

Theoretical Study of ion mobility of isomers in different drift gases

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Abstract: A new dimension for ion analysis has been added to Mass Spectrometry, via its coupling with ion mobility spectrometry (IMS), where the separation of isomers occurs while the ions migrate through a drift gas. The use of other gases in place of helium has allowed the separation of isomeric species in a much more efficient way. In this work, we study isomeric systems aiming to understand, from the molecular point of view, the separation in different drift gases [1-2]. The chosen system was the *ortho*, *meta* and *para* isomers of the chlorophenyl piperazine. The collision cross sections were calculated by using three different methods: trajectory method (TM), exact hard-sphere scattering approximation (EHSS) and projection approximation (PA). To take account all configurations of an isomer when it is moving through the gas, we have performed a conformational analysis by varying the angle between the two aromatic rings by 10 degrees in the interval from 0 to 180°. The calculations were performed by using the RM1 semiempirical model and the DFT methodology with B3LYP/6-31G(d,p). Then we had performed the calculation of population distributions seeking to estimate the contribution of cross sections calculated for each conformer. The results showed that the final cross sections (weighted average) obtained for each isomer by RM1 and DFT methodology were very similar. The calculation of the collision cross sections using N₂ or CO₂ as drift gas through the EHSS and PA approximation showed a good agreement with experimental data. According to these data the crescent order of the ionic mobility was: *ortho* > *para* > *meta*. However, when TM method was carried out, we observed an order inversion of the results regarding from the experimental data. In the case of the results for N₂, as gas drift, the order found was: *para* (178.59Å²) > *meta* (177.33Å²) > *ortho* (175.82Å²). The *ortho* compound has a larger theoretical cross section, in contrast with experimental data. When CO₂ was used as drift gas the results found for TM method was: *para* (294.15Å²) > *ortho* (292.83Å²) > *meta* (290.50Å²). These discrepancies can be explained due to ϵ and σ parameters of Lennard-Jones potential, which were not optimized in the TM method for this kind of system.



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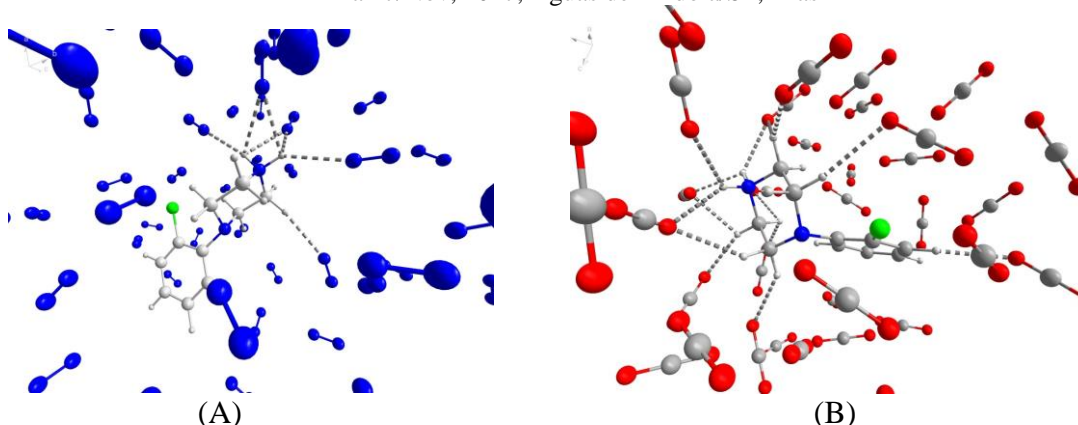


Figure 1. Hydrogen bonds between the ortho - chlorophenyl piperazine isomer with (A) N₂ and (B) CO₂ as drift gas.

To explain why the drift time is longer when CO₂ is used as drift gas, calculations were performed for each isomer. As Figure 1(A) shows, when N₂ was used as a drift gas, the formation of seven hydrogen bonds between the isomer specie and N₂ gas molecules were observed. The Figure 1(B) shows the formation, on average, of 13 hydrogen bonds between the CO₂ molecules and the isomeric species. The larger number of interactions when CO₂ was used as a drift gas explains why experimentally the drift time increases by approximately 1.5 ms when CO₂ is used instead of N₂.

Key-words: Ion Mobility Spectrometry, Isomers, Drift Gas

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