}_{if}^-(\mathbf{b}, \omega_E)|^2, \quad (10)$$

the doubly differential cross section (DDCS),

$$\frac{d^2 \sigma_i}{dE_e d\Omega_e} = \int d\mathbf{b} \frac{d^3 P_i(b)}{dE_e d\Omega_e}, \quad (11)$$

and the total cross section (TCS) for the i th molecular orbital,

$$\sigma_i = \int dE_{el} \int d\Omega_{el} \frac{d^2 \sigma_i}{dE_{el} d\Omega_{el}}, \quad (12)$$

can be found in detail in [33,34,37]. We note that the integral over ω_E in Equation (10), $\int d\omega_E = \int_0^{2\pi} d\alpha \int_0^\pi d\beta \sin \beta \int_0^{2\pi} d\gamma$, is analytic owing to the orthogonal properties of the $D_{l\nu}^m$ functions [39]. In the following we describe only the calculation of the spherically averaged potential of the molecular core

$$V_T(x) = V_{nuclei}(x) + V_{electron}(x), \quad (13)$$

which is used to derive $\phi_{\mathbf{k}_e}(\mathbf{x})$, the unperturbed continuum orbitals of the emitted electron centered on the target core [34]. In (13),

$$V_{electron}(x) = \frac{1}{n_{occ}} \sum_{i,j}^{n_{occ}} n_{i,j} \int d\mathbf{x}_1 \frac{|\phi_i(\mathbf{x}_1)|^2}{x_{>}}, \quad x_{>} : \max(x_1, x) \quad (14)$$

and

$$V_{nuclei}(x) = \sum_k \begin{cases} -\frac{Z_m}{x} & \text{if } x > R_k, \\ -\frac{Z_m}{R_k} & \text{if } x < R_k, \end{cases} \quad (15)$$

where k runs over the atoms of the molecule, and so it denotes the C and H atoms, along with their nuclear charges Z_k and distances R_k from the COM. n_{occ} denotes the number of occupied molecular orbitals and $n_{i,j} = 2$ if $i \neq j$ and $n_{i,j} = 1$ if $i = j$. In this treatment of V_T , the nuclei form a uniformly distributed, charged sphere with a radius of R_k around the CMO. Figure 1 shows $V_T(x)$ for the coronene molecule; note that $x \cdot V_T(x)$ is shown, which is the x -dependent effective charge. The R_k distances of the C and H rings of nuclei are also shown in Figure 1. $\phi_{\mathbf{k}_e}(\mathbf{x})$ is evaluated numerically on the the potential V_T as described in [37].

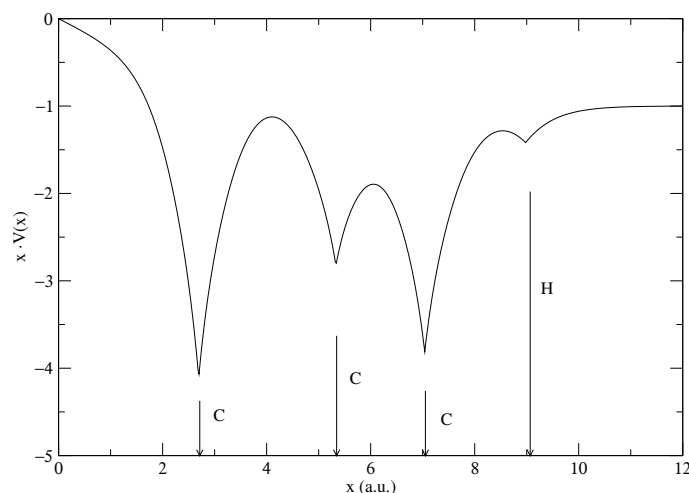


Figure 1. Effective charge for the $C_{24}H_{12}$ molecule. The arrows point to the values of R_m (see text).

The spherically averaged V_T potential represents a significant limitation of the method, the application of which is justified by the limitations of computational capacity. Non-spherical potential in the exit channel was applied for ionization of water molecules [41]. This study revealed that the multi-center geometric effect in the exit channels is important in the region of low-energy electron emission. However, the computational demands associated with molecules having a large number of orbitals, like $C_{24}H_{12}$, exceed the scope of this study.

The Hartree–Fock method, applied to molecular orbitals or electron densities, makes it possible to determine the contribution of individual atoms to a given ground-state molecular orbital. This is a population analysis (PA) that decomposes each molecular orbital into the contributions of individual atoms, which are computed from the MO coefficients and overlap matrix of the basis function using a Mulliken-like scheme [42,43]. In the LCAO procedure, a given MO is expressed as

$$\phi_i = \sum_{j_\mu} C_{j_\mu i} \chi_{j_\mu}, \quad (16)$$

where χ_{j_μ} is the j th orbital on atom μ and $C_{j_\mu i}$ is the expansion coefficient (the sum runs over all j and all atoms μ). The number of electrons assigned to the j_μ th atomic orbital is

$$N_{j_\mu}^i = n_i \sum_{k_\nu} C_{j_\mu i} C_{k_\nu i} S_{j_\mu k_\nu}, \quad (17)$$

where $S_{j_\mu k_\nu}$ is the overlap matrix between the j_μ and k_ν atomic orbitals and n_i is the occupation number of the i th MO. In Mulliken partitioning, each overlap term is equally divided between the two atomic orbitals centered on different atoms:

$$N_{j_\mu}^i = n_i \left[C_{j_\mu i}^2 + \frac{1}{2} \sum_{k_\nu \neq j_\mu} C_{j_\mu i} C_{k_\nu i} S_{j_\mu k_\nu} \right]. \quad (18)$$

If we add up the $N_{j_\mu}^i$ values for a given type j of atomic orbital, regardless of which atom in the molecule it belongs to, we obtain the number of effective electrons,

$$\zeta_{j,i} = \sum_{\mu} N_{j_\mu}^i, \quad (19)$$

associated with the j th atomic component. Using these effective electron occupation numbers, the ionization probability for the i th MO is obtained as

$$\frac{d^3 P_i(b)}{dE_e d\Omega_e} = \sum_j \zeta_{j,i} \frac{d^3 P_{i,j}^{at}(b)}{dE_e d\Omega_e} \quad (20)$$

where $P_{i,j}^{at}$ is the differential ionization probability of the j th (nlm) orbital of the C and H atoms. The DDCS and TCS values can be obtained as described in Equations (11) and (12). Only s and p atomic orbitals were included in the expansion, and $\sum_j \zeta_{j,i} \approx 2$. It is evident from Equation (19) that the geometric information of the molecule is lost in the population-analysis approach; therefore, this treatment of MOs is hereafter referred to as LCAO-HF-PA. Note that in the calculation of $\sigma_{i,j}^{at}$ for the j th atomic orbital, the binding energy of the i th MO is used.

In the following sections, the results for the single ionization of the $C_{24}H_{12}$ molecule induced by 100 keV proton impact are discussed. The DDCS and TCS values are evaluated only for the valence orbitals, ranging from $i = 25$ to 78. Orbitals with $i < 25$ make a negligible contribution to the total DDCS or TCS (i.e., the sum over all orbitals). Finally we note that the expansions of the initial MOs $\phi_i(x')$, see (2), were performed only for a limited range of l_i values ($l_i = 0, 1 \rightarrow l_{i,max}$). Convergent DDCS were obtained with $l_{i,max} = 16$ for all the considered ejection parameters and collision energies.

3. Comparison of Results Obtained in the LCAO-HF and LCAO-HF-PA Descriptions of the MOs

Figure 2 shows the total ionization cross sections for the valence MOs in the range of $i = 25$ –78, which provide the dominant contributions to the single ionization of $C_{24}H_{12}$. Calculations performed using both the LCAO-HF and LCAO-HF-PA descriptions of the molecule show that the orbital TCS values (OTCSs) generally increase as the binding energy decreases (or, equivalently, as the MO number increases). This trend can also be observed in the TCSs evaluated for the 2s and 2p orbitals of the C atoms, denoted as C_{2s} -MO and C_{2p} -MO, respectively, using the orbital energies of the corresponding MOs, (see the dashed curves in Figure 2).

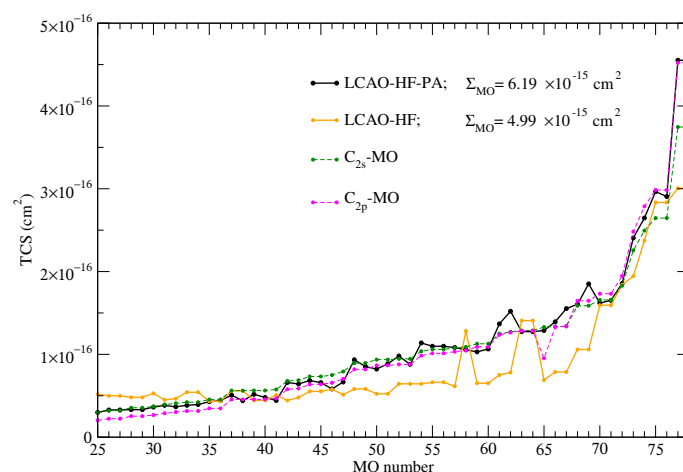


Figure 2. Total cross sections for the single ionization of the different molecular orbitals of coronene by impacts of 100 keV protons, where the ground state MOs are described the LCAO-HF-PA and LCAO-HF description of the molecule. The dashed lines are OTCS for the 2s and 2p orbitals of the C atom with MO binding energies (see the text). The lines are only to guide eyes.

Note also that the C_{2s} -MO is normalized to the LCAO-HF-PA at $i = 25$, while the C_{2p} -MO at $i = 78$ due to their relevant contributions to the MOs. It is not surprising that the OTCS curve for the LCAO-HF-PA treatment is in close agreement with those of C_{nk} -MOs.

However, this trend is not reproduced by the LCAO-HF treatment. In the $i = 25\text{--}60$ range, the slope of the LCAO-HF curve is significantly smaller than that of the LCAO-HF-PA curve. Moreover, for some individual MOs or small groups of MOs, the calculated TCS values are substantially higher than those of the neighboring orbitals. As shown in Figure 2, the LCAO-HF-PA description of the MOs generally yields higher OTCS values than the LCAO-HF treatment. This is reflected in the larger total ionization TCS of the molecule (obtained as the sum of the OTCSs), whose values are also presented in Figure 2 (see Σ_{MO}).

The differences between the LCAO-HF and LCAO-HF-PA methods used to describe the molecular orbitals become even more striking when the corresponding ionization probabilities are compared (see Equation (10)). Figures 3–5 show the ionization probabilities for selected orbitals together with their orbital diagrams, illustrating their spatial distributions. The selection of these molecular orbitals is intended to illustrate the variation in electron density. As can be seen from these figures, the ionization probabilities derived using the LCAO-HF description more closely reflect the electron-density distributions than those obtained using the LCAO-HF-PA approach. In the latter method, because the molecular geometry is neglected, the MO transition probabilities are identical to specific combinations of the ionization probabilities of the hydrogen and carbon atomic orbitals.

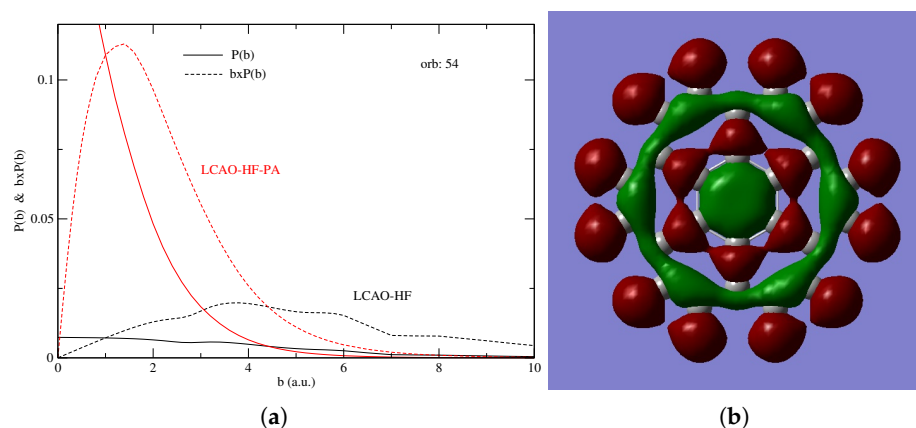


Figure 3. One electron ionization probabilities (a) and iso surfaces (b) for the 54th MO. Panel (a) shows $P(b)$ (solid l.) and $b \times P(b)$ (dashed l.) evaluated with LCAO-HF and LCAO-HF-PA description of the MOs. In panel (b) the large gray spheres represents the C atoms; their inner, middle and outer circles are located at distances of 2.69, 5.33, and 7.04, respectively, from the CMO. The outermost ring marked by small grey spheres is the ring of H atoms, which are located at distance of 8.98 from the CMO (see also Figures 4 and 5).

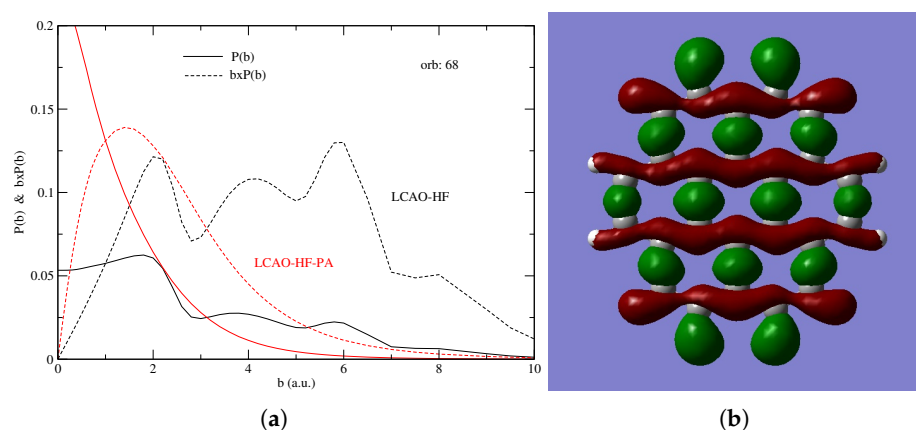


Figure 4. Panel (a) same as for panel (a) in Figure 3 but for the 68th MO. Panel (b) same as for panel (b) in Figure 3 but for the 68th MO.

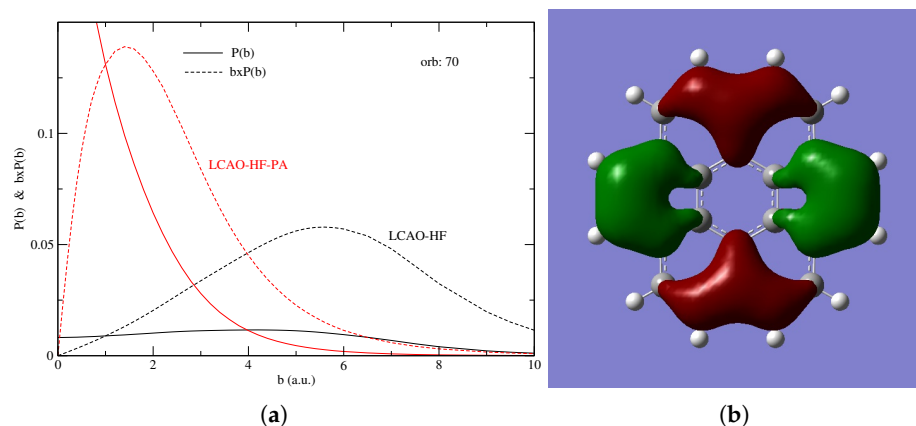


Figure 5. Panel (a) same as for panel (a) in Figure 3 but for the 70th MO. Panel (b) same as for panel (b) in Figure 3 but for the 70th MO.

It is also worth comparing the momentum distributions of MOs obtained using the two treatments of the molecule. The momentum space wave function of an orbital is given

$$\Phi_i(\mathbf{p}) = (1/2\pi)^{3/2} \int \phi_i(\mathbf{x}) e^{-i\mathbf{p}\cdot\mathbf{x}} d\Omega_p, \quad (21)$$

and the spherically averaged momentum density is defined as $\gamma_i(p) = \int |\Phi_i(\mathbf{p})|^2 d\Omega_p$. The $\gamma_i(p)$ distributions for the $C_{24}H_{12}$ (left panel) and CH_4 (right panel) molecules, as well as for the C and H atoms, and are presented in Figure 6. Only a few characteristic orbitals of the coronene molecule are shown in the figure. It is clear that large variations can be observed among the different orbitals. However, due to the large number of MOs, the orbital-specific structures disappear (i.e., are averaged out) in the p distribution for the entire molecule (black curve). For comparison, we also show the $\gamma_i(p)$ distribution for the methane molecule, which has far fewer valence orbitals (see the right panel). The figure also shows the $\gamma_i(p)$ distributions of the corresponding atomic orbitals. The characteristics of the 1s, 2s, and 2p orbitals of the H and C atoms that contribute to the $2a_1$ and $1t_2$ MOs are much more easily identifiable than in the case of the $C_{24}H_{12}$ molecule. In other words, the $2a_1$ orbital is largely composed of ns atomic orbitals, whereas p-type orbitals also play a significant role in the formation of the $1t_2$ hybrid orbitals. This is less evident in the case of coronene molecule, whose orbital structures involve a substantially larger number of atomic orbitals. Moreover, the molecule contains enough electrons to exhibit certain statistical properties, as discussed later. Interestingly, the shapes of the total (sum over i) $\gamma_i(p)$ distributions are similar for the CH_4 and $C_{24}H_{12}$ molecules, see the blue and green curves in the right panel.

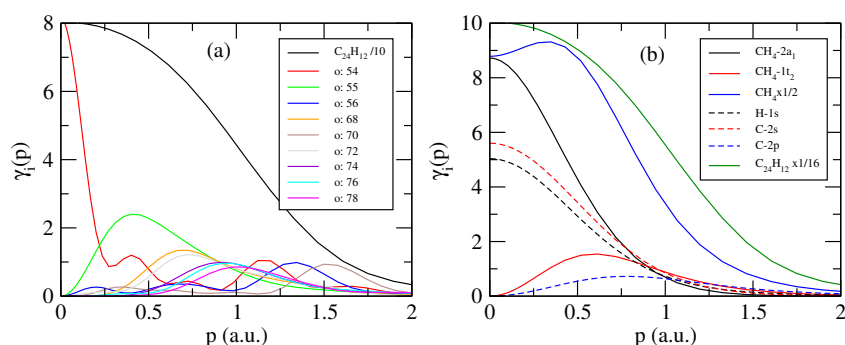


Figure 6. Momentum distributions (a) for $C_{24}H_{12}$ molecule and (b) CH_4 molecule and for the C and H atoms. For CH_4 , the $2a_1$ and $1t_2$ orbitals are selected, while for $C_{24}H_{12}$ selected orbitals denoted by o:nn only are presented (note the sum of $\Phi(p)$ for $C_{24}H_{12}$ is scaled).

Figure 7 shows the momentum distributions of selected MOs of the $C_{24}H_{12}$ molecule obtained within the LCAO-HF framework, together with the corresponding results from the LCAO-HF-PA approach. Similar to the ionization probabilities and momentum distributions, the LCAO-HF-PA description reproduces the characteristic features of the s- and p-orbitals of the H and C atoms. However, it does not account for the molecular geometry and therefore cannot capture the orbital structures arising from the specific arrangement of the atoms within the molecule.

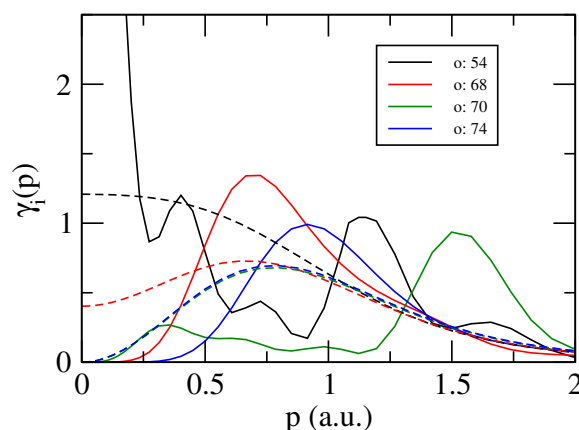


Figure 7. Momentum distributions for some MOs of the $C_{24}H_{12}$ molecule. The MOs are obtained using the LCAO-HF (solid lines) and LCAO-HF-PA (dashed lines) methods.

4. Information Theory and Molecular Orbitals

Figure 8 shows the OTCSs of the coronene molecule calculated using the LCAO-HF description of the MOs. The symmetries of the MOs are also indicated, with crosses denoting the one-dimensional IRs and dots denoting the two-dimensional IRs. As noted above, the TCSs of certain orbitals deviate from the general trend, exhibiting OTCS values that are 2–3 times larger than those of neighboring orbitals. Orbital 58 provides a notable example of this behavior. Figure 9 shows the orbital diagrams of the MOs for $i = 57–59$. In the case of the 58th orbital, it can be seen that the electron density is distributed much more evenly and is concentrated primarily around the carbon atoms, in contrast to the neighboring orbits. This example demonstrates that the details of the electron distribution can significantly influence the ionization cross section of a given molecular orbital. Therefore, it is worthwhile to analyze the electron distribution from a statistical perspective.

The information-theoretic approach is an important tool for measuring correlations, predicting statistical quantities, and determining the atomic and molecular complexity of systems [15]. Here, we consider the Shannon information entropy [19], Fisher information [20] and Onicescu information energy [21] to gain further insight into the MO structure of the $C_{24}H_{12}$ molecule. These information-theoretic quantities are determined from the electron density distribution and can be evaluated in both position and momentum spaces [44]. In the present work, however, we restrict our analysis to their values calculated in position space. The single particle charge density of the molecule is defined as [45]

$$\rho(\mathbf{r}) = \int |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_n)|^2 d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{r}_n = 2 \sum_{i=1}^{n_{occ}} |\phi_i(\mathbf{r})|^2 = 2 \sum_{i=1}^{n_{occ}} \rho_i(\mathbf{r}), \quad (22)$$

where Ψ_i , the many-particle wave functions of the molecule, is described by a single Slater determinant built from n_{occ} occupied one-electron MOs, see ϕ_i of Equation (2). In our treatment, total ionization of a molecule is described as the sum of ionization contributions from its molecular orbitals. We therefore evaluate and analyze information-theoretic quantities for each molecular orbital separately, based on its electron density. The

Fisher information includes the density distribution and its gradient. For the i th MO it is evaluated as

$$I_{\rho}^i = \int d\mathbf{r} \frac{|\nabla \rho_i(\mathbf{r})|^2}{\rho_i(\mathbf{r})}. \quad (23)$$

This quantity characterizes the localization of the density distributions. The Shannon information

$$S_{\rho}^i = - \int d\mathbf{r} \rho_i(\mathbf{r}) \ln \rho_i(\mathbf{r}) \quad (24)$$

measures the spatial delocalization of the electron density. The Onicescu information energy is the integral of the second power of the density distribution

$$E_{\rho}^i = \int d\mathbf{r} |\rho_i(\mathbf{r})|^2 \quad (25)$$

Since the single-particle charge densities are evaluated numerically, the above integrals are also calculated numerically. It is well known that the Hartree–Fock method does not account for electron correlation. However, given the variations in the electron distributions of MOs (see the iso surfaces in Figures 3–5 and 9), it is worth considering these distributions in terms of the information quantities introduced above. In general the Shannon entropy is very insensitive to small changes in the distribution over a short region and thus measures the spatial delocalization of the electronic cloud. On the other hand, Fisher information is a measure of local changes or sharpness in the distribution. Consequently, these two information measures provide complementary descriptions of disorder (smoothness) and the uncertainty of electron localization in the MO, i.e., I_{ρ}^i and S_{ρ}^i are the local and global measures of smoothness, respectively [14]. The Onicescu information energy is an attempt to define a finer measure of dispersion distribution than that of Shannon information entropy.

Figure 10 shows the Shannon, Fisher, and Onicescu information measures for the MOs of the coronene molecule, with i ranging from 25 to 75. These quantities were evaluated from the orbital electron densities, which were derived from wave functions calculated using 6-311G(d,p) basis set. This figure supports the above statement that these information-theoretic approaches capture different features of the charge density associated with the molecular orbitals. Calculations using all three approaches generally predict different values for different MOs, with the largest relative deviations observed for the Fisher and Onicescu measures. However, a common feature of these methods is the presence of MOs or groups of MOs for which the calculated quantities are significantly higher or lower than those obtained for neighboring orbitals. See orbitals 58, 63, and 64 for example. These orbitals also exhibit outlying TCS values in Figure 8, indicating a connection between the information measure of a given orbital and its ionization properties.

We now consider the OTCS values based on the LCAO-HF description of MOs from the perspective of the Fisher method, similar conclusions can be drawn when the other methods are considered. Based on observations for the MOs 58 and 63 and 64, it can be concluded that a low I_{ρ}^i value, which corresponds to sharply localized electron density, is associated with a large TCS value. First let us analyze the general trend in the OTCS values. The OTCS values may be expected to depend on the orbital binding energy in a manner similar to that observed above for the LCAO-HF-PA model. Any deviations from this behavior can be attributed to the information content of the corresponding molecular orbital. Considering the values of I_{ρ}^i , we observe a slight increase with increasing i in the range of MOs $i = 25$ –65, provided that certain orbitals are excluded from the analysis. This suggests that the OTCS values exhibit a weaker dependence on orbital binding energy than that observed for the LCAO-HF-PA treatment. Note the different slopes of the OTCS curves obtained using the LCAO-HF and LCAO-HF-PA models for the MOs in Figure 2. In this region, excluding some MOs, the OTCS values can also be fitted by a linear curve, see the

dashed line in Figure 8. For MOs with numbers greater than 70, the I_{ρ}^i values are relatively low. Consequently, the OTCS values increase more strongly than it would be expected on the basis of the binding energies alone. In this region, the OTCS results are comparable with those obtained using the LCAO-HF-PA model of MOs. The OTCS curve can also be fitted with a linear curve in this region, as shown by the dashed line in Figure 8. The slope of this line is considerably steeper than that in the $i = 25$ –65 region. It can also be seen that I_{ρ}^i is relatively large for MOs 66–69, which accounts for the change in slope of the OTCS curve. Orbitals 58, 63, and 64 are characterized by I_{ρ}^i values that lie well below the general trend, see the middle panel in Figure 10. These low I_{ρ}^i values generate the high TCS values in Figure 8.

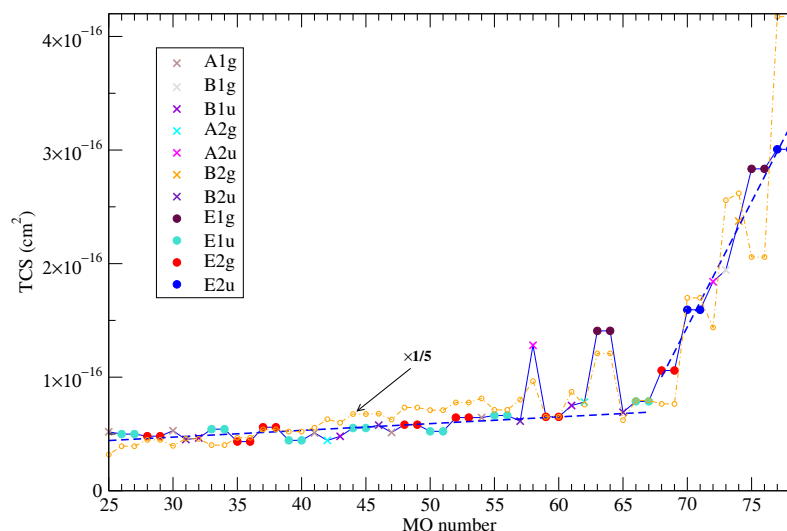


Figure 8. Total cross sections for the single ionization of the different molecular orbitals of coronene by impacts of 100 keV protons, where the ground state MOs are described by the LCAO-HF method. The lines are only to guide eyes and the dots and crosses denote the one- and two-dimensional IRs of MOs. Dashed blue lines are linear fits of TCS data. The dot-dashed orange lines with open circles at the MOs are results of the B1 model, note they are multiplied by the factor 1/5.

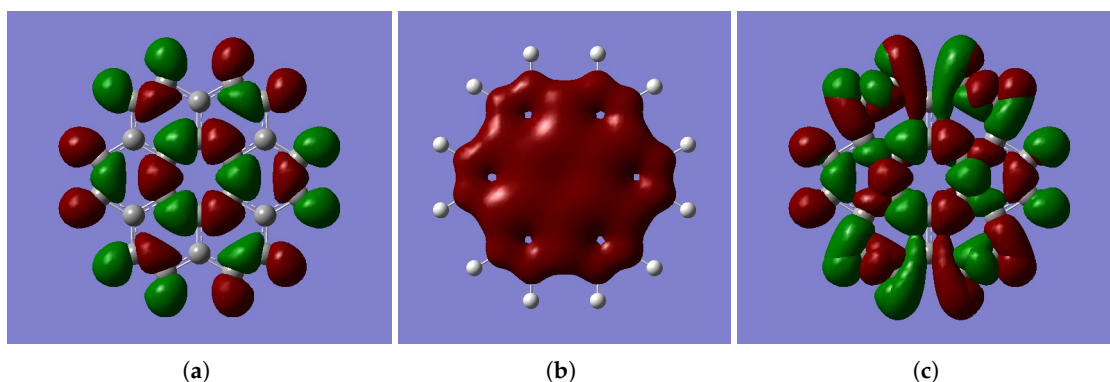


Figure 9. Orbital diagrams of the 57th (a), 58th (b) and 59th (c) MOs.

Figure 8 also shows the results obtained within the first Born (B1) approximation. In B1, the transition amplitude can be given as [46]

$$\mathcal{A}_{i\mathbf{k}_e}^{B1}(\mathbf{b}, \omega_E) = -i \int_{-\infty}^{\infty} dt \left\langle \phi_{\mathbf{k}_e}(x, t) \left| \frac{-Z_p}{x} \right| \phi_{i, \omega_E}(x, t) \right\rangle, \quad (26)$$

Note that the transition amplitude in the B1 model can also be obtained from Equation (4) by neglecting the distortion factors given in Equation (5) provided that unperturbed orbitals

in the entrance and exit channels are orthogonal. The shape of the OTCs curve calculated within the B1 approximation is seen to exhibit the same overall characteristics as the corresponding CDW-EIS curve. The slight discrepancies observed in the low- and medium-MO regions arise from the fact that the first few terms of the series expansion in Equation (2) already provide a realistic description of the process in these regions. In other words, the global characteristics of the electron distribution, as quantified by the Shannon entropy, play a more significant role in this range. For MOs above approximately 55–60, however, the higher-order terms of the expansion become increasingly important. This indicates that fine details of the electron distribution have a greater influence on the calculated OTCs values. Interestingly, the influence of I_p^i is more apparent in this region for the B1 approximation than for the CDW-EIS model. It should also be noted that the transition amplitude in the CDW-EIS formalism contains the gradient operator, which may enhance the role of Fisher information for certain molecular orbitals. The significant differences in the absolute OTCS values predicted by the B1 and CDW-EIS approaches are related to the fact that the orbitals in the initial and final channels are not orthogonal.

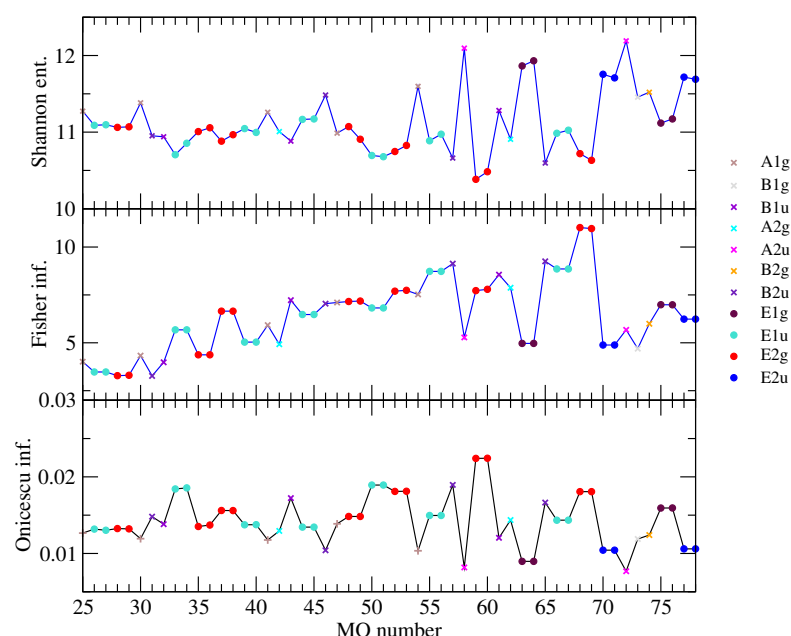


Figure 10. Shannon information entropy, Fisher information and Onicescu information energy for different orbitals of $C_{24}H_{12}$ in position space. The lines are only to guide eyes.

5. Conclusions

In this paper, we analyzed the doubly differential and total cross sections for the single ionization of electrons in 100 keV $H^+ + C_{24}H_{12}$ collisions. The scattering quantities were evaluated within the framework of the CDW-EIS model. The ground-state molecular orbitals were calculated using the Gaussian 16 quantum chemistry program within the LCAO-HF framework, employing the 6-311G basis set. The continuum orbitals for the final state were derived from a potential obtained from the spherically averaged potential of the molecular ion core. The 156 electrons of the coronene molecule occupy 78 molecular orbitals, however only the valence MOs ranging from 25 to 78 were included in the present treatment, as these orbitals provide the dominant contribution to the molecule's total ionization cross section. The ionization cross sections were also evaluated using a simplified LCAO-HF-PA description of the molecule, in which the molecular geometry was neglected. This approximation of MOs is commonly employed in the literature to evaluate the scattering quantities of large molecules. In the present 100 keV $H^+ + C_{24}H_{12}$ system, the calculated TCS value is 24% higher than the value based on a description of the molecule using

the LCAO-HF method. Significant discrepancies can be observed between the two MO treatments when comparing the orbital ionization transition probabilities and the orbital momentum distributions. These quantities clearly reveal signatures of the molecular geometry in the results obtained using the LCAO-HF model.

Different descriptions of the molecule result in different orbital ionization cross sections. The results obtained using the LCAO-HF-PA model can be interpreted in terms of the ionization cross sections of the atomic orbitals involved in forming of a given molecular orbital, regardless of the molecular geometry. The differences between the results obtained using the LCAO-HF-PA and LCAO-HF descriptions arise not only from the different treatment of the molecular geometry but also from the different information content associated with the corresponding orbitals. The values of the Shannon entropy, Fisher information, and Onicescu information energy were determined. Shannon entropy captures the global spatial delocalization of the electron density, whereas Fisher information reflects its local structure and sensitivity to spatial variations. Onicescu information energy exhibits qualitative behavior similar to that of Fisher information but is opposite in nature to Shannon entropy. The trends observed in the total orbital cross sections obtained using the LCAO-HF-PA description of the MOs were interpreted on the basis of the Fisher information measure. This study analyses the ionization of coronene under the impact of 100 keV protons. Calculations were also performed for 1 MeV proton impacts, and the conclusion drawn from comparing the results of LCAO-HF and LCAO-HF-PA treatment, as well as the structures found in OTCs, were consistent with those obtained for 100 keV protons.

Finally, it should be noted that the current frozen-core description of MOs in the exit channels is probably a rough approximation of the real situation. It is unrealistic to expect that, in an interaction between a high-energy heavy ion and a many-electron target, only one of the particles involved will undergo a change of state. Changes in the states of other electrons may also have a significant effect on the state of the ejected electron. A more accurate description can be obtained within the framework of Dyson orbitals [47,48], but this is beyond the scope of the present study.

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