

Supporting Information

for

Isomers and Rotamers of DCM in Methanol and in Gas Phase Probed by Ion Mobility Mass Spectrometry in Combination with High Performance Liquid Chromatography

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Experimentally derived collision cross-section values

The instrument used in the present study, Agilent 6560 Ion Mobility Quadrupole Time-of-Flight (IM-QTOF) mass spectrometer, measures the drift time (t_D) of the ions as recorded by the ion detector. After exiting from the drift cell, the ions have to travel through a certain distance (through the rear ion funnel, quadrupole analyzer, collision cell and flight tube) to reach to the ion detector. Thus, the actual drift time of an ion, i.e., the time it actually spends in the drift cell (t_d), is smaller than the drift time measured by the ion detector (t_D). The CCS value (Ω) of a particular ion is derived by putting the corrected drift time (t_d) value in the following equation,¹

$$\Omega^{(avg)} = \frac{3q}{16N} \sqrt{\frac{2\pi}{\mu k_B T}} \frac{t_d V}{L^2} \left(\frac{760}{P} \right) \left(\frac{T}{273} \right) \text{-----} (1)$$

Where q is the charge of the ion, N is the number density of the buffer gas, k_B is the Boltzmann gas constant and μ is the reduced mass of the colliding ion-neutral pair (with respective masses of m and M). The parameters T , P , L and V represent the effective temperature, pressure, length and applied voltage of the drift gas cell, respectively.

Now, the corrected drift time (t_d) can be obtained as,

$$t_d = t_D - t_0 \quad (2)$$

where t_0 corresponds to the time taken by an ion to travel the distance between the exit of the drift tube and detector. For the present study, the time t_0 has been considered as composed of two components, a fixed delay time (t_{fix}) and a mobility dependent drift time outside the drift cell ($t_{d(out)}$).¹ Thus, t_0 can be written as,

$$t_0 = t_{fix} + t_{d(out)} \quad (3)$$

According to equ (1), any type of mobility dependent drift time depends on some instrumental and experimental parameters (gas pressure, electric field and geometry of the drift cell and other ion optics) which can be expressed by an instrument dependent proportionality coefficient and it is considered as β_1 in case of $t_{d(out)}$. Thus, $t_{d(out)}$ can be considered to be equivalent to $\beta_1\gamma\Omega$, where γ is the modified reduced mass related coefficient given by,

$$\gamma = \frac{1}{q} \sqrt{\frac{m}{m+M}} \quad (4)$$

Similarly, the corrected drift time (t_d) can be considered as the mobility dependent drift time inside the drift cell and it can be expressed as $\beta_2\gamma\Omega$ (β_2 is also an instrument dependent proportionality coefficient that depends on gas pressure, electric field and geometry of the drift cell only)

Thus, equ (2) can be written as,

$$\begin{aligned} t_D &= t_{fix} + \beta_1\gamma\Omega + \beta_2\gamma\Omega \\ &= t_{fix} + (\beta_1 + \beta_2)\gamma\Omega \\ t_D &= t_{fix} + \beta\gamma\Omega \quad (5) \end{aligned}$$

In our experimental arrangement, a calibrant solution, 'Agilent tune mix' (containing compounds within the mass range of m/z 122 to 1522), was run at the same experimental

conditions as the sample, either prior to the sample run or after that. The CCS values of the calibrant ions are known for a particular drift gas under the same instrumental conditions as the sample. Therefore, the plot of t_D vs. $\gamma\Omega$ for these calibrant ions provides t_{fix} and β as the intercept and slope values, respectively. These values were then used to calculate the corrected drift time (t_d) of the sample ion. Then the t_d value was used to calculate the CCS value of the sample ion according to equ (1). The CCS calculation procedure was executed by using the *IM-MS Browser Software*, version *B.07.01*, supplied by Agilent.

Theoretical calculation of collision cross-section values

To calculate the CCS (Ω_c) values of the ions, the trajectory method was originally developed by Jarrold and co-workers² considering interaction of the ions with the drift gas He. In this method, the interaction potential was considered to be the sum of the Lennard-Jones 12-6 potential (short-range van der Waals interactions) and the ion induced-dipole interaction (long-range attractive interaction). Later on, this method was modified in order to calculate the CCS values for the use of N₂ drift gas and in the present study, we have used the method described by Kim and co-workers.³⁻⁵ Particularly, in the expression of Lennard-Jones 12-6 potential, the value of the polarizability (α) of the neutral drift gas was set as 1.710×10^{-24} cm², i.e., the experimentally determined value of the polarizability of N₂ gas.⁶ In order to take into account of the non-spherical geometry (linear geometry) of N₂, two additional terms were incorporated in the interaction potential. One of these terms represents the ion-quadrupole interaction, whereby the quadrupole moment of N₂, $(-4.65 \pm 0.08) \times 10^{-40}$ C cm²,⁷ is expressed as summations of partial charges on the two nitrogen atoms (negative charge 0.4825e on each atom) and one positive ($2 \times 0.4825e$) charge at the center of the nitrogen molecule. The other term takes into account of the orientation of the linear N₂ molecule

during the ion-neutral collision process. In this case, all possible orientations of the colliding N₂ molecule were considered in the three-dimensional rotational space and the orientation averaged interaction potential was calculated using Boltzmann weighting.

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