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Newly calculated absolute cross-section for the electron-impact ionization of $C_2H_2^+$

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Abstract. New measurements of the cross-section for electron impact ionization of the molecular ion $C_2H_2^+$ have been carried out recently. These data differ significantly from earlier data, because cross-sections corresponding to all the possible dissociative ionization processes were determined. The new data in conjunction with the significant discrepancies between the earlier data and the results of various calculations, which disagreed among themselves by a factor of 3, motivated a renewed attempt to apply the semi-classical Deutsch-Märk (DM) formalism to the calculation of the absolute electron-impact ionization cross-section of this molecular ion. A quantum chemical molecular orbital population analysis for both the neutral molecule and the ion revealed that in the case of $C_2H_2^+$ the singly occupied molecular orbital (i.e. the "missing" electron) is highly localized near the site of a C atom in the molecule. This information is explicitly incorporated in our formalism. The results obtained by taking the ionic character directly into account are in excellent agreement with the recent experimental data.

PACS. 34.80.Gs Molecular excitation and ionization by electron impact – 52.20.Fs Electron collisions

1 Introduction

Collisions between electrons and neutral molecules have been the subject of intense experimental and theoretical studies since the early days of atomic collision physics. By contrast, studies of electron collisions with singly (and multiply) positively or negatively charged molecular ions as targets have not nearly received as much attention despite the importance of molecular ions in environments such as low-temperature plasmas, fusion plasmas, planetary and cometary atmospheres, and mass spectrometry. Electron impact ionization of a molecular ion is a particularly challenging process for experimentalists because of the fact that both the projectile and the target are charged, which poses difficulties not encountered in experiments with neutral targets. The ionization process results in the formation of doubly charged molecules in states which may easily dissociate into pairs of singly charged fragments. In addition, there are competing channels for the formation of particular fragment ions involving dissociative *excitation* (DE) vs. dissociative *ionization* (DI), which cannot be separated experimentally unless all reaction products of the collision are detected and a specific procedure is developed, which is based on the shape of the cross-section or on the shape of the kinetic energy distribution.

Calculations of cross-sections for the ionization of molecular ions are also challenging. Up to now, we are only aware of the application of semi-rigorous methods such as the Deutsch-Märk (DM) formalism [1] and the Binary-Encounter-Bethe (BEB) method of Kim and coworkers [2] to the calculation of ionization cross-sections of a few selected molecular ions [3–5]. Comparisons of the calculated cross-sections with available experimental data for the ions H_2^+, N_2^+, O_2^+, CD^+, CO^+, CO_2^+, H_3O^+/D_3O^+, and CD_4^+ [4,5] were in reasonable agreement only in the case of N_2^+ [3–5]. In this latter case, the experiment was able to determine separately (i) the cross-section for the production of N_2^{2+} (simple ionization, SI) and (ii) the cross-section for the production of N^+ due to DI only. The calculation concerns the ionization process only, dissociation being not taken into account, so that serious

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disagreements for the other ions were often attributed to the inability of the experiment to separate contributions due to DE from contributions due to DI. However, it should also be noted that the application of the DM formalism to molecular ions requires certain assumptions and additional approximations that are not required in the case of neutral molecular targets (as discussed in Sect. 2) and whose validity is entirely based on plausibility arguments which may not be valid in all cases. This may also have contributed to the significant discrepancies between calculated and measured data for certain molecular ions. Similar arguments apply to application of the BEB model to molecular ions and the level of agreement/disagreement between calculated BEB cross-sections and experimental data [2–5].

In this paper, we present the results of the calculation of electron-impact ionization cross-sections of molecular ions using a variant of our method that has been improved in two key aspects compared to the earlier calculations [4,5]. First, we use the revised high-energy behavior of the calculated cross-sections as described in [1]. Second, the weighting factors that are inherent to the DM formalism (see below) have been modified, so that the 'ionic' component of the target is now represented by 'ionic' weighting factors rather than by the corresponding 'neutral' weighting factors. We have selected $C_2H_2^+$ as a first test case for this approach, which takes into account details of the ionization process obtained from a comparison of the quantum chemical molecular orbital population analyses for the neutral molecular and the molecular ion. The choice of $C_2H_2^+$ was motivated by the availability of new and improved experimental data for the electron impact ionization of this molecular ion [6]. First, data were obtained for the formation of the doubly-charged molecule $C_2H_2^{2+}$ only [8]. Previous calculations disagreed among themselves by a factor of 3 (with maximum cross-section values in the range of $1{-}3 \times 10^{-20}$ m^2) and none of the calculated cross-sections agreed with these early experimental data (maximum cross-section value of 0.5×10^{-20} m^2). In a second step, the experiment concentrated on the detection of all possible fragments and the analysis of these data led to the accurate determination of the DI cross-sections. Finally, the ionization cross-section was obtained by adding the cross-sections corresponding to SI and to all the DI processes, respectively.

2 Background

The DM formalism was originally developed [9] for the calculation of atomic ionization cross-sections and has been modified and extended several times (see e.g. Ref. [1]). The DM formula expresses the atomic ionization cross-sections σ as the sum over all partial ionization cross-sections corresponding to the removal of a single electron from a given atomic sub-shell labeled by the quantum numbers n and l as

$$\sigma(u) = \sum_{n,l} g_{nl} \pi r_{nl}^2 \xi_{nl} b_{nl}^{(q)}(u)\ [\ln(c_{nl}u)/u] \tag{1}$$

where r_{nl} is the radius of maximum radial density of the atomic sub-shell characterized by quantum numbers n and l (as listed in column 1 in the tables of Desclaux [10]) and ξ_{nl} is the number of electrons in that sub-shell. The sum extends over all atomic sub-shells labelled by n and l. The factors g_{nl} are weighting factors which were originally determined from a fitting procedure [9,11] using reliable experimental cross-section data for the rare gases and uranium. The quantity u refers to the "reduced" energy $u = E/E_{nl}$, where E denotes the incident energy of the electrons and E_{nl} is the ionization energy in the (n,l) sub-shell. The energy-dependent function $b_{nl}^{(q)}(u)$ has the form

$$b_{nl}^{(q)} = \frac{A_1 - A_2}{1 + (u/A_3)^p} + A_2 \tag{2}$$

where the four quantities A_1, A_2, A_3, and p are constants that were determined from reliable measured cross-sections for the various values of n and l [1]. The superscript "q" refers to the number of electrons in the (nl) sub-shell. The constant c_{nl} in equation (1) was found to be identical to one except for d-electrons.

Our formula can be extended for the case of a molecular ionization cross-section calculation provided one carries out a Mulliken (or other) molecular orbital population analysis [12,13] which expresses the molecular orbitals in terms of the atomic orbitals of the constituent atoms. Various orbital population analyses can be obtained routinely using standard quantum chemistry codes, many of which are available in the public domain. These codes can also be used to obtain the necessary molecular structure information in cases where this information is not available accurately otherwise. The application of the DM formalism to molecular ions as described in our earlier publications [4,5] required several modifications as well as additional assumptions and approximations:

(i) the energy-dependent part in formulas (1) and (2), which was derived for neutral targets, was extended to ions in a straightforward fashion by replacing the neutral ionization energy E_{nl} by the corresponding ionization energy of the ion. This neglects the fact that the Coulomb interaction between the incident electron and the target may affect the impact energy. However, this is not expected to be a serious problem, except perhaps for impact energies very close to the ionization threshold;
(ii) the weighting factors g_{nl} for the ionic component of the molecular ion were derived semi-empirically from a fitting procedure using well-established ionization cross-sections of atomic ions;
(iii) the data base of radii r_{nl} for atomic ions is much less developed than the corresponding data base for neutral atoms. In cases where no calculated radii for atomic ions were available, neutral radii were used. This is an acceptable substitution as the cross-sections depend on the product of g_{nl} and $(r_{nl})^2$ and this product is obtained from a fitting procedure.

Therefore, the ionic character of the target was only reflected in the population analysis of the molecular orbitals

Table 1. Mulliken analysis of the MO populations of C_2H_2. See text for details.

	Orbital 1	Orbital 2	Orbital 3	Orbital 4	Orbital 5
$C(2s)$	1.544	0.568	0.052	—	—
$C(2p_x)$	—	—	—	—	2.000
$C(2p_y)$	—	—	—	2.000	—
$C(2p_z)$	0.304	0.728	1.216	—	—
$H(1s)$	0.152	0.704	0.732	—	—
	2.000	2.000	2.000	2.000	2.000

Table 2. Mulliken analysis of the MO population of $C_2H_2^+$. See text for details.

	Orbital 1	Orbital 2	Orbital 3	Orbital 4	Orbital 5
$C(2s)$	1.460	0.632	0.148	—	—
$C(2p_x)$	—	—	—	—	1.000
$C(2p_y)$	—	—	—	2.000	—
$C(2p_z)$	0.448	0.752	1.160	—	—
$H(1s)$	0.096	0.616	0.692	—	—
	2.004	2.000	2.000	2.000	1.000

as a 'missing' electron which resulted in different populations ξ_{nl} and different energies E_{nl}. In essence, the previous DM calculation for e.g. CO_2^+ treated the ion as an iso-electronic neutral BO_2 molecule with the orbitals of the CO_2^+ ion.

In this paper, we attempt to remedy some of the limitations of the approach described above. In a first step, we carry out a Mulliken population analysis for both the molecular ion and the neutral molecule in an effort to "localize" the positive charge in the molecular ion, if possible. In the present case of $C_2H_2^+$ this means trying to identify whether the ionic character can be associated with a H^+ ion in the target or a C^+ ion. If the ionization can be localized in this fashion, the second step involves the determination of the weighting factors for the corresponding atomic ion, i.e. we attempt to use 'ionic' rather than 'neutral' weighting factors for the ionic component. This can be done by applying the DM formalism to experimentally determined cross-sections for the ionization of the corresponding singly charged ion, e.g. see [14]. Such a comparison yields a value for the product $(r_{nl}^2 g_{nl})$ for the atomic ion, which, in turn, yields directly a value for the weighting factors g_{nl} for the atomic ion, if the ion radii r_{nl} are known. If these radii are not known, neutral radii are used (see above). With this information, the DM formalism can now be applied to the ionization of a molecular ion with far fewer assumptions and approximations compared to our previous approach. This is illustrated in the following section for the molecular ion $C_2H_2^+$.

3 Application of the DM formalism to the ionization of $C_2H_2^+$

We have only considered the acetylene cation H–C≡C–H$^+$ and not other possible isomers since it is by far the most stable one. MP2 calculations with the aug-cc-pVTZ [15] basis set showed, for example, the isomer $C{=}CH_2^+$ to be less stable than the acetylene cation by about 14 eV. The results of the Mulliken analyses for C_2H_2 and $C_2H_2^+$ are summarized in Tables 1 and 2 for the valence orbitals where orbital 5 is the highest-lying one. They were performed on molecular geometries optimized at the MP2/aug-cc-pVTZ level by means of ROHF calculations with the small CEP-4G [16] basis set. Two facts are obvious: (1) the two outermost orbitals (orbital 5 and 4) are of pure $C(2p)$ character and (2) the electron that is removed in the ionization process from orbital 5 can be attributed to the C atom to 100%. For this simple molecule this is already a consequence of the fact that its carbon atoms are not hybridized and that the lowest-lying energy state of H–C≡C–H$^+$ has $D_{\infty h}$ point group symmetry like the neutral molecule. This has the following consequences for the values of the parameter ξ_{nl} in equation (1):

orbital 5:	ξ_{nl} to C^+ (100%)
orbital 4:	ξ_{nl} to C (100%)
orbitals 3, 2, 1:	ξ_{nl} to C^+ (50%) and to C (50%)

whereas the H atoms are not affected by the distribution of the ξ_{nl} to C and C^+.

Now we need to determine the weighting factors for the C^+ ion. This was done by fitting a DM cross-section for the process $C^+ + e^- \rightarrow C^{++} + 2e^-$ to measured data [17,18]. This yields the following values for the so-called 'reduced weightings factors' $g_{nl}E_{nl}$ [9]: 16.64 eV for the two $(2s)$-electrons and 10.02 eV for the one $(2p)$-electron. In this derivation we used the atomic radii for the ionic orbitals. All relevant parameters for the cross-section calculation are summarized in Table 3.

4 Results and discussion

Recently, a full set of experimental data has become available for the electron impact ionization of $C_2H_2^+$ by Defrance and coworkers [6]. In these measurements, great care was exercised to separate the contributions attributable to dissociative *excitation* and to dissociative *ionization*, so that the ionization cross-section was determined by summing the SI (simple ionization) and all the DI contributions. Figure 1 shows the comparison between the result of the present calculation and the new experimental data [6].

The numerical values are given in Table 4. As can be seen, the agreement for these two new data sets is quite good over the entire range of electron energies. There appears to be a minor discrepancy in the cross-section shape. The calculated cross-section rises somewhat faster than the measured cross-section, reaches its maximum value at a slightly lower energy, and subsequently declines a little more gradual with increasing impact energy. However, the deviation at any given energy is well within the quoted error margin of the experimental data. The main effect of taking into account the details of the ionization process in terms of the exact location of the missing electron in the

Table 3. Summary of all relevant parameters for the application of our formalism to the calculation of the $C_2H_2^+$ ionization cross-section.

Molecular orbital number	ξ_{nl}	E_{nl}(eV)	g_{nl}	r_{nl}(m)	Atom orbital
5	1	20.92	0.4780	6.44×10^{-11}	$C^+(2p)$
4	2	22.29	1.3460	6.44×10^{-11}	$C(2p)$
3	0.074	27.66	0.7230	6.46×10^{-11}	$C(2s)$
	0.580	27.66	1.0850	6.44×10^{-11}	$C(2p)$
	0.074	27.66	0.6016	6.46×10^{-11}	$C^+(2s)$
	0.580	27.66	0.3622	6.44×10^{-11}	$C^+(2p)$
	0.692	27.66	1.3810	5.29×10^{-11}	$H(1s)$
2	0.310	29.90	0.6688	6.46×10^{-11}	$C(2s)$
	0.370	29.90	1.0030	6.44×10^{-11}	$C(2p)$
	0.316	29.90	0.5565	6.46×10^{-11}	$C^+(2s)$
	0.376	29.90	0.3344	6.44×10^{-11}	$C^+(2p)$
	0.616	29.90	1.2780	5.29×10^{-11}	$H(1s)$
1	0.730	38.97	0.5132	6.46×10^{-11}	$C(2s)$
	0.224	38.97	0.7698	6.44×10^{-11}	$C(2p)$
	0.730	38.97	0.4270	6.46×10^{-11}	$C^+(2s)$
	0.224	38.97	0.2566	6.44×10^{-11}	$C^+(2p)$
	0.096	38.97	0.9800	5.29×10^{-11}	$H(1s)$

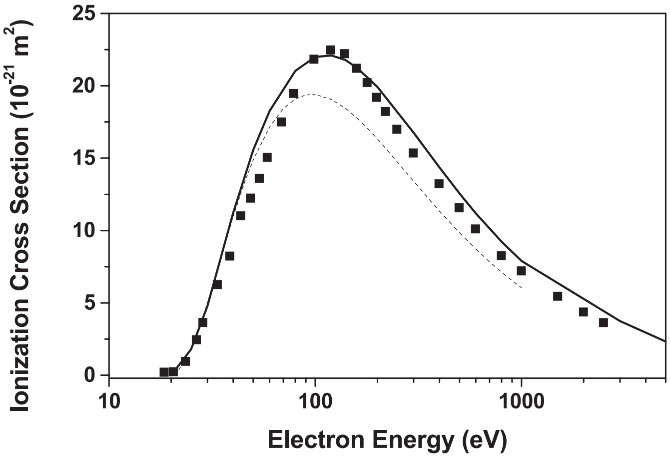

Fig. 1. Calculated absolute cross-section for the electron-impact ionization of $C_2H_2^+$ as a function of electron energy using the present formalism (thick solid line) in comparison with the recently measured cross-section of Defrance and co-workers [6] (solid squares) and the calculated cross-section of Kim et al. [3] (dotted line).

molecular ion and, as a consequence, using 'ionic' rather than 'neutral' weighting factors for the ionic component, is a 20% reduction in the maximum value of our calculated cross-section. The effect of implementing the revised high-energy behavior of the calculated cross-section [1] is by comparison rather minor. We also included in Figure 1 the results of the previous BEB calculation of Kim et al. [3] for reasons of completeness. The three curves shown in Figure 1 represent the current state-of-the-art in terms of the measured and calculated total $C_2H_2^+$ ionization cross-section. The BEB cross-section begins to deviate from our calculated cross-section above about 50 eV and lies below our curve and the experimental data for all energies above about 50 eV. At energies above about 200 eV it appears that the experimental data lie between our curve and the BEB curve, which are separated by about 20%.

Table 4. Absolute calculated cross-section for the ionization of $C_2H_2^+$ as a function of electron energy using the present formalism.

Electron energy (eV)	Ionization cross-section (10^{-20} m^2)
25	0.18
30	0.48
40	1.12
50	1.56
60	1.83
80	2.10
100	2.20
120	2.21
140	2.18
160	2.12
180	2.06
200	1.99
300	1.68
400	1.44
500	1.26
600	1.12
800	0.92
1000	0.79
3000	0.35

5 Conclusions

In this paper, we present the results of the calculation of electron-impact ionization cross-sections of the $C_2H_2^+$ molecular ion using a modified variant of the DM formalism calculation. The choice of $C_2H_2^+$ was motivated by the availability of new and improved experimental data for the electron impact ionization of this molecular ion [6].

Previous calculations disagreed with earlier experimental data [8] as well as among themselves by a factor of 3, because the dissociation of doubly charged molecules could not be taken into account. As shown by a quantum chemical molecular orbital population analysis for both the neutral molecule and the ion, in the case of the acetylene cation $C_2H_2^+$ the electron is removed from a $(2p)$ orbital of carbon and thus is mainly localized near the site of a C atom in the molecule. This information is explicitly incorporated in our formalism. The results obtained by taking the ionic character directly into account are in excellent agreement with the recent experimental data [6].

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