Ab initio study of energy characteristics of small polyatomic molecules in threshold electron-impact dissociative ionization processes

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Synopsis A joint theoretical study of electron-impact dissociative ionization (DI) processes of small polyatomic molecules is presented. Different organic (CH_4 and C_2H_6) and inorganic (SF_6 and S_n, n = 2-8) target molecules were examined. The investigated dissociative ionization processes take place at threshold energies, so our main focus is to study the appearance energies (E_{ap}) of different ion fragments as well as to analyse the corresponding DI reaction pathways.

The appearance energy characterizes that minimal collision energy in a DI process, which is necessary in order to observe the appearance of a concrete ion fragment. While the main ion products in electron impact measurements are usually well-known, it is challenging to measure by spectroscopy the different secondary products, which are mainly consists of neutral fragments. So, if one would like to characterize the complete reaction channels in such DI experiments, one should utilize different high-level *ab initio* methods [1].

In order to obtain the energy characteristics of the reaction products in threshold processes, i.e. the appearance energy (E_{ap}) or the more general ionization energy (I) and electron affinity (E_a), we performed total energy calculations by the GAMESS-US software package [2]. The corresponding molecular energy characteristics are derived from these data simply. They are considered as the reaction enthalpy change, and calculated as the total energy difference of the initial and final products [3]. So the E_{ap} value is valid for particular fragmentation channels.

The systematic theoretical study of the various neutral and ion fragments of CH_4, C_2H_6, SF_6 and S_n target molecules was performed by means of higher level *ab-initio* theories, such as CCSD(T), DFT or MP2. We used large basis sets in the calculations, e.g. aug-cc-pVTZ. The total energies of all molecular species are calculated as the sum of total electronic and zero-point vibrational energies. Some relevant energy characteristics of the observed fragments in a DI processes of ethane molecule are shown in Table 1.

Table 1. Calculated energy characteristics of the neutral and ion fragments of ethane molecule.

Energy char.		Calc.	Exper.
$E_a(C_2H)$		2.91	2.97
$I(C_2H_4)$		10.33	10.52
$I(C_2H_2)$		11.13	11.40
DI reaction channel: $C_2H_6 + e^- \rightarrow$			
E_{ap}	$\rightarrow C_2H_5^+ + H + 2e^-$	12.43	12.45
E_{ap}	$\rightarrow C_2H_3^+ + H_2 + H^- + e^-$	14.52	13.76
E_{ap}	$\rightarrow CH_4^+ + C + H_2 + 2e^-$	20.01	20.40
E_{ap}	$\rightarrow CH_3^+ + CH_3 + 2e^-$	13.54	13.65
E_{ap}	$\rightarrow CH_3^+ + CH_3^- + e^-$	13.64	13.56
E_{ap}	$\rightarrow C_2^+ + 6H + 2e^-$	34.88	31.50

The theoretical values in Table 1 are calculated by CCSD(T)/aug-cc-pVDZ theory [2]. The experimental values are taken from the NIST database [4]. Our results are in a fairly good agreement with these measurements, which indicates the validity of the proposed theoretical approach for the description of electron-impact DI processes. More detailed results will be presented at the conference.

References

[1] Gross J H 2011 *Principles of Ionization and Ion Dissociation in Mass Spectrometry*. Berlin, Springer-Verlag, pp. 21-66
[2] Schmidt M W, Baldridge K K *et al.* 1993 *J.Comp. Chem.* **14** 1347
[3] Demesh S and Remeta E 2015 *Eur. Phys. J. D* **69** 168
[4] https://webbook.nist.gov/chemistry/form-ser/

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