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Electron scattering cross-sections for molecular iodine

Alejandro L García-Muñoz^{1,2} , Nicolas Sisourat² , Zdeněk Mašín^{1,*} , Oliver Bramley³, Gregory S J Armstrong³ , Jonathan Tennyson^{3,4,*} and Trevor Lafleur⁵

¹ Institute of Theoretical Physics, Faculty of Mathematics and Physics, Charles University, V Holešovičkách 2, 180 00 Praha 8, Czech Republic

² Sorbonne Université, CNRS, Laboratoire de Chimie Physique Matière et Rayonnement, UMR 7614, F-75005 Paris, France

³ Quantemol Ltd, 320 City Road, EC1V 2NZ London, United Kingdom

⁴ Department of Physics and Astronomy, University College London, Gower Street, WC1E 6BT London, United Kingdom

⁵ School of Engineering and Technology, University of New South Wales Canberra, Canberra ACT 2600, Australia

* Authors to whom any correspondence should be addressed.

E-mail: zdenek.masin@matfyz.cuni.cz and j.tennyson@ucl.ac.uk

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Abstract

Iodine is an emerging alternative propellant for high-performance electric propulsion systems and has also been proposed as a novel feed gas for the dry etching of III-V semiconductor materials. For both of these applications, electron impact collisional processes, and their associated reaction cross sections, are critical inputs required for plasma modeling, as well as the interpretation and analysis of certain diagnostics. Here, updated cross sections for electron scattering from molecular iodine (I_2) over an extended energy range up to 50 eV are calculated using the *R*-matrix method with scalar relativistic effective core potentials. The first estimates of cross sections for spin-orbit split states are also presented. In particular, electron impact cross sections are determined for: elastic scattering (total and momentum transfer), electronic excitation, neutral dissociation, ion pair formation, direct and dissociative ionization, and dissociative electron attachment. Potential energy curves for the main excited molecular states are computed and multiple dissociation pathways are identified. Kinetic energy release during dissociation is found to be significant (reaching over 1 eV per atom for some reaction pathways) and may contribute to strong neutral gas heating as previously observed in some iodine plasma discharges.

1. Introduction

Xenon is typically the propellant of choice for electric propulsion systems, such as gridded ion and Hall effect thrusters, because of its attractive physical properties [1]. In particular, it is chemically benign, has a relatively low ionization threshold energy (12.13 eV), and can be stored as a supercritical fluid above about 7 MPa with a density higher than liquid water. However, xenon is also expensive (of the order of \$5000/kg) and world production is only about 60 metric tons per year [2]. In addition, given the rapid growth of the space industry over the last 10 years, demand for xenon may outpace supply in the near future, and so the investigation of alternative propellants has become an important research area [3, 4].

One possible viable alternative is iodine. First demonstrated in space as a propellant for gridded ion thrusters in 2020 [3], iodine is approximately 50–100 times cheaper than xenon and can be stored unpressurized in a solid state with a density 2–3 times higher [4]. Iodine has attracted strong interest in recent years with a wide range of prototype electric propulsion systems having been designed and tested including gridded ion thrusters [3, 5, 6], Hall effect thrusters [7–9], and ambipolar thrusters [10]. Because iodine has a significantly more complex plasma chemistry than xenon, a number of theoretical and numerical models have been developed to better understand the underlying plasma discharge behavior [11–18]. In addition to space propulsion applications, iodine plasmas have also been used in a number of ground-based applications such as the dry etching of type III-V semiconductors, where the

resulting etch product is volatile at a much lower surface temperature compared with other halogens such as chlorine [19, 20].

Regardless of the application, modeling of iodine plasmas is important for understanding the basic underlying processes and system operation, as well as device optimization. Such models not only require the main reaction processes as an input, but also the associated collision cross sections. For low-temperature plasmas, electron impact scattering typically represents the dominant set of processes as the electron temperature is much higher than ion or neutral temperatures, and is therefore effectively responsible for sustaining the plasma discharge [21]. In an iodine plasma, vapor is initially fed into a chamber as a diatomic molecule (I_2) produced through thermal sublimation of solid crystals or pellets [3, 15]. Consequently, it is critical to understand and accurately describe electron scattering from molecular iodine. In particular, electron impact dissociation is important as it is the main process that leads to the formation of atomic iodine, which can then itself be ionized through subsequent electron collisions. Indeed, several experiments and numerical models have shown that I^+ is typically the dominant positive ion in low-pressure discharges [12, 22, 23], and which is largely produced from ionization of atomic iodine.

As highlighted in a recent review article on iodine plasmas [4], although electron scattering cross sections for many processes are now available, there are still a number that are either unknown or inconsistent. For molecular iodine, the most important knowledge gap is associated with electron impact dissociation. At present, only a single cross-section dataset is available based on calculations originally performed in [24], and where the maximum electron energy is limited to only 10 eV. Given that the electron temperature in many low-pressure iodine discharges is of the order of 5 eV or higher [12, 15], this energy limit is far too low and necessitates an extrapolation to higher energies [4]. Additionally, atomic iodine is an interesting element because spin-orbit coupling produces a metastable excited state, $I(^2P_{1/2}^o)$, only 0.9427 eV above the ground state, $I(^2P_{3/2}^o)$. Consequently, this excited state is long-lived and can be highly populated. Dissociation is usually a multi-step process whereby an electron first transfers energy exciting the molecule and placing it into one of several possible bound or repulsive states. The repulsive states then dissociate and the resulting atomic iodine products can be a combination of $I(^2P_{3/2}^o)$ and $I(^2P_{1/2}^o)$ states, or even ionic states in the case of dissociative attachment. These different dissociation pathways are currently not well known, and the original calculations in [24] assumed that the dissociation products were both in the ground state. Furthermore, dissociative electron attachment is an important reaction as it is one of the main processes leading to the formation of I^- . While there is a wide range of previously calculated and measured cross sections, there is significant disagreement among them, particularly for electron energies below 1 eV. As also noted in [25], the resulting neutral atomic dissociation product is predicted to be the $I(^2P_{1/2}^o)$ state, which seems to contradict most works on electron attachment in other halogens [26]. Therefore, improved knowledge of electron scattering from molecular iodine is vital for enabling more accurate plasma discharge models. It is also expected to be important for the interpretation and analysis of some diagnostics, such as optical emission spectroscopy [27, 28].

The importance of updated electron scattering cross sections is also motivated by several previous and unexplained observations in low-pressure iodine discharges. For example, while the wall temperature of some electric propulsion systems can reach between 400–900 K during operation [3, 29], laser fluorescence measurements indicate that the atomic iodine gas temperature may exceed 1500 K [30]. At present, this anomalous gas heating is not understood, but is hypothesized to occur because of the unique iodine plasma chemistry. In particular, kinetic energy release (KER) in several dissociation and neutralization reactions may be significant and lead to bulk gas heating. Although the dissociation threshold energy of the molecular ground state is 1.542 eV [31], electrons can initially transfer more energy and place the molecule into a repulsive state that eventually splits and releases the energy difference. This energy difference can either excite one or both of the resulting atomic iodine products, and/or is shared as kinetic energy. These hot fragments can then lead to gas heating via successive heavy particle collisions. Such energy release has been implicated in gas heating with other diatomic molecules such as hydrogen, oxygen, and chlorine [32–34], and may therefore also be important for iodine.

In this work, we explicitly address the shortcomings above by calculating updated cross sections for electron scattering from molecular iodine. Crucially, we provide the first estimates of the cross sections for spin-orbit (SO) split states and for an extended energy range up to 50 eV. While a relatively complete set of cross sections is obtained for a wide range of collisional processes (such as elastic scattering, ionization, excitation, etc), an important focus is on dissociation where a number of different dissociative pathways are identified, along with the resulting KER. Section 2 gives a brief overview of the numerical methods used, while section 3 presents the main results, followed by Conclusions in section 4.

Table 1. Summary of electron scattering processes studied. Here, I_2^* represents an electronically excited state above the $I_2(X^1\Sigma_g^+)$ ground state (denoted simply as I_2 for convenience). And $I^+ \cdots I^-$ represents the Coulomb attraction without the formation of a covalent bond, as characteristic of ion pairs.

ID	Reaction	Process	Threshold energy (eV)
R1	$I_2 + e^- \rightarrow I_2 + e^-$	Elastic scattering	—
R2	$I_2 + e^- \rightarrow I_2^* + e^-$	Electronic excitation	See table 3
R3.1	$I_2 + e^- \rightarrow I(^2P_{3/2}) + I(^2P_{3/2}) + e^-$	Neutral dissociation	See table 3
R3.2	$I_2 + e^- \rightarrow I(^2P_{3/2}) + I(^2P_{1/2}) + e^-$	Neutral dissociation	See table 3
R3.3	$I_2 + e^- \rightarrow I(^2P_{1/2}) + I(^2P_{1/2}) + e^-$	Neutral dissociation	See table 3
R4.1.1	$I_2 + e^- \rightarrow I^+(^3P_0) \cdots I^-(^1S_0) + e^-$	Ion pair formation	See section 3.6
R4.1.2	$I_2 + e^- \rightarrow I^+(^3P_1) \cdots I^-(^1S_0) + e^-$	Ion pair formation	See section 3.6
R4.1.3	$I_2 + e^- \rightarrow I^+(^3P_2) \cdots I^-(^1S_0) + e^-$	Ion pair formation	See section 3.6
R4.2	$I_2 + e^- \rightarrow I^+(^1D_2) \cdots I^-(^1S_0) + e^-$	Ion pair formation	See section 3.6
R4.3	$I_2 + e^- \rightarrow I^+(^1S_0) \cdots I^-(^1S_0) + e^-$	Ion pair formation	See section 3.6
R5	$I_2 + e^- \rightarrow I_2^+ + 2e^-$	Impact ionization	9.30
R6	$I_2 + e^- \rightarrow I(^2P) + I^+(^1S_0) + 2e^-$	Dissociative ionization	11.94
R7	$I_2 + e^- \rightarrow I(^2P) + I^-(^1S_0)$	Dissociative electron attachment	—
R8	$I_2 + e^- \rightarrow I^+ + I^-(^1S_0) + e^-$	Polar dissociation	9.94

2. Numerical methods

Potential energy curves and cross sections for I_2 have been published in [25, 35–37] and serve as a useful benchmark. Potential energy curves with both relativistic and non-relativistic models are available in [35] using the all-electron cc-pVTZ basis set. Potential energy curves calculated with a semi-empirical approach are available in [36]. The calculations in [37] used the all-electron 3-21G basis set, while those given in [25] used the all-electron 6-311G basis set. Additionally, ionization cross sections have been reported in [38–40] and polar dissociation fragment data is available in [41].

Throughout this work, the scalar-relativistic effective core potential ECP46MWB [42] is used to describe the 46 innermost electrons (up to the $n = 4$ shell) in each iodine atom, drastically reducing the computational cost compared to all-electron calculations. The remaining seven valence electrons on each atom are described using an optimized triple-zeta basis set (ECP46MWB_VTZ) [43]. An additional SO calculation for the target electronic structure used the cc-ECP46+SO [44] ECP together with an optimized triple-zeta basis set (cc-pVTZ) for the valence electrons.

The potential energy curves presented here have been calculated using the MOLPRO [45, 46] quantum chemistry program. The target molecule structure obtained is then used in the R -matrix calculation. The cross sections presented in this work have been calculated using the UKRmol+ molecular R -matrix suite of codes [47–51] and the Quantemol electron collisions (QEC version 2.0) software package [52] designed for electron-molecule scattering calculations.

I_2 belongs to the $D_{\infty h}$ point group, but is treated using its highest Abelian subgroup, D_{2h} , which consists of eight irreducible representations ($A_g, B_{3u}, B_{2u}, B_{1g}, B_{1u}, B_{2g}, B_{3g}, A_u$). Nevertheless, all the results presented below were subsequently translated into $D_{\infty h}$.

3. Results

The electron scattering processes studied in this work are summarized in table 1 and include Elastic scattering (R1), Electronic excitation (R2), Neutral dissociation (R3), Ion pair formation (R4), Impact ionization (R5), Dissociative ionization (R6), Dissociative electron attachment (R7), and Polar dissociation (R8). The target (I_2) electronic structure is presented in section 3.1. The scattering calculations in this work were performed for the ground-state equilibrium geometry using the ab initio R -matrix method [50, 51]. The scattering models are described in section 3.2. The resulting cross sections for elastic scattering, impact excitation, neutral dissociation and ion pair formation at low energies up to 15 eV are presented in sections 3.3–3.6 respectively. In subsection 3.7 we attempt a simple estimation of the relativistic inelastic cross section based on the non-relativistic scattering results. The R -matrix results obtained using UKRmol+ [47–51] are supplemented with a presentation of the high-energy part of the cross sections up to 50 eV, and a comparison with previous results obtained using various extrapolations.

Cross sections for impact ionization, dissociative ionization and Dissociative Electron Attachment (DEA) derived using QEC [52] from the R -matrix results are presented in sections 3.10–3.12.

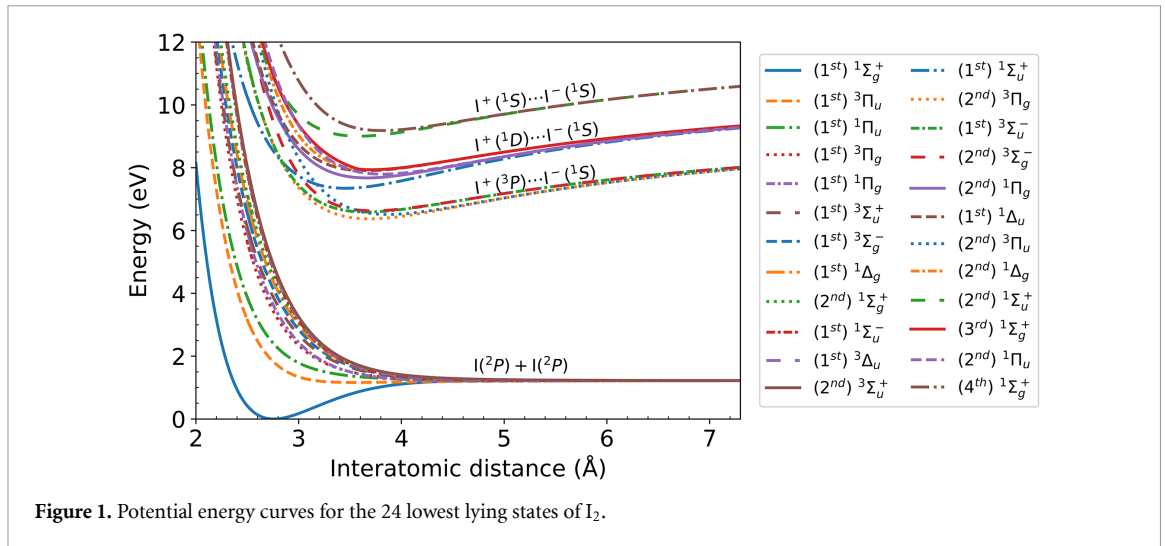


Figure 1. Potential energy curves for the 24 lowest lying states of I_2 .

Table 2. Vertical excitation energies for I_2 states converging to the $^2P+^2P$ non-relativistic threshold. Results are provided for this work, together with the results of de Jong *et al* [35], Yadav *et al* [37], and Ambalampitiya *et al* [25].

Term ($D_{\infty h}$)	Vertical excitation energy (eV)			
	This work	Reference [35]	Reference [37]	Reference [25]
$1^{st} 1\Sigma_g^+$ (X)	0.00	0.00	0.00	0.00
$1^{st} 3\Pi_u$	1.82	2.25	2.18	2.18
$1^{st} 1\Pi_u$	2.40	2.92	2.99	3.00
$1^{st} 3\Pi_g$	3.41	4.17	10.88	
$1^{st} 1\Pi_g$	3.60	4.53	11.16	
$1^{st} 3\Sigma_u^+$	3.86	4.17	12.25	
$1^{st} 3\Sigma_g^-$	4.12	5.03	5.44	5.18
$1^{st} 1\Delta_g$	4.36	5.30	6.26	
$2^{nd} 1\Sigma_g^+$	4.51	5.54	6.80	5.70
$1^{st} 1\Sigma_u^-$	4.75	5.87		
$1^{st} 3\Delta_u$	4.82	5.95		
$2^{nd} 3\Sigma_u^+$	4.90	6.04		

3.1. Target electronic structure

In this work, both non-relativistic and relativistic potential energy curves are computed. Relativistic effects beyond those included in the scalar relativistic ECPs are not yet explicitly implemented in UKRmol+, and therefore only non-relativistic cross sections can be obtained. Nevertheless, in section 3.7 we describe how approximate relativistic cross sections can be obtained from the non-relativistic ones with the help of the relativistic states computed in MOLPRO.

The active space chosen for the calculations was complete active space (CAS) (14,8), where the active orbitals, in D_{2h} , were: $1-2a_g$, $1-2b_{1u}$, $1b_{2u}$, $1b_{3u}$, $1b_{2g}$ and $1b_{3g}$. Hence, all available electrons (7 per atom) are included in the active space defined by the 5 s and 5p orbitals of both atoms. This CAS configuration generates 44 ($D_{\infty h}$) states, all of which are included in the R -matrix calculations.

The non-relativistic potential energy curves for the ground and first 23 excited states are shown in figure 1. They can be classified into four groups: those converging to the lowest asymptote of neutral dissociation and those converging to the three possible ion pairs associated with the reactions R4.1, R4.2, and R4.3 in table 1 respectively. Higher-lying states do not contribute to these processes.

The calculated neutral dissociation energy is 1.22 eV which is about 0.3 eV lower than the more accurate value of 1.542 eV obtained spectroscopically [31]. Vertical excitation energies for the ground equilibrium bond length are shown in table 2 together with available non-relativistic results from the literature.

The three groups of ion pair states contribute to the yield of I^+ and I^- in dissociative collisions. The state labels were assigned by analyzing the configuration of each state, and comparing with the literature (e.g. [36, 53]). The equilibrium distances for the ion pair states lie between 3.5–3.7 Å.

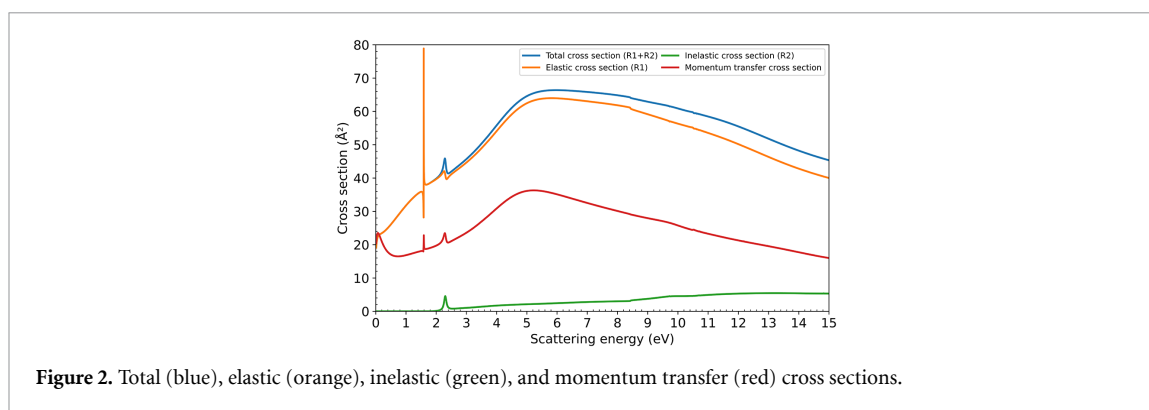


Figure 2. Total (blue), elastic (orange), inelastic (green), and momentum transfer (red) cross sections.

3.2. Scattering models

The I_2 bond length of 2.756 Å was obtained as the minimum of the ground state potential energy curve, presented in figure 1. This value was used in the subsequent UKRmol+ and QEC calculations.

In the R -matrix calculation, the unbound electron was described using a pure Gaussian type orbital (GTO) continuum basis with a maximum angular momentum of $l_{\max} = 6$. The deletion thresholds for the symmetric orthogonalization were set to 10^{-7} , and the R -matrix radius was set to 15 Bohr. The resulting basis set was sufficient to describe the continuum up to a scattering energy of about 15 eV.

We employed the Born correction to top up the angular momentum expansion in the calculation of the dipole-allowed electronically inelastic cross sections. The correction was negligible in the low-energy region and we included it only in the high-energy cross sections presented in section 3.8.

The electronic configurations of the scattering model were based on the CAS with three types of configurations included: $CAS^N \times (\text{continuum})^1$, $CAS^{(N+1)}$, and $CAS^N \times (\text{virtual})^1$, where N is the number of target electrons (see [50] for further details). All available target molecular orbitals were included in the calculation.

We performed calculations with scattering models of varying complexity. Here, only the results obtained with the CAS(14,8) Close-Coupling model including 44 states are presented. We refer the reader to the appendix for a more detailed comparison and analysis of the different models.

3.3. Elastic scattering

The total, elastic, inelastic, and momentum transfer electron-impact scattering cross sections for I_2 are shown in figure 2. The cross sections are presented for scattering energies up to 15 eV.

The dominance of elastic processes over inelastic ones is evident for the energy range studied. In order to further investigate the two resonances observed, an analysis of the eigenphase sums was carried out. The first resonance at 1.59 eV is a Feshbach resonance decaying into the ground state and the second one at 2.30 eV corresponds to a Feshbach resonance decaying into both the ground and the first excited molecular term ($^3\Pi_u$). The first resonance appears in $^2\Pi_u$ scattering symmetry and the second one in $^2\Sigma_g^+$. Additional calculations to study the position of the resonances as a function of the CAS model and the number of states included place the first peak in the energy range between 1.59–2.19 eV and the second peak between 2.30–3.08 eV (see also the appendix).

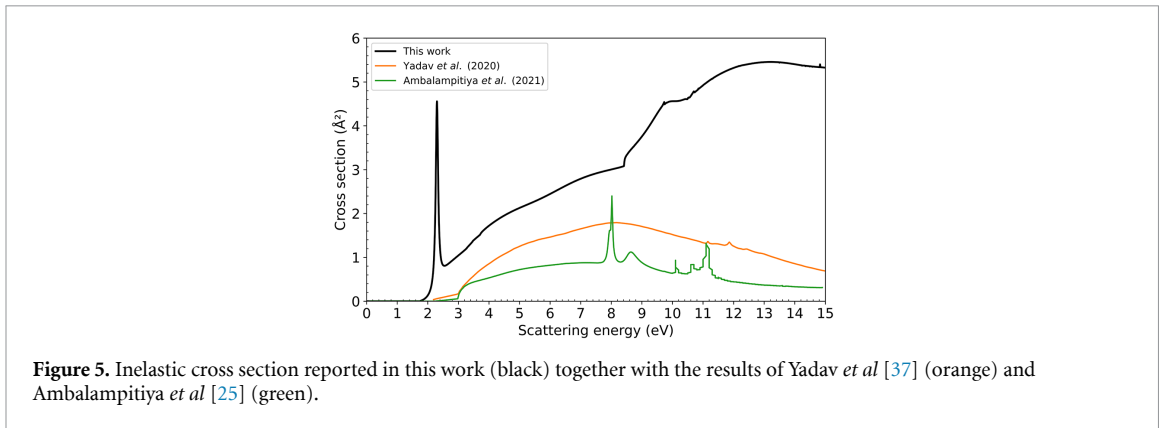
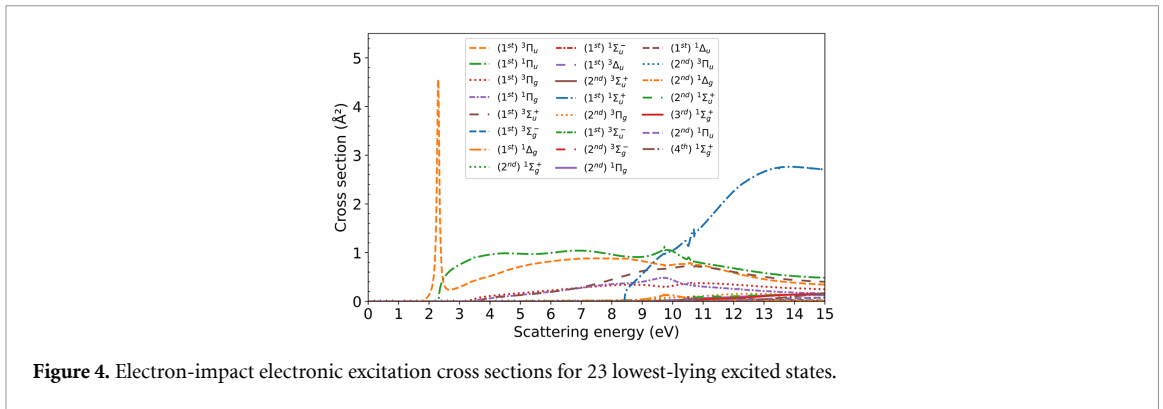
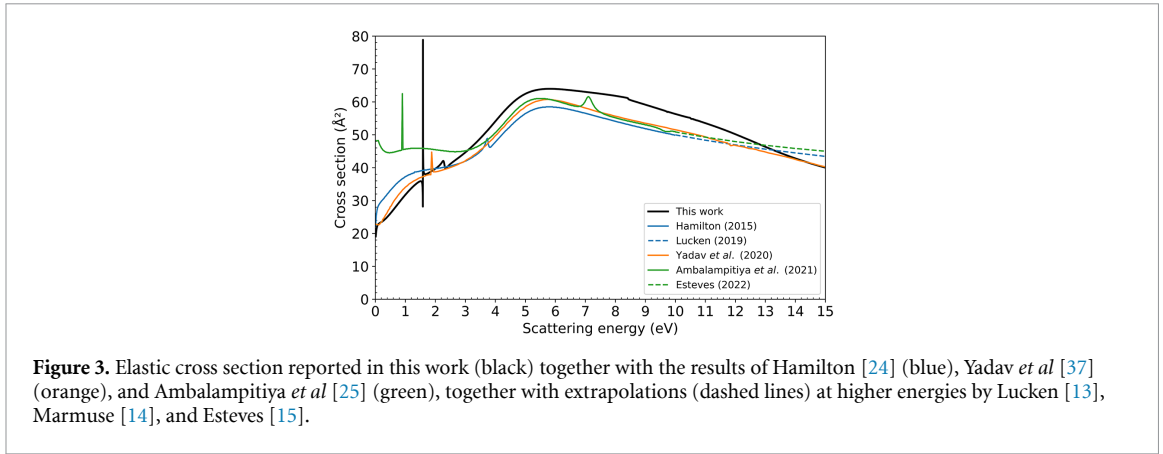
Having analyzed the resonances, we now compare our calculated cross-section data with previously published calculations. In figure 3 we show the computed elastic cross section, together with previous calculations from the literature in the low-energy range.

There are three main differences between the previous calculations and the new ones presented here. Firstly, the previous calculations of Hamilton [24] were computed for a maximum angular momentum of 4, while in this work a maximum angular momentum of 6 was included. Secondly, Hamilton's calculations used a CAS with only 6 active electrons⁶ while our CAS(14,8) is larger and includes all available states: i.e. more than the maximum number of states accessible in previous CAS calculations. Finally, our calculations use ECPs to represent the core and inner-valence electrons and include scalar relativistic effects.

3.4. Electronic excitation

The electron impact electronic excitation cross sections were calculated for excitation from the I_2 ground state ($1\ ^1A_g$) to the 43 excited states included in the calculation. Figure 4 shows the state-to-state cross

⁶ The report specifies CAS(8,6) which is probably a typo and the use of CAS(10,6) seems more likely.



sections for the lowest 23 excited states. The remaining states, generated by our model, lie higher in energy and do not contribute to the range of energies shown.

The contribution of the resonance at 2.3 eV is associated with the first $^3\Pi_u$ state. Another important contribution comes from the first $^1\Sigma_u^+$ state: it becomes the main contributor to the inelastic cross section above 12 eV.

Figure 5 shows the total inelastic cross section computed in this work together with previous calculations. Two main differences can be observed. Firstly, the cross sections from the previous calculations have a significantly smaller magnitude than ours (by a factor of approximately 2 at low energies and rising up to a factor of approximately 5 at higher energies), which can be traced to the smaller number of states included in the previous calculations as discussed in detail in the appendix. Secondly, the previous calculations are unable to capture the rapid rise of the cross section around 8 eV, since they do not include all the states that contribute significantly at this energy range.

At energies above approximately 9 eV, we cannot discount some distortion of the results due to the opening of the impact ionization channel which is missing from all the calculations, including the previous ones.

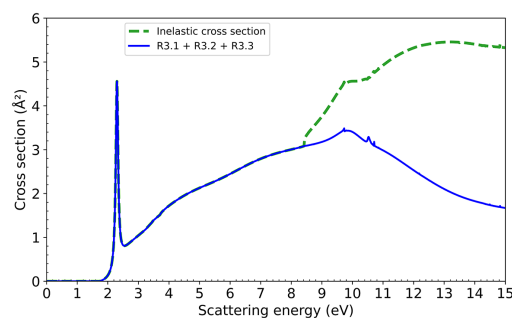


Figure 6. Neutral dissociation cross section (solid) and the total electronically inelastic cross section (dashed). The neutral dissociation cross section corresponds to the reactions labeled R3.1–R3.3 in table 1.

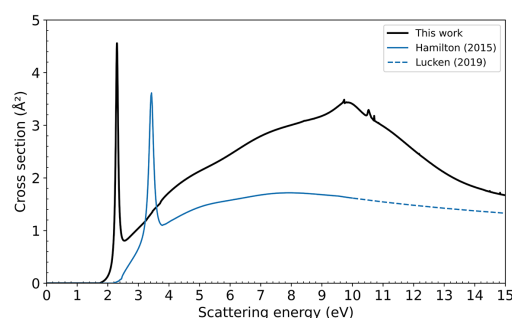


Figure 7. Total neutral dissociation cross section reported in this work (black) together with the results of Hamilton [24] (blue) including the extrapolation to higher energies by Lucken [13] (dashed lines).

3.5. Neutral dissociation

In a neutral dissociation process, energy from the incoming electron is transferred to the molecule to generate an excited state that relaxes by dissociation into neutral fragments. In I_2 , neutral dissociation occurs for the first 11 excited states (see figure 1). All of those states are purely repulsive in the non-relativistic picture. Therefore, the inelastic impact excitation cross section into this group of states, shown in figure 6, is equal to the neutral dissociation cross section.

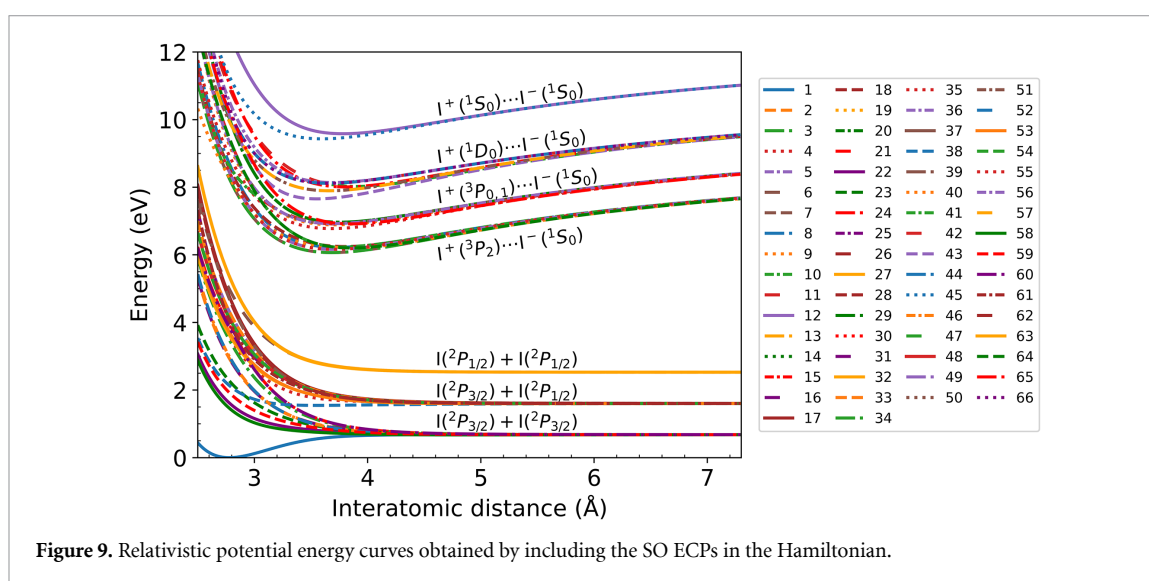
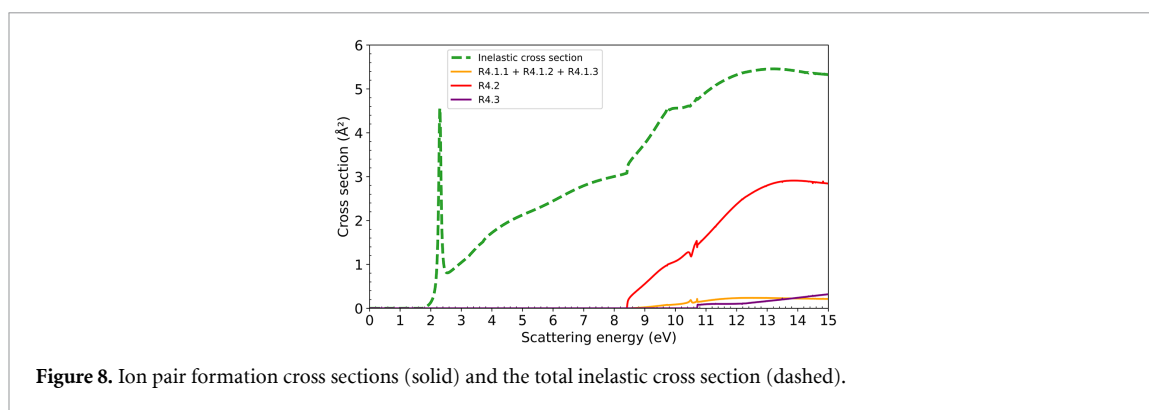
It can be seen that up to energies of around 8.5 eV, where the ion pair formation channels open, all electronically inelastic processes lead to neutral dissociation. It is also confirmed that the resonance at 2.3 eV contributes to neutral dissociation. The next peak in the cross section appears around 10 eV, close to the ionization energy, and is not connected with resonance formation as confirmed by eigen-phase sum analysis.

Figure 7 compares our neutral dissociation cross section with previous calculations in the literature. The resonance appears almost 2 eV higher in the earlier results of Hamilton [24] and the second maximum at around 10 eV is completely absent in their results. Consequently, the cross sections of Hamilton, and the extrapolation of Lucken [13], appear to underestimate the cross section by more than a factor of 2 in the vicinity of the ionization threshold.

Both the shift of the resonance position to higher energies, and underestimation of the cross section magnitude, have the same origin as in the case of elastic scattering discussed in section 3.3: insufficient modeling of correlation and polarization and retention of a lower number of electronically excited states than in the current calculations.

3.6. Ion pair formation

In inelastic processes, energy from the incoming electron is transferred to the molecule to, for example, generate charged atomic fragments (I^+ and I^-): i.e. polar dissociation. As opposed to the excited states converging to the neutral dissociation threshold, the ion pair states ($I^+ \cdots I^-$) exhibit pronounced minima (see figure 1). Consequently, excitation of these states may lead to vibrational excitation too. For that reason, we have not computed cross sections for polar dissociation.



The cross section for the ion pair formation process, and the total inelastic cross section, are compared in figure 8. We can see that the dominant contributor to the formation of ion pairs appears to be reaction R4.2, which is mainly composed of the $1\ ^1\Sigma_u^+$ term (see figure 4).

A further step to improve accuracy of the inelastic cross sections would be to include the effects of vibrational excitation, for example by means of Franck–Condon factors. The significant relative shift of the minima of the potential energy curves of the ground state and the ion-pair states, see figures 1 and 9, would probably lead to small Franck–Condon factors between the vibrational ground state and the vibrational states of the ion-pair states. Therefore, unless the target molecule is significantly vibrationally excited, the fixed-nuclei ion-pair impact excitation cross sections are most likely an upper limit to the accurate ones. Overestimation of inelastic cross sections by fixed nuclei results has been observed in other molecules too (see e.g. [54]).

The energy thresholds for the three polar dissociation processes are: 9.94 eV for $I^+(^3P)$, 11.26 eV for $I^+(^1D)$, and 12.55 eV for $I^+(^1S)$. Therefore, at energies lower than 9.94 eV, only vibrationally excited ion pairs will be generated. At higher energies, the polar dissociation channel opens and nuclear motion needs to be included to accurately describe the dynamics. This effect was not included in the calculations presented here.

3.7. Relativistic estimation

Relativistic effects are included in a separate set of calculations of the relativistic potential energy curves by including the SO ECPs. The results are shown in figure 9 and can be compared with their non-relativistic counterparts from figure 1. A total of 66 D_{2h} relativistic states were obtained. Since these relativistic states are formed as a linear combination of non-relativistic states, the assignment of specific D_{2h} states, and then of $D_{\infty h}$ states, is not possible.

Table 3. Vertical excitation energies for I_2 states converging to $^2P_{3/2} + ^2P_{3/2}$, $^2P_{3/2} + ^2P_{1/2}$, and $^2P_{1/2} + ^2P_{1/2}$ relativistic thresholds. Results of this work, sorted by energy, are presented together with the results of Mulliken [36] and de Jong *et al* [35], grouped by molecular terms.

State index	Vertical excitation energy (eV)			Term ($D_{\infty h}$)
	This work	Reference [35]	Reference [36]	
1	0.00	0.00	0.00	$X\ ^1\Sigma_g^+$
37, 58	1.46	1.78	1.66	$1\ ^3\Pi_u$
22, 13	1.61	1.95	1.79	
59	1.92	2.34	2.34	
38	2.13	2.50	2.37	
23, 14	2.27	2.72	2.38	$1\ ^1\Pi_u$
31, 2	2.93	3.62	3.2	$1\ ^3\Pi_g$
52, 46	2.98	3.71	3.4	
3	3.48	4.21	4.1	
4	3.61	4.34	4.1	
32	3.62	4.49	4.1	$1\ ^1\Pi_g$
53, 7	3.71	4.64	4.5	$1\ ^3\Sigma_u^+$
60	3.84	4.71	4.57	
15, 24	3.91	4.36	3.8	$1\ ^3\Sigma_g^-$
25, 16	4.03	4.84	3.9	
61	4.05	5.07	4.2	$1\ ^1\Delta_g$
48, 54	4.12	5.79	4.4	$2\ ^1\Sigma_g^+$
33, 5	4.31	5.02	5.4	$1\ ^1\Sigma_u^-$
62, 39	4.68	5.00	4.7	$1\ ^3\Delta_u$
17, 26	4.76	5.66	5.3	
6	4.98	6.34	5.9	
63	5.35	5.76	5.5	$2\ ^3\Sigma_u^+$
27, 18	5.36	6.65	5.6	

Clearly, relativistic effects play an important role in I_2 . Both the lowest and the ion pair asymptotes display significant SO splitting of approximately 1 eV and one of the states converging to the $^2P_{3/2} + ^2P_{1/2}$ asymptote even displays a very shallow minimum at a bond distance of about 3 Å.

The agreement with previous results available in the literature, such as [35] or [36], is excellent. The dissociation energy difference between $I(^2P_{3/2})$ and $I(^2P_{1/2})$ fragments is expected to be 0.9427 eV, and differences of 0.93 eV are obtained. Nevertheless, due to the approximations made in this relativistic estimate, the ground state minimum is not as deep as that previously observed in the literature, which produces absolute dissociation energies lower than earlier results. The assignment of the terms for each group of states was done by direct comparison with the aforementioned literature. Furthermore, the vertical excitation energies for the neutral dissociative states obtained in this work, and the ones reported by Mulliken [36] and de Jong *et al* [35], are shown in table 3.

Implementation of SO coupling into the UKRmol+ suite is currently underway. Therefore SO effects were not explicitly included in the calculation of the cross sections. Nevertheless, we attempted a simple estimation of the relativistic cross sections with the help of the relativistic states obtained with MOLPRO.

First, the relativistic target states, ψ_i^R , can be obtained as a linear combination of the non-relativistic states, ψ_j^{NR} , by diagonalization of the ECP-SO Hamiltonian in this basis

$$\psi_i^R = \sum_j c_{ij} \cdot \psi_j^{NR}, \quad (1)$$

where c_{ij} represents the contribution of every non-relativistic state j to each relativistic state i (see figure 24 in the appendix).

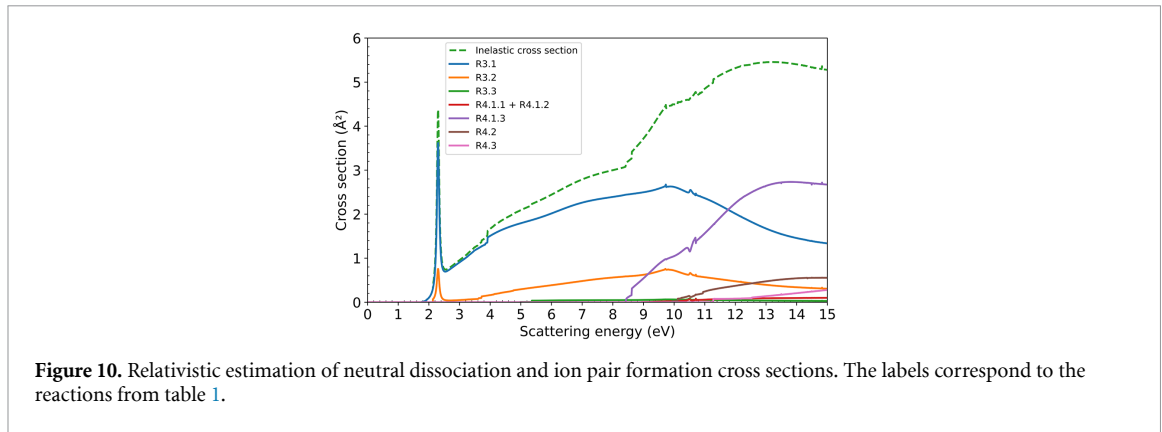


Figure 10. Relativistic estimation of neutral dissociation and ion pair formation cross sections. The labels correspond to the reactions from table 1.

Under the approximations detailed in the appendix, the relativistic state-to-state cross sections ($\sigma_{i \rightarrow f}^R$) can be estimated as a linear combination of the non-relativistic state-to-state cross sections ($\sigma_{i \rightarrow q}^{NR}$) as follows

$$\sigma_{i \rightarrow f}^R \approx \sum_q \frac{1}{(2S_q + 1)} |c_{fq}|^2 \cdot \sigma_{i \rightarrow q}^{NR}, \quad (2)$$

where S_q is the spin of the q th non-relativistic state. Thanks to unitarity of the transformation (1), the total, elastic, and inelastic relativistic cross sections are almost identical to the non-relativistic ones. However, the inelastic contribution can now be associated with the different relativistic SO split dissociation limits. The relativistic estimations of the inelastic, neutral dissociation, and ion pair formation cross sections are shown in figure 10.

The dominant neutral dissociation appears to be the formation of $I(^2P_{3/2}) + I(^2P_{3/2})$ fragments, while formation of $I(^2P_{1/2}) + I(^2P_{1/2})$ fragments seems to be negligible. This is consistent with the results for other halogen atoms [26] but contradicts [25]. In respect of ion pair formation, the dominant process for the whole range of energies studied is the formation of $I^+(^3P_2) \cdots I^-(^1S_0)$, differing from what the results without SO effects suggest (see section 3.6).

The results included here constitute the first attempt to calculate cross sections for SO split states of I_2 . More accurate calculations that explicitly include SO effects in the scattering calculation are needed.

3.8. Extension of the scattering energy range

A Kaufmann–Baumeister–Jungen (KBJ) basis [55] was used for an extended description of the continuum and the molecular integrals were computed in quadruple precision, increasing significantly the computational cost but allowing us to extend the calculations to higher scattering energies. The set of continuum GTO exponents is included in the appendix. The deletion thresholds for the symmetric orthogonalization of the continuum basis were set to 10^{-14} . All other parameters of the scattering model, such as the maximum angular momentum, the R -matrix radius, and the CAS model, were kept unchanged and are described in section 3.2. Born correction for the inelastic dipole-allowed transitions was included. Additionally, a smoothing procedure, detailed in the appendix, was applied to deal with appearance of some very narrow nonphysical (pseudo-)resonances resulting from numerical artifacts of the continuum basis. Results obtained in this way are called smoothed KBJ (sKBJ) in what follows.

The total, elastic, inelastic, and the momentum transfer electron-impact scattering cross sections for I_2 , extended for scattering energies up to 50 eV, are shown in figure 11.

The magnitude of the inelastic Born correction is demonstrated by comparison to the uncorrected cross sections. The correction is negligible for energies below approximately 15 eV and starts to dominate at higher energies towards the end of the studied range. Nevertheless, the correction is dominated by a single ion-pair state, R4.2, with a large transition dipole moment (3.7 a.u.) with the ground state. The accuracy of this dipole moment therefore determines the magnitude of the Born correction. Excluding the contribution of this state reduces the Born correction by an order of magnitude to a negligible value of approximately 0.1 Å^2 at 50 eV. As discussed in section 3.6 above, the contribution of this state would probably be significantly reduced by the Franck–Condon factors. As a result, the accurate value of the inelastic cross section is probably closer to the uncorrected value.

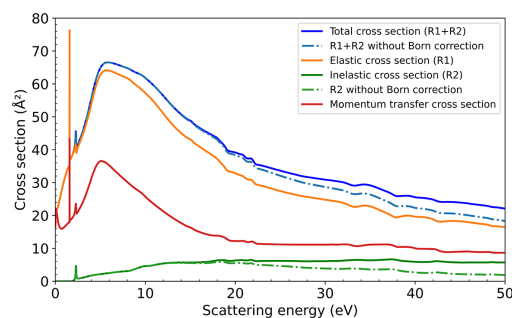


Figure 11. Total (blue), elastic (orange), inelastic (green), and momentum transfer (red) cross sections for I_2 up to 50 eV. Results with and without the inclusion of the Born correction for the dipole-allowed transitions are shown.

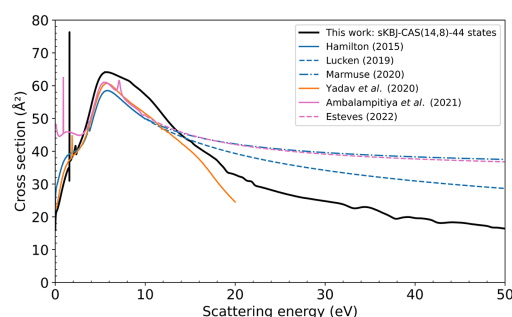


Figure 12. Elastic cross sections for I_2 reported in the present work (black) together with the results of Hamilton [24] (blue), Yadav [37] (orange), and Ambalampitiya [25] (pink), with extrapolations to higher energies by Lucken [13], and Marmuse [14] (dashed blue), and Esteves [15] (dashed pink). The extrapolations represented by the dashed lines are based on the low-energy data plotted with the solid line of the same color.

It is important to note that the CAS(14,8) model includes target states of I_2 with vertical energies up to 40 eV. At energies beyond the ionization threshold our calculations ignore the impact ionization channel which may affect the elastic and inelastic channels. The states in our calculations with energies above the ionization potential may effectively couple to the ionization channel too. This may lead to a further overestimation of our impact excitation cross sections, but it is not possible to quantify this effect. Nevertheless, we expect that the effect of the ionization channel on the elastic channel will be small because the impact ionization cross section is at least a factor 2–5 smaller than the elastic cross section, see section 3.10.

In figure 12, the smoothed elastic cross section computed with the KBJ basis is shown together with previous results from the literature. Our elastic cross section is the first ab initio result computed for energies larger than 20 eV.

We observe that at low energies between 5–15 eV, previous calculations underestimate the elastic cross section, while at energies above 15 eV the extrapolations significantly overestimate it. The reason for this is a smooth continuation of the low-energy curve with an inaccurate slope. The results of Yadav *et al* are the only other calculation going beyond 15 eV and confirm the general rapid drop of our cross section at energies above 15 eV.

We have applied the methodology of section 3.7 to extend the relativistic estimation of the inelastic processes to higher energies. In figure 13, the relativistic estimation of the cross sections for neutral dissociation (reactions R3.1–R3.3) and ion pair formation (reactions R4.1–R4.3) are shown.

The results obtained suggest that ion pair formation from reaction R4.1.3 (producing $I^+(^3P_2) \dots I^-(^1S_0)$) is the dominant process in the high energy range with the reservations related to the possible effects of vibrational motion discussed above.

3.9. KER

As noted in several other diatomic gases [32–34], KER during electron impact dissociation of molecular iodine can produce hot fragments that may lead to significant neutral gas heating. Consider the neutral dissociation reactions R3.1–R3.3 in table 1. Although the dissociation threshold energy, $\varepsilon_{\text{diss}}$, of the molecular ground state is 1.542 eV, an incident electron can initially transfer a higher energy and place the molecule into an excited repulsive state. The energy required (and which the electron also losses),

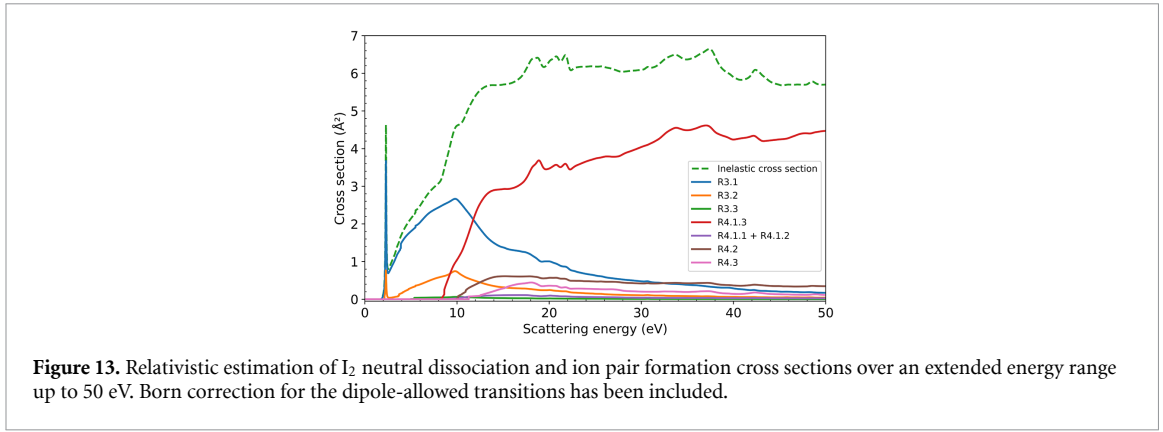


Figure 13. Relativistic estimation of I_2 neutral dissociation and ion pair formation cross sections over an extended energy range up to 50 eV. Born correction for the dipole-allowed transitions has been included.

Table 4. Total kinetic energy release (KER) from neutral dissociation (R3) of relevant excited molecular states. Here, values have been computed from the equilibrium interatomic distance, R .

Term ($D_{\infty h}$)	KER (eV per atom)
1 st $^3\Pi_u$	0.30
1 st $^1\Pi_u$	0.59
1 st $^3\Pi_g$	1.10
1 st $^1\Pi_g$	1.19
1 st $^3\Sigma_u^+$	1.32
1 st $^3\Sigma_g^-$	1.45
1 st $^1\Delta_g$	1.57
2 nd $^1\Sigma_g^+$	1.64
1 st $^1\Sigma_u^-$	1.77
1 st $^3\Delta_u$	1.80
2 nd $^3\Sigma_u^+$	1.84

is the vertical excitation energy, ε_{vee} . Making use of the Franck–Condon principle, the internuclear distance, R , is assumed to remain fixed during the electron collision. Thus, the vertical excitation energy is

$$\varepsilon_{\text{vee}} = \varepsilon_{\text{pe}}^*(R) - \varepsilon_{\text{pe}}(R), \quad (3)$$

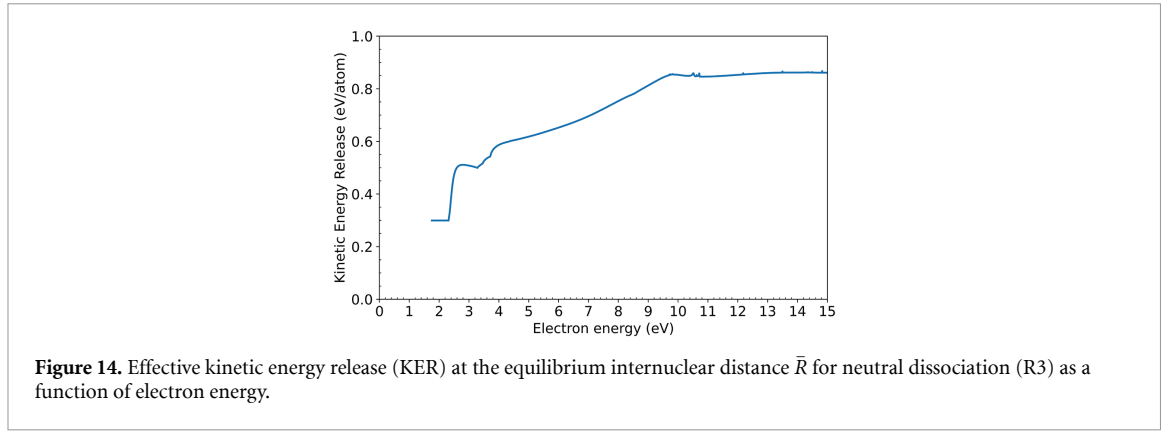
where $\varepsilon_{\text{pe}}^*(R)$ and $\varepsilon_{\text{pe}}(R)$ are the potential energies of the excited and ground states respectively at an internuclear distance R . The repulsive state, being unstable, will dissociate and the combined potential energy of the resulting atomic fragments is equal to the asymptotic value of the potential energy curve at large internuclear distances (i.e. $R \rightarrow \infty$) denoted by $\varepsilon_{\text{pe}}^*(\infty)$. As a result, the excited repulsive state initially has a potential energy, $\varepsilon_{\text{pe}}^*(R)$, higher than this asymptotic value, and thus to conserve energy, the excess energy, $\Delta\varepsilon_{\text{ker}}$, must be carried away in the form of kinetic energy of the dissociation fragments

$$\Delta\varepsilon_{\text{ker}} = \varepsilon_{\text{pe}}^*(R) - \varepsilon_{\text{pe}}^*(\infty). \quad (4)$$

The lowest vibrational level (denoted $\nu = 0$) of the molecular ground state has an energy approximately equal to 0.0133 eV. Nevertheless, in the present analysis we only consider the vertical transition from the ground equilibrium configuration and neglect vibrational effects leading to a KER distribution. Based on the potential energy curves presented in section 3, equation (4) is used to determine the KER for the equilibrium internuclear distance, $\bar{R}$. These results are summarized in table 4.

For plasma discharge modeling, it is more convenient to have effective KER values that include all excitation processes leading to dissociation so that separate excitation and dissociation pathways do not need to be individually treated. An effective KER is therefore defined based on a cross-section-weighted value determined from

$$\langle \Delta\varepsilon_{\text{ker}} \rangle = \frac{\sum_j \Delta\varepsilon_{\text{ker},j} \sigma_j}{\sum_j \sigma_j}, \quad (5)$$



where σ_j is the cross section for an individual dissociation pathway contributing to one of the main dissociation reactions (i.e. reaction R3 in table 1), and $\Delta\epsilon_{\text{ker},j}$ is the KER associated with this individual pathway. Because the cross section varies with incident electron energy, the effective KER will also vary, as shown in figure 14. Over the energy range studied, the effective KER varies between about 0.3–0.9 eV per atom. This range is consistent with values assumed in previous plasma models [15]. The dominant neutral dissociation reaction based on the cross-section magnitude is reaction R3.1.

In this work, detailed excited states of neutral molecular iodine have been computed, but not excited molecular positive or negative ion states. Thus, an accurate estimate of the KER for dissociative ionization and dissociative electron attachment are not presented. Nonetheless, some general statements can still be made. For atomic iodine, the electron affinity, $\epsilon_a = 3.059$ eV, is higher than the ground state dissociation threshold. Thus, there is no threshold energy for dissociative electron attachment and even low energy electrons can participate.

If the dominant neutral dissociation product is the $\text{I}(^2\text{P}_{3/2})$ configuration, as suggested in this work (see section 3.12), the resulting KER is at least equal to approximately $\epsilon_{a,\text{I}} - \epsilon_{\text{diss}}$. Considering also the initial incident electron energy, ϵ_e , the KER is

$$\Delta\epsilon_{\text{ker}} = \epsilon_e + \epsilon_{a,\text{I}} - \epsilon_{\text{diss}} \approx \epsilon_e + 1.517 \text{ eV}. \quad (6)$$

If the neutral dissociation product is instead the $\text{I}(^2\text{P}_{1/2})$ configuration, as indicated by previous calculations [25], the excitation threshold of 0.9426 eV needs to be subtracted, and the KER becomes $\Delta\epsilon_{\text{ker}} \approx \epsilon_e + 0.574$ eV. In either case, the excess energy can be significant.

3.10. Impact ionization

The total electron-impact ionization cross section is calculated using the Binary Encounter Bethe (BEB) method [56], including the same ECP used in the *R*-matrix calculation [57]. In the BEB method, the contribution to the ionization cross section from each orbital k within a set of Hartree–Fock orbitals is given by

$$\sigma_k = \frac{S_k}{t + u_k + 1} \left[\frac{1}{2} \left(1 - \frac{1}{t^2} \right) \ln t + 1 - \frac{1}{t} - \frac{\ln t}{1 + t} \right], \quad (7)$$

where t , u_k and S_k depend on the binding energy B , the incoming electron energy T , the orbital kinetic energy U_k , and the orbital occupation number N_k as: $t = T/B$, $u_k = U_k/B$, and $S_k = 4\pi a_0^2 N_k R^2 / B^2$, where a_0 is the Bohr radius and R the Rydberg constant. The total ionization cross section is found by summing the contributions from all occupied orbitals.

Seven Hartree–Fock orbitals are included. The orbital kinetic energies used are 0.378 192 au, 0.508 596 au, 0.186 007 au, 0.283 221 au, 0.574 244 au, 0.659 060 au and 0.823 630 au respectively.

As shown in [58], the above expression may be modified to account for dissociative ionization pathways, such as reaction R6 in table 1, as well as the non-dissociative pathway in reaction R5.

3.11. Dissociative ionization

The total ionization cross section may be further separated into contributions for all fragments, which account for both dissociative and non-dissociative ionization processes (reactions R5 and R6 in table 1). These partial ionization cross sections are defined for each fragment, f , and are deduced using a modified version of the BEB cross section given in [58]. In this modified expression, the contribution to the

Table 5. Branching ratios for I_2^+ and I^+ , derived from the mass spectrum [59], and appearance thresholds of the fragments obtained from NIST [60].

Species	Branching Ratio	Threshold (eV)
I_2^+	0.645	9.30
I^+	0.355	11.94

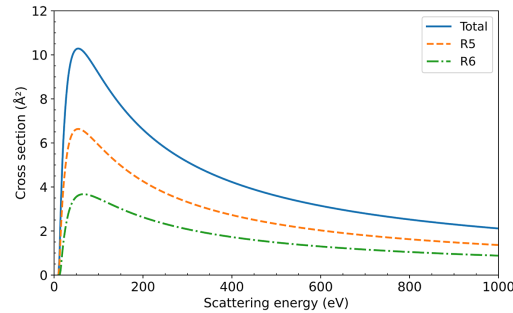


Figure 15. Total and estimated partial ionization cross sections for I_2 .

ionization cross section for fragment f from each orbital k is given by

$$\sigma_k^f = \frac{\Gamma_f S_k}{t_f + u_k + 1} \left[\frac{1}{2} \left(1 - \frac{1}{t_f^2} \right) \ln t_f + 1 - \frac{1}{t_f} - \frac{\ln t_f}{1 + t_f} \right], \quad (8)$$

where Γ_f is the branching ratio for fragment f , and $t_f = t/(B - D_f)$, where D_f is the appearance threshold for fragment f . In the case of I_2 , evaluation of this expression requires the branching ratio and appearance thresholds for I_2^+ and I^+ . Branching ratios are predicted through analysis of the electron-ionization mass spectrum, which is given for I_2 in [59]. The predicted branching ratios are given in table 5, with appearance thresholds for the fragments obtained from [60].

The total and partial ionization cross sections for I_2 are shown in figure 15.

3.12. Dissociative electron attachment

The dissociative electron attachment (DEA; reaction R7) cross section is calculated using the semi-analytical DEA estimation method described in [61] that uses the bond dissociation energy, vibrational frequency, electron affinity of the dissociating fragment (to which the electron attaches), and the resonance positions and widths as input parameters. In this work, the method uses an electron affinity of 3.06 eV, a bond dissociation energy of 1.542 eV, and a vibrational frequency of 214 cm^{-1} [25]. The DEA cross section is shown in figure 16, together with the individual contributions to the cross section from the two resonances observed, and the DEA cross section calculated in [25]. Since the two resonances that enable DEA to occur are nearby in energy, their combined contributions form a single broad feature in the DEA cross section for energies between 1–3 eV.

In [25], the DEA cross section was calculated using two methods, namely the local complex potential (LCP) approximation, and the static-exchange plus polarization (SEP) method within the molecular R -matrix codes implemented in the Quantemol software package QN. The SEP calculation showed two distinctly separated peaks in the DEA cross section that were attributed to $^2\Pi_g$ and $^2\Pi_u$ resonances, while our calculation finds that the two resonances at low energy are associated with $^2\Sigma_g^+$ and $^2\Pi_u$ scattering symmetries (see figure 20). These resonances are found at around 0.6 eV and 2.0 eV in the LCP calculation in [25], and are found at around 0.85 eV and 2.5 eV in the SEP calculation. Given the impact of excited target states on the other cross sections calculated in this work, it is not surprising that our resonance positions differ from the SEP calculation, which only includes a single target state. The contribution to the cross section from the $^2\Pi_u$ resonance in the LCP calculation of [25] is in better agreement with our calculation, both in terms of position and magnitude.

Additionally, since we find no resonances at higher energies, the DEA cross section tends to zero after the peak at 2.3 eV. In [25], a resonance appears in the elastic scattering cross section at around 7.5 eV, and this may be the source of the significant DEA cross section at higher energies.

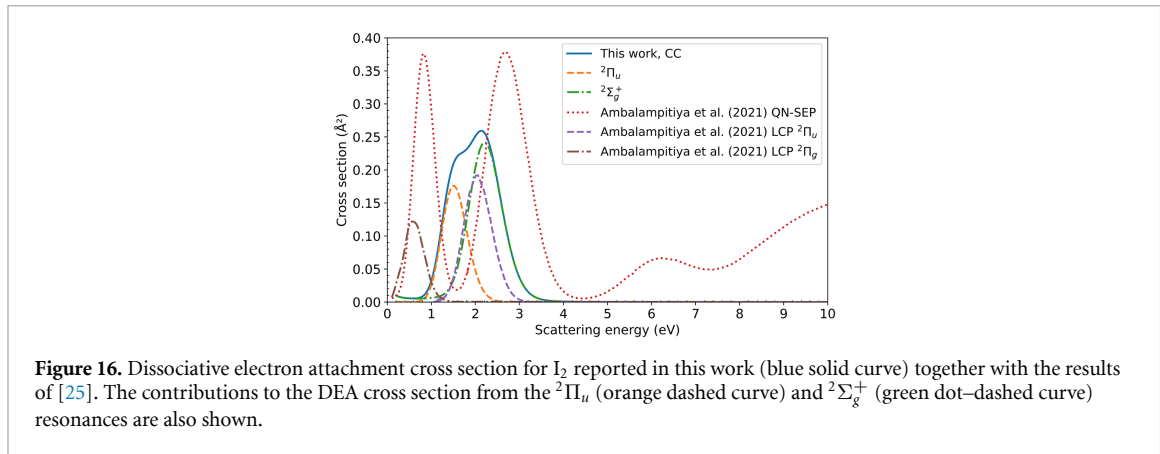


Figure 16. Dissociative electron attachment cross section for I_2 reported in this work (blue solid curve) together with the results of [25]. The contributions to the DEA cross section from the $^2\Pi_u$ (orange dashed curve) and $^2\Sigma_g^+$ (green dot-dashed curve) resonances are also shown.

4. Conclusions

The present study provides updated electron scattering cross sections for I_2 : accounting for higher angular momentum ($l_{\max} = 6$), an expanded CAS(14,8) including more states, and scalar relativistic ECPs. These improvements address gaps in the earlier literature, such as the limited angular momentum ($l_{\max} = 4$) and smaller CAS(10,6) models used in previous calculations. While experimental results are still required to definitively validate the theoretical framework, the model presented here is likely to be more accurate because it includes a more complete description of polarization, correlation, and angular momentum expansion.

The analysis of scattering symmetries identifies two Feshbach resonances in the low energy region: the first at 1.59 eV (with a width lower than 0.01 eV) decaying to the ground state through $^2\Pi_u$ scattering symmetry, and the second at 2.30 eV (with a width of 0.10 eV) decaying to the first $^3\Pi_u$ term through $^2\Sigma_g^+$ scattering symmetry. The resonance positions exhibit a significant dependence on model size, decreasing in energy as the size of the CAS and the number of included states increases. The position of the resonances in our calculations is therefore estimated to be in the range 1.59–2.19 eV for the first resonance and in the range 2.30–3.08 eV for the second resonance. These resonances may contribute to produce a large KER of around 1 eV per atom during dissociation. This energy release might provide a critical physical explanation for the anomalous neutral gas heating (>1500 K) previously observed in some iodine plasma discharges [15].

Furthermore, our relativistic estimation identifies the dominant subprocesses in the complex plasma chemistry of I_2 . We confirm that neutral dissociation primarily follows the $I(^2P_{3/2}) + I(^2P_{3/2})$ pathway, while the $I(^2P_{1/2}) + I(^2P_{1/2})$ channel is almost negligible. It suggests therefore that the dominant configuration in processes such as DEA would be $I(^2P_{3/2})$. These findings align with observations in other halogen atoms, but contradict the results reported in [25]. In ion pair formation, $I^+(^3P_2) \cdots I^-(^1S_0)$ was identified as the main product. However, in the non-relativistic picture, $I^+(^1D_2) \cdots I^-(^1S_0)$ seems to be the dominant pathway instead. This phenomena is related to the non-relativistic first $^1\Sigma_u^+$ state and its low vertical excitation energy (see figure 1).

Finally, we provide the first ab initio results for scattering energies up to 50 eV, revealing that previous extrapolations are largely faulty due to inaccurate slopes of the low-energy cross sections. Nonetheless, the produced results need to be contrasted with calculations involving a larger CAS with more states included, as well as an angular momenta beyond $l = 6$. For high-energies, the novel full-potential Born approximation method [62] may serve as a viable alternative to the current R -matrix approach. Despite these advances, a truly comprehensive description of electron-impact I_2 scattering will require inclusion of nuclear dynamics and more rigorous relativistic methods to account for polar dissociation and SO effects in the continuum dynamics, which are omitted at present. Nevertheless, this work serves as a necessary preparatory step for more accurate future calculations of KER, DEA, and even photodetachment from negative ions.

Acknowledgments

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Data availability statement

The data that support the findings of this study will be openly available following an embargo at the following URL/DOI: <https://doi.org/10.5281/zenodo.20395295> [64]. Data will be available from 2 September 2026.

Appendix A. Scattering models

Different complete active space (CAS) models were studied, together with a simpler static exchange (SE) model with all 14 available electrons frozen in 7 doubly occupied 5p orbitals. The SE calculations describe only elastic scattering with no polarization of the target molecule and allow for formation of shape resonances only, if present in the target molecule. The calculations used Hartree–Fock orbitals and included 50 virtual orbitals available for capture of the incoming electron. Additionally, a static exchange plus polarization (SEP) was considered. It includes, on top of the SE configurations, configurations allowing two electrons in the virtual orbitals. The different scattering models considered in this work are summarized in table 6. They include the SE and SEP mentioned above, and two CAS Close-Coupling models: CAS(10,6) with 10 active electrons in the 5p shell of both atoms ($1a_g$, $1b_{1u}$, $1b_{2u}$, $1b_{3u}$, $1b_{2g}$, $1b_{3g}$), and CAS(14,8) with 14 electrons in the 5 s and 5p shells ($1-2a_g$, $1-2b_{1u}$, $1b_{2u}$, $1b_{3u}$, $1b_{2g}$, $1b_{3g}$).

Table 6. Scattering models studied in this work.

Model	Number of states
SE	1
SEP	1
CAS(10,6)	12
CAS(10,6)	24 (all available)
CAS(14,8)	24
CAS(14,8)	44 (all available)

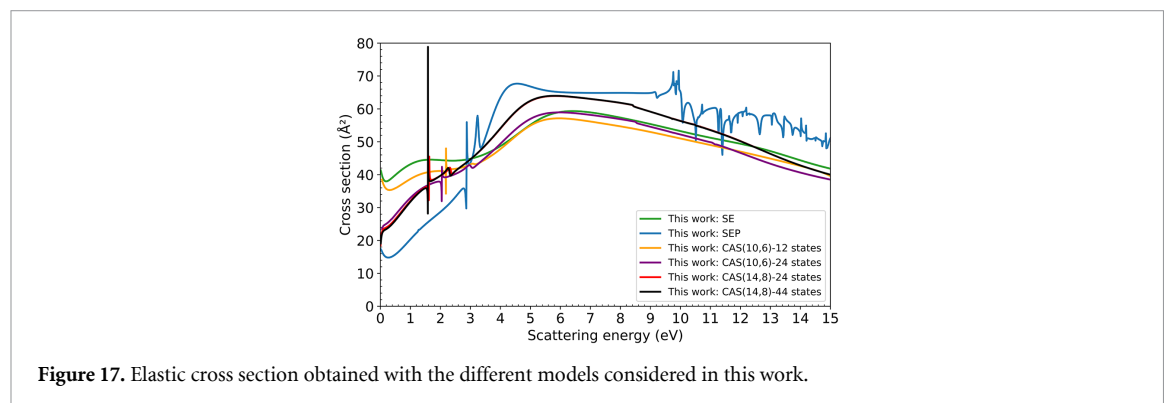
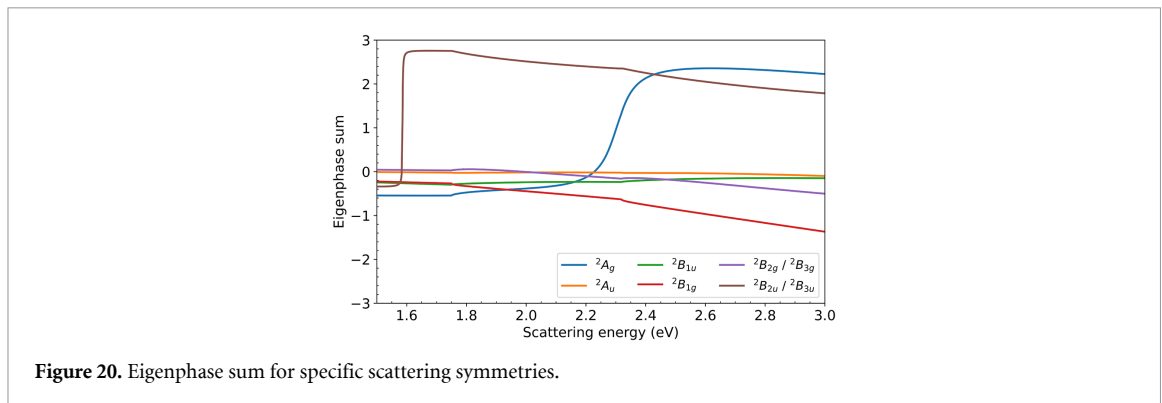
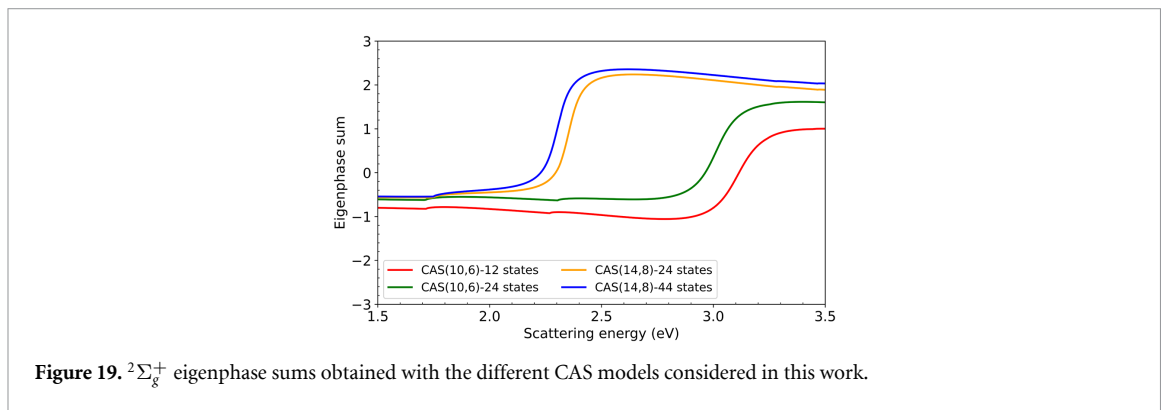
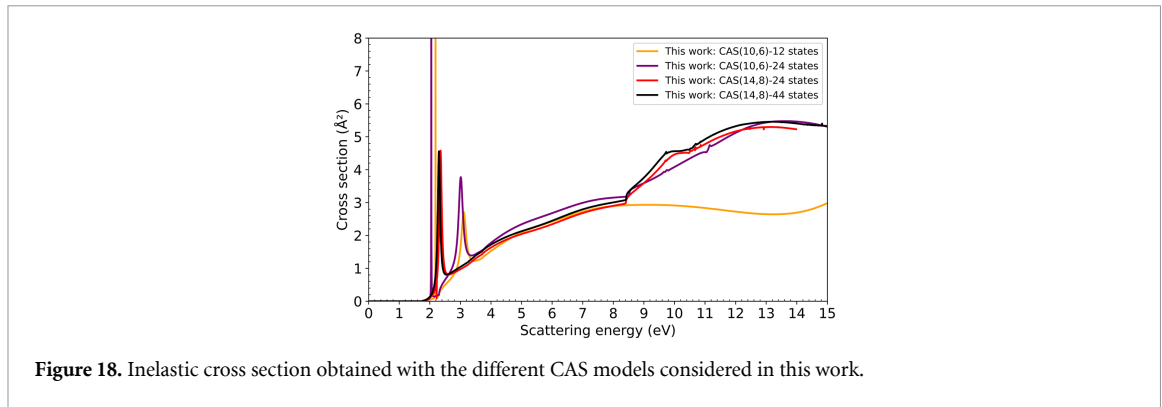


Figure 17. Elastic cross section obtained with the different models considered in this work.

Figure 17 compares the elastic cross sections from all models used. The absence of resonances in the SE results shows that both resonances appearing in the CAS results are Feshbach resonances. In the SEP results, the first two peaks (at 2.77 eV and 3.24 eV) correspond to the Feshbach resonances obtained with the CAS model, because the scattering symmetries are the same. The peaks observed at higher energies (above 9 eV) are unphysical pseudoresonances characteristic for SEP calculations. Additionally, the dependence of the energy position of the resonance on the CAS model can be analyzed, where we conclude that the larger the CAS, the lower the resonance energy. Moreover, for the same CAS, the more



states included, the lower the resonance energy. The difference in the positions of the first resonance between the smallest and the largest model is 0.60 eV, confirming the important role of polarization/correlation in the description of this resonance. In the absence of any experimental reference, we can only provide an estimate of the resonance position within the range 1.59–2.19 eV.

Similarly, the inelastic cross sections obtained with the different models are shown in figure 18. The same effects as in the elastic cross sections can be seen. Although the cross sections in the low-energy range are sufficiently converged with respect to the number of states included on the level of 36 states, including only 18 states in the calculation results in a significant underestimation of the cross sections at energies beyond 8 eV.

Finally, for the study of the resonances, the eigenphase sum for the scattering symmetry $^2\Sigma_g^+$ obtained with the different models is shown in figure 19 to exemplify the sensitivity of the resonance parameters on the model size. The same effects as reported for the $^2\Pi_u$ resonance can be seen here and the general shape of the Breit–Wigner resonance is preserved across the different models with a small decrease of the resonance width with an increasing size of the CAS model and the number of states included. This second resonance is expected to lie in the range 2.30–3.08 eV.

The results with the resonances at lower energies are the ones presented in the main text. In figure 20, we show the eigenphase sums in the energy region where scattering resonances form, using the model presented in the main text: CAS(14,8) including 44 states.

Table 7. Resonance parameters obtained from the CAS(14,8) model with 44 states.

Symmetry	E_{res} (eV)	Γ (eV)
$^2\Pi_u$	1.59	< 0.01
$^2\Sigma_g^+$	2.30	0.10

The first resonance at 1.5 eV is a Feshbach resonance decaying into the ground state and the second peak at 2.3 eV corresponds to a Feshbach resonance decaying into both the ground and the first excited molecular term ($^3\Pi_u$). The first resonance appears in the degenerate $^2B_{2u}$ and $^2B_{3u}$ scattering symmetries, with the second resonance appearing in the ^2A_g symmetry. The degenerate B_{2u} and B_{3u} symmetries in D_{2h} can be directly related to the Π_u term in $D_{\infty h}$, but for the A_g symmetry there are two options: Σ_g^+ and Δ_g . However, as the latter requires a contribution of B_{1g} symmetry and no resonance is observed in this symmetry, this option can be discarded, and the resonance may be assigned to the Σ_g^+ term.

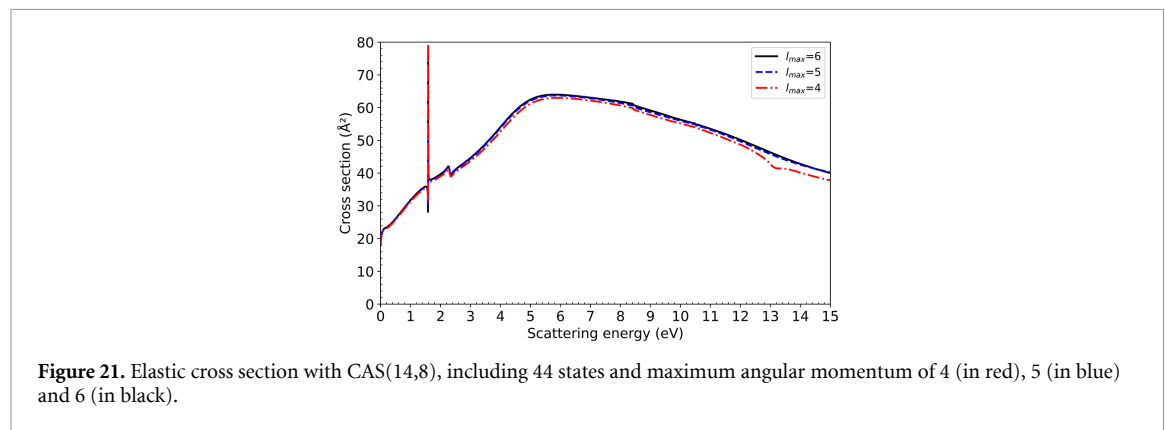
For this model, resonance parameters were extracted by fitting the eigenphase sums to the Breit–Wigner formula:

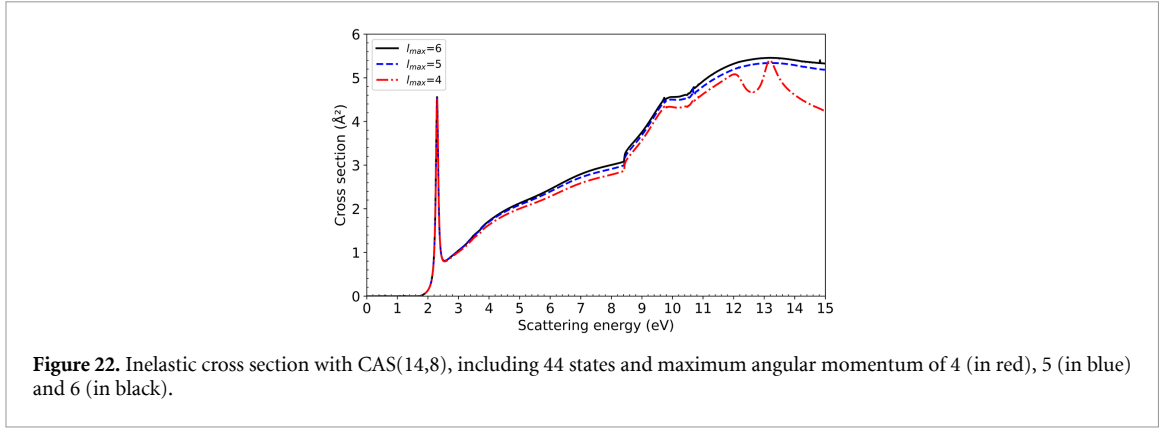
$$\delta = \delta_{bg}(E) + \arctan\left(\frac{\Gamma/2}{E_{\text{res}} - E}\right), \quad (9)$$

where δ represents the eigenphase sum, $\delta_{bg}(E) = \delta_0 + aE$, is the linearly-varying background eigenphase, Γ is the width of the resonance, E_{res} is the resonance energy, and E is the scattering energy. The resulting resonance energy position (E_{res}) and width (Γ) for both resonances are given in table 7.

Appendix B. Partial-wave convergence

An important parameter to converge in the scattering calculations is the maximum angular momenta included. The previous calculations included angular momentum contributions up to 4. In this work, we studied convergence of the angular momentum expansion in the low-energy region. In figure 21, the elastic cross sections using the CAS(14,8), 44 states, and including angular momentum up to 4, 5, and 6 are shown. In figure 22, the inelastic cross section for the same model and including angular momentum up to 4, 5, and 6 are shown. For energies between 4 eV and 12 eV, the cross section appears to be sufficiently converged with respect to continuum angular momentum. For energies beyond 12 eV, the inclusion of higher angular momentum is crucial for a proper description of the scattering process. The results for $l_{\text{max}} = 4$ are not only smaller in magnitude, but also possess some unphysical structures which disappear when the angular momentum expansion is converged.



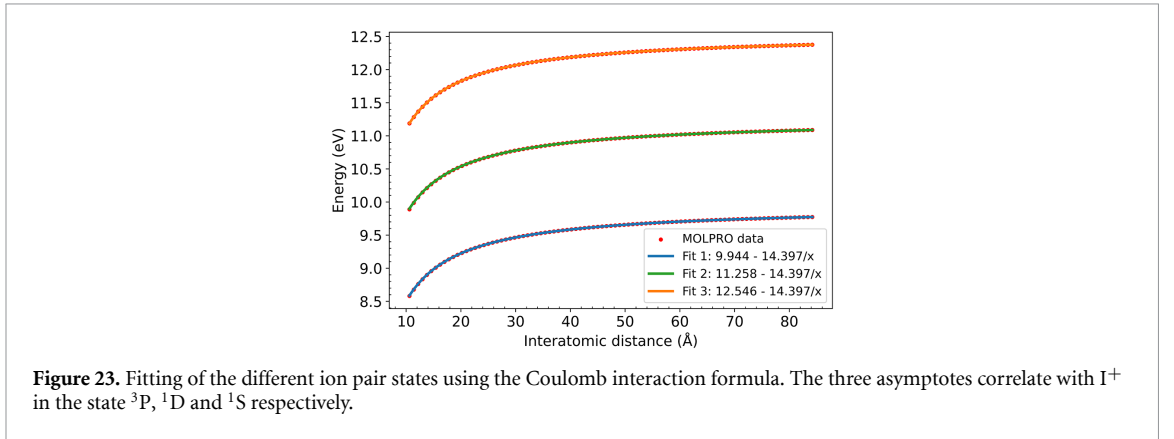


Appendix C. Polar dissociation thresholds

At large interatomic distances, the ion pair state energies can be described by the Coulomb interaction formula

$$y = A - B/x, \quad (10)$$

where A represents the asymptotic (dissociation) energy of the state and B represents the Coulomb constant. The results of the fits of the state energies to the Coulombic form for the three groups of ion-pair states are shown in figure 23. The Coulomb interaction as the only component defining the states at large interatomic distances is confirmed: i.e. the three groups of states above the neutral dissociation limit correspond to ion pair formation.

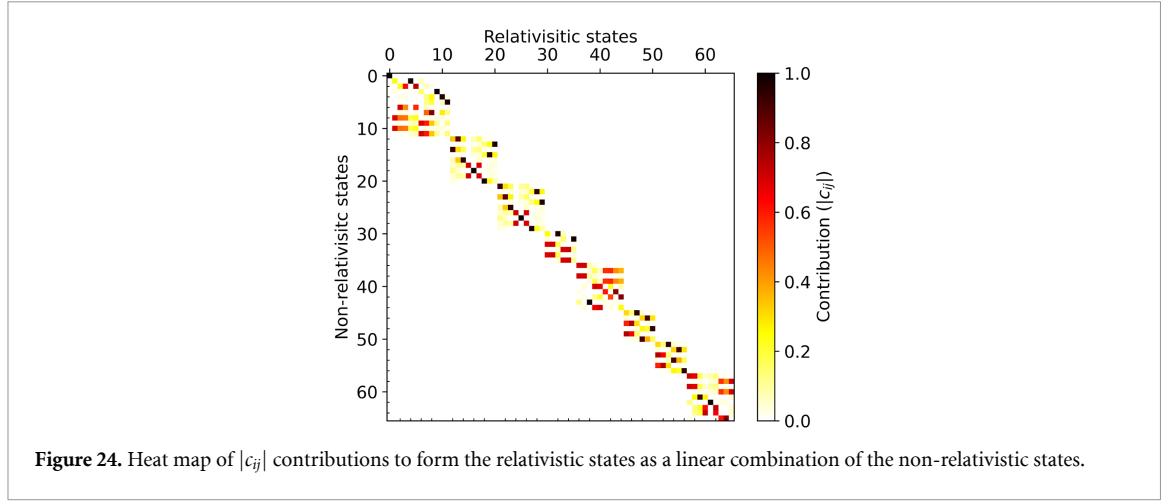


Appendix D. Relativistic estimation

To construct the relativistic states as a linear combination of the non-relativistic ones, the real-valued coefficients c_{ij} from equation (1) are used and plotted in figure 24 as a heat map. They represent the decomposition of the relativistic states in terms of the non-relativistic ones. The quasi diagonal shape of the heat map is due to the expected fact that the relativistic states are formed mainly from the neighboring non-relativistic states.

The non-relativistic cross sections are constructed in terms of the T -matrix elements in the basis of the target states

$$\sigma_{i \rightarrow f}^{NR} = \frac{\pi}{k_i^2} \frac{2S+1}{2S_i+1} \sum_{l_i, m_i} \sum_{l_f, m_f} |T_{i, l_i, m_i, f, l_f, m_f}^{NR}|^2, \quad (11)$$



where S is the total spin of the scattering wavefunction, S_i is the spin of the initial state and k_i is the momentum in the initial channel. The set of the non-relativistic states used in the expansion of the relativistic ones includes the degenerate states from the same spin multiplet. Consequently, the cross section for a final state f with a fixed spin projection is given by $\sigma_{i \rightarrow f}^{NR} / (2S_f + 1)$.

We make the transition to the basis of the relativistic states and write for the modulus squared of the T -matrix element

$$|T_{i,l_i,m_i,f,l_f,m_f}^R|^2 = \left| \sum_{p,q} c_{ip} c_{fq} T_{p,l_i,m_i,q,l_f,m_f}^{NR} \right|^2 \quad (12)$$

$$\approx \left| \sum_q c_{fq} T_{i,l_i,m_i,q,l_f,m_f}^{NR} \right|^2 \quad (13)$$

$$\approx \sum_q |c_{fq}|^2 |T_{i,l_i,m_i,q,l_f,m_f}^{NR}|^2, \quad (14)$$

where in the first step the T -matrix in the basis of the relativistic target states was expressed as a linear combination of the non-relativistic T -matrices. Then, we have approximated the relativistic ground state, i , with the non-relativistic one by setting $c_{ip} = \delta_{i,p}$. Expanding the resulting modulus squared would yield phase-sensitive cross-terms which we have neglected, resulting in an expression requiring only moduli squared of the combination coefficients and the non-relativistic T -matrices.

Finally, the relativistic cross section is estimated by combining (14) with (11)

$$\sigma_{i \rightarrow f}^R \approx \frac{\pi}{k_i^2} \frac{2S+1}{2S_i+1} \sum_{l_i,m_i} \sum_{l_f,m_f} |T_{i,l_i,m_i,f,l_f,m_f}^R|^2 \quad (15)$$

$$= \frac{\pi}{k_i^2} \frac{2S+1}{2S_i+1} \sum_q |c_{fq}|^2 \quad (16)$$

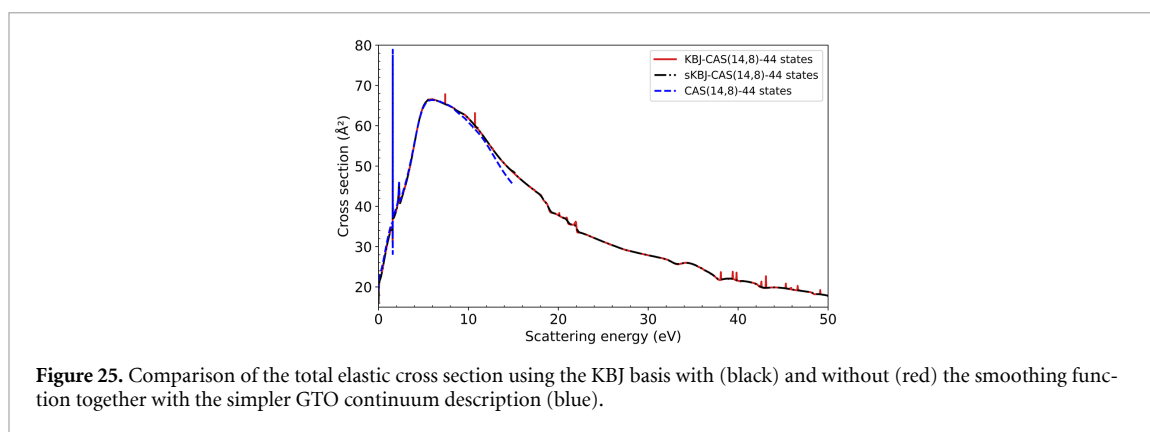
$$\times \sum_{l_i,m_i} \sum_{l_f,m_f} |T_{i,l_i,m_i,q,l_f,m_f}^{NR}|^2 \quad (17)$$

$$= \sum_q |c_{fq}|^2 \frac{\sigma_{i \rightarrow q}^{NR}}{2S_q+1}. \quad (18)$$

Appendix E. Smoothed Kaufmann–Baumeister–Jungen (KBJ) cross sections

The KBJ basis generated very narrow unphysical peaks in the cross sections, due to numerical artifacts of the continuum description. In order to deal with these nonphysical contributions, a smoothing procedure [63] for the cross sections was employed. The following function is used in a self-consistent iterative smoothing process

$$f_{\text{smooth}}(x_i) = \sum_j \frac{g(x_i - x_j) f(x_j)}{\sqrt{1 + |f(x_j) - f_{\text{smooth}}(x_j)|^2}}, \quad (19)$$



where f represents the input cross section with the artifacts (KBJ), f_{smooth} is the smoothed cross section (sKBJ), and g represents a Gaussian function where a pre-exponential factor of 1 and an exponential factor of 0.5 was used. The smoothing procedure was applied starting at the energy 5.5 eV, sufficiently above the energy of the higher-lying resonance. Furthermore, at energies below 5.5 eV no artifacts were present in the KBJ results, obviating the need for the smoothing procedure.

In figure 25, the KBJ total cross section up to 50 eV with (KBJ) and without (sKBJ) smoothing is presented together with the cross section obtained with the regular continuum for energies up to 15 eV. We observe a perfect match of the two sKBJ results with the regular continuum results for energies up to approximately 10 eV, with the sKBJ results starting to deviate slightly at 15 eV. We found that the KBJ basis is able to describe the continuum well up to energies of about 50 eV, while the results start to break down at energies approaching 60 eV.

Appendix F. From D_{2h} to $D_{\infty h}$ symmetry

For conversion from the 64 D_{2h} states used in MOLPRO and UKRmol+ to the 44 $D_{\infty h}$ molecular terms, the relation detailed in table 8 was used.

Table 8. Correlation of $D_{\infty h}$ irreducible representations (Molecular Terms) to D_{2h} irreducible representations.

$D_{\infty h}$ Term	D_{2h} state(s)
Σ_g^+	A_g
Σ_g^-	B_{1g}
Π_g	$B_{2g} \oplus B_{3g}$
Δ_g	$A_g \oplus B_{1g}$
Σ_u^+	B_{1u}
Σ_u^-	A_u
Π_u	$B_{2u} \oplus B_{3u}$
Δ_u	$A_u \oplus B_{1u}$

ORCID iDs

Alejandro L García-Muñoz 0009-0000-5739-095X

Nicolas Sisourat 0000-0002-8567-5263

Zdeněk Mašín 0000-0001-9382-4655

Gregory S J Armstrong 0000-0001-5949-2626

Jonathan Tennyson 0000-0002-4994-5238

Trevor Lafleur 0000-0002-9926-2187

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