Development of Models for the Calculation of Collision Cross Section

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Abstract: Ion mobility spectrometry (IMS) consists of an analytical technique that can separate gas phase ions based on their size, shape and polarizability [1]. In turn, the mobility can be used to determine the collision cross section (Ω), which is a measure of an ion's conformation in the gas phase. As the number of collisions is dependent on the conformations of an analyte, ions of identical composition with different conformations may be separated by using IMS. When Ω is utilized in conjunction with computational modeling, comparisons between theoretical and experimental data can be used to deduce the gas phase structures of analyte ions. Hence, various simulation methods have been applied to generate low-energy structures for correlating with experimentally determined collision cross section (CCS) [2]. The computational procedure follows the steps: i) calculation of molecular structure in gas phase, ii) application of an approximate method for calculating theoretical Ω by using the projection approximation (PA), the exact hard-sphere scattering approximation (EHSS), or the trajectory method (TM). In the PA approximation, the ion is modeled by a collection of overlapping hard spheres with radii equal to hard sphere collision distances. Differently of the PA approximation, in the EHSS approximation the orientationally-averaged momentum transfer cross section is calculated by determining the scattering angles between the incoming buffer gas atom trajectory and the departing buffer gas atom trajectory. The trajectory method treats the ion as a collection of atoms, each one represented by a 12-6-4 potential. In theory, the experimental drift time should be correlate well with the theoretical cross section. However, many tests carried out by our research group showed that this trend is not always obeyed. This way, the main of this work is to develop models based on the PA, EHSS, and TM method, which is implemented into the MOBCAL code [3], to improve the correlation between structure and theoretical cross section. The database that was used in the development procedure of our models consisted of values of the experimental collision cross sections reported by Campuzano et al [4]. Due to the limited number of compounds, we have decided to include all them as training set. Moreover, at the first moment, the helium was used as the drift gas. The geometry of each considered compound was then optimized with DFT method by using B3LYP/6-311++G(d,p). The atomic charges used in the TM method were the Mulliken charges calculated with the same DFT method. We have decided re-written the Fortran 77 code of MOBAL for the Fortran 90 standard with the intention of allowing further implementations. Consequently, this new code was applied in the parametrization process. For now, we have only considered compounds containing the H, C, O, and N atoms. For the PA and EHSS approximations the atomic radii were treated as parameters; whereas for the parametrization of the model based on the TM method the ε

and σ parameters of the Lennard-Jones potential, regarding to each atom, were treated as adjustable parameter in the development of the model. The results obtained after months of parametrization using the GSA algorithm are shown in the below table. The mean relative percentage errors for the PA, EHSS, and TM method are 1.3%, 2.3%, and 2.3%, respectively, regarding the experimental results. It is worth highlighting that a difference of 1% for a mean relative percentage error suggests that all three models developed by us have satisfactory quality for general purpose.

Table 1. Experimental and theoretical collision cross sections calculated by using the models developed by us.

	Ω_{EXP} ($\mathring{A}^2$)	Ω_{PA} ($\mathring{A}^2$)	Ω_{EHSS} ($\mathring{A}^2$)	Ω_{TM} ($\mathring{A}^2$)
N-ethylaniline	63.0	62.2	60.8	61.3
acetaminophen	67.0	67.0	67.0	67.0
alprenolol	96.9	100.7	104.1	105.3
tetramethylammonium	48.5	47.0	46.0	47.6
tetraethylammonium	65.9	64.5	64.5	65.7
tetrapropylammonium	88.9	87.5	89.2	89.6
tetrapentylammonium	133.5	132.2	136.9	139.2
tetrahexylammonium	154.9	154.9	161.5	162.5
tetraheptylammonium	174.5	178.3	185.6	192.5
naphthalene	59.4	59.9	58.7	59.2
anthracene	73.9	74.0	73.0	73.1
phenanthrene	71.9	73.1	72.4	71.7
pyrene	76.4	76.7	75.8	76.4
triphenylene	83.8	85.5	84.9	84.8
C60	122.6	122.6	122.6	122.6
C70	135.0	134.4	134.7	135.0

Key-words: Ion mobility spectrometry. Collision cross section. Development of models.

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