

Simulation of Ion Mobility and Diffusion of Sodium Ions based on Revised Ion-Molecule Collision Models

Dimitris Papanastasiou¹; Alexander Lekkas¹; Emmanuel Raptakis¹; Mikhail Sudakov²;
¹Fasmatech, Athens, GREECE; ²Ryazan State Radioengineering University, Ryazan, RUSSIA

INTRODUCTION

In Ion Mobility Spectrometry (IMS) and Differential Mobility Spectrometry (DMS) separation depends on mobility variations with electric field and pressure. The non-linear dependence of the ion mobility on E/N is partly attributed to the nature of ion-molecule interactions defined to a first approximation by the interaction potential. A revised collision model has been developed¹ where high-order polynomials used to describe complex variations of cross section dependence on relative velocity of collision partners are employed to reflect interaction potentials. In this work experimental data of sodium ion mobility as a function of electric field at fixed pressure are used to determine the cross section dependence curve. Further tests explore the extent of ion diffusion at different field conditions and simulated results are compared to experimentally determined diffusion coefficients.

METHODS

Ion trajectory computations are performed in AXSIM². The procedure involves the calculation of reduced ion mobility for sodium using the average drift velocity of large ion populations accelerated in methane gas obtained by simulation. Coefficients of higher-order polynomials used to describe the dependence of sodium cross section on relative velocity of the collision partners are adjusted in order for the simulated ion mobility to match experimental data. Once the ion mobility curve is reproduced and the cross section is determined, large populations of sodium ions are accelerated at different electric field strengths and diffusion coefficients are determined and contrasted against experimental results. The additional step of calculating diffusional effects in this work is used to further validate the accuracy of the collision model. Hard sphere and Langevin collision models are also employed to highlight discrepancies observed between the different approaches. The cross section $Q(V_R)$ appears in the calculation of the collision probability $dP = Q(V_R) V_R dt dN$. The dependence of Q on the relative velocity of the collision partners V_R can take several forms. For hard sphere collisions the cross section is constant $Q(V_R)=c_0$ and ions exhibit a constant mean free path, independent of ion velocity. In the Langevin collision model the cross section is inversely proportional to the relative velocity, $Q(V_R) = c_1/V_R$ and in this case it is the collision frequency which becomes independent of ion velocity. The revised collision model is capable of accepting complex cross section curves described using polynomial expressions. For the sodium-methane system this dependence is determined using an expression of the form: $Q(V_R)=c_0 + c_1/V_R + c_2/u_R^{1/2} + c_3/u_R^{1/4}$

RESULTS

Experimental data of ion mobility and longitudinal diffusion coefficients for the sodium-methane ion-molecule system investigated are available up to 500 Td at 0.5 Torr³. The cross section dependence on the relative velocity of collision partners is adjusted based on a trial and error procedure in order to reproduce ion mobility values determined experimentally over an extended range of electric field intensities. The cross sections employed in hard-sphere and Langevin collision models and the corresponding ion mobility curves, including the cross section dependence tailored to match experimental data using simulations are shown in Figures 1 and 2 respectively.

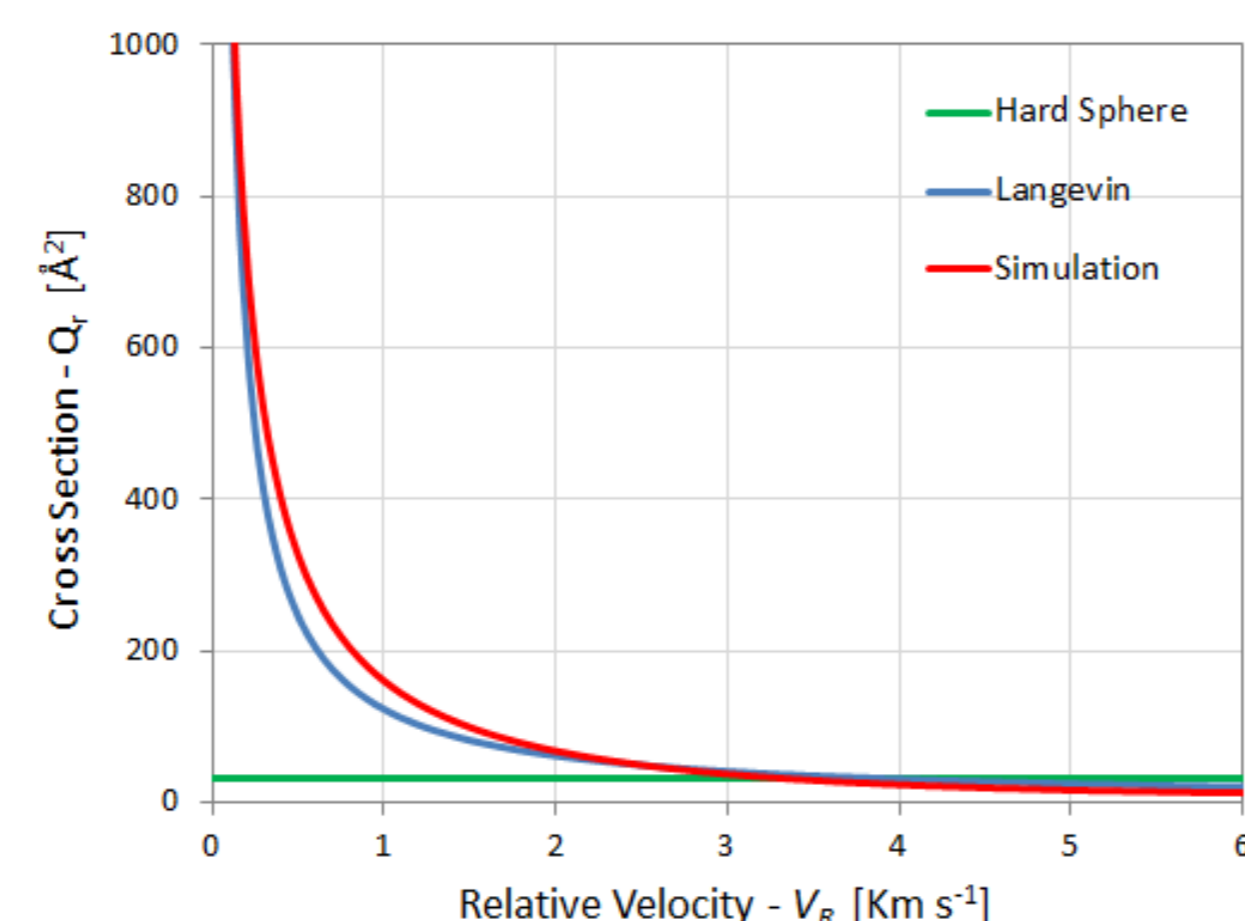


FIGURE 1. Collision cross section as a function of relative velocity for Langevin and hard sphere collision models. The extrapolated cross section used in the simulation to reproduce ion mobility values determined experimentally is also shown.

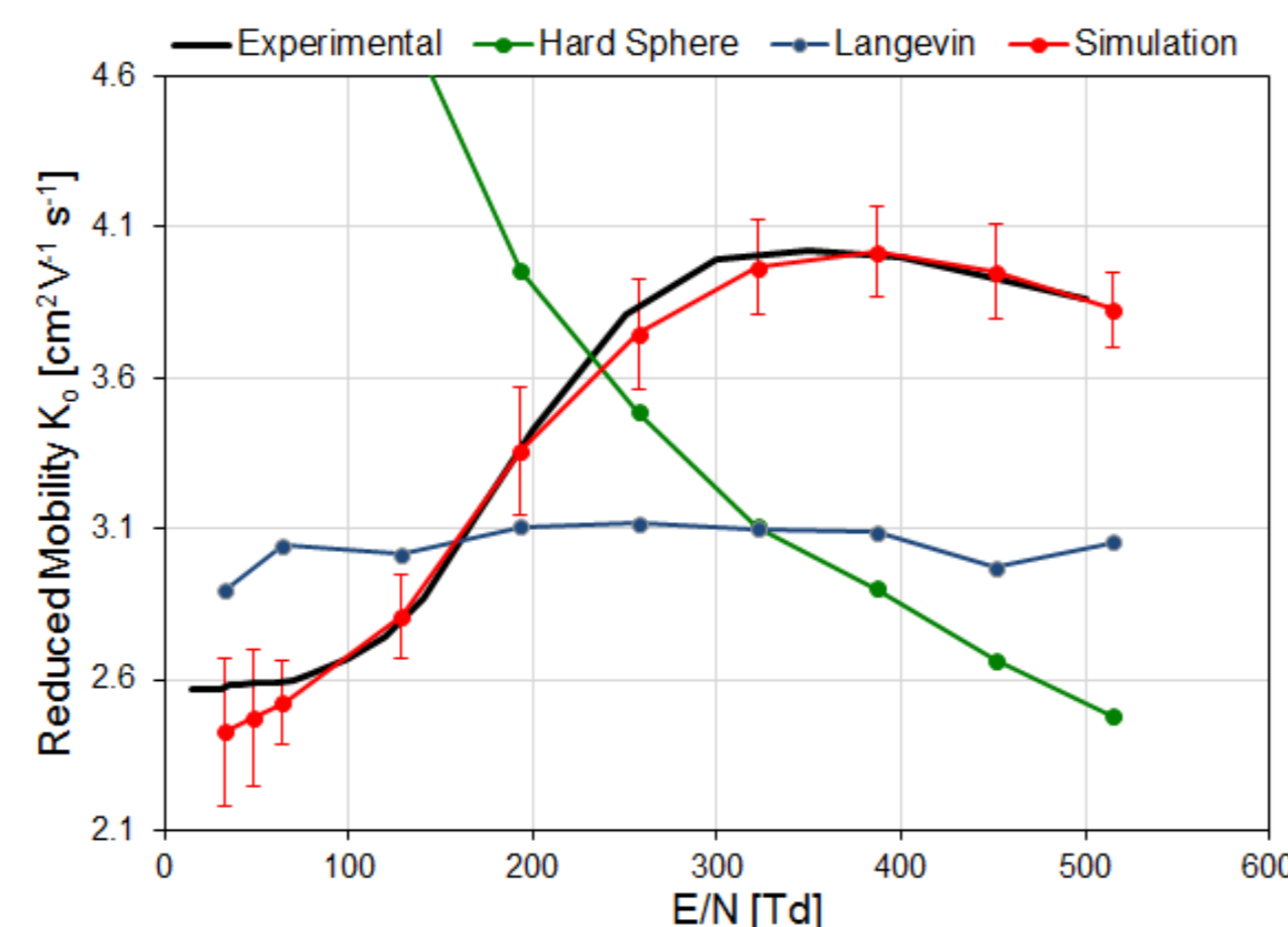


FIGURE 2. Reduced ion mobility for Na⁺ in CH₄ at 0.5 Torr determined experimentally and simulated ion mobility dependence using the tailored cross section shown in Figure 1. Results for the hard sphere and Langevin collision models are also shown.

Simulations for the determination of the longitudinal diffusion coefficient over a wide range of electric field intensities are carried out using the cross section determined using ion mobility simulations and results are shown in Figures 3 and 4. These are compared with longitudinal diffusion coefficients determined experimentally³ and the analytical expression used to determine the spatial distribution of ions, which reflects the extent of diffusion as a function of time. The number density of ions at the low field limit is given by⁴ :

$$n = \frac{S}{\sqrt{4\pi Dt}} e^{-x^2/4Dt}$$

where S is the number of ions, D is the diffusion coefficient (longitudinal or lateral) measured in m²s⁻¹, and x is the direction ions spread over time t . The assumption is that the number of ions S is small so that gas pressure remains unchanged and also that space charge effects are negligible.

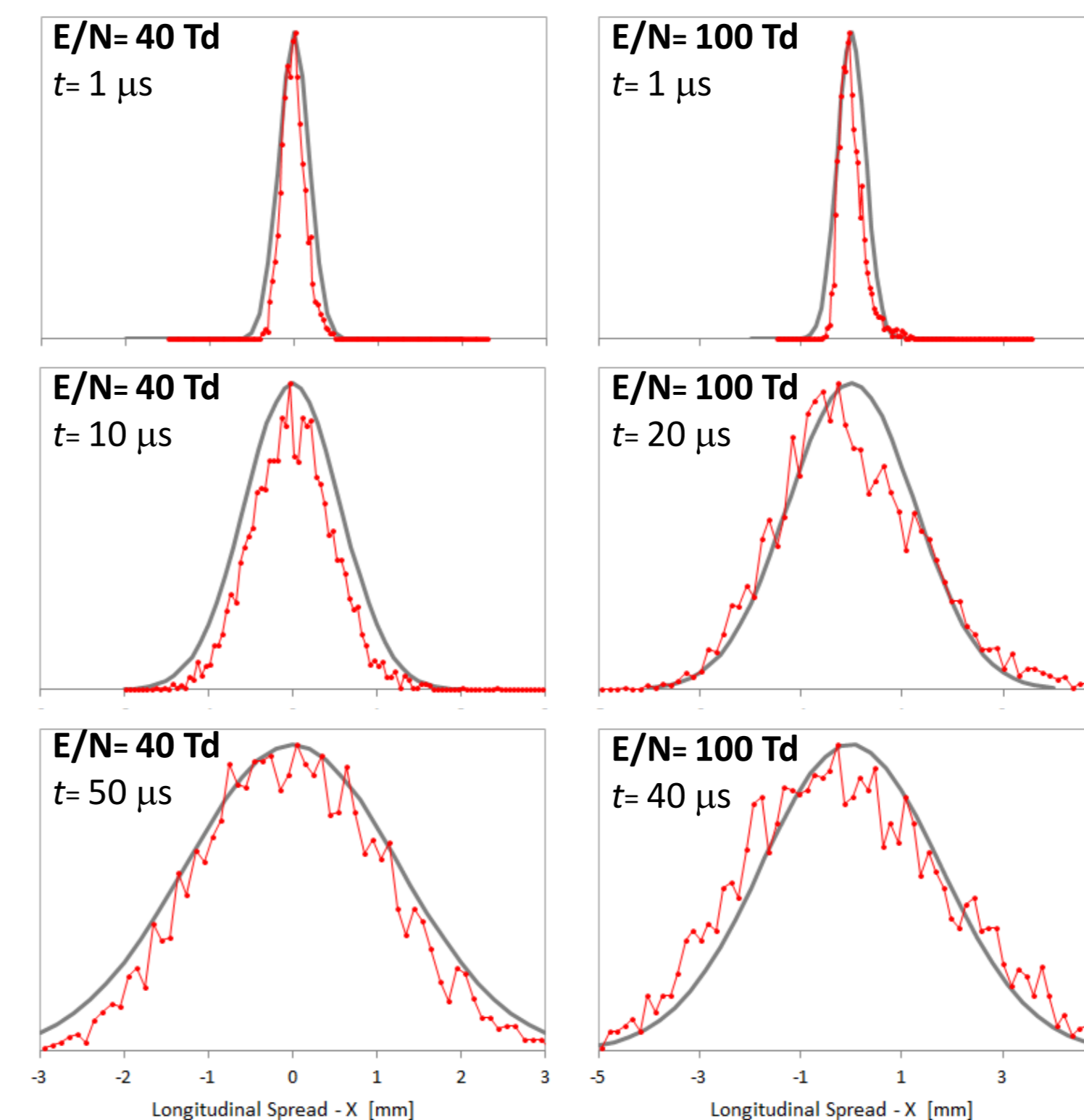


FIGURE 3. Simulated longitudinal spatial distribution of Na⁺ at 40 Td and 100 Td recorded as a progression of time. Distributions obtained using the analytical expression and experimentally determined diffusion coefficients are also shown.

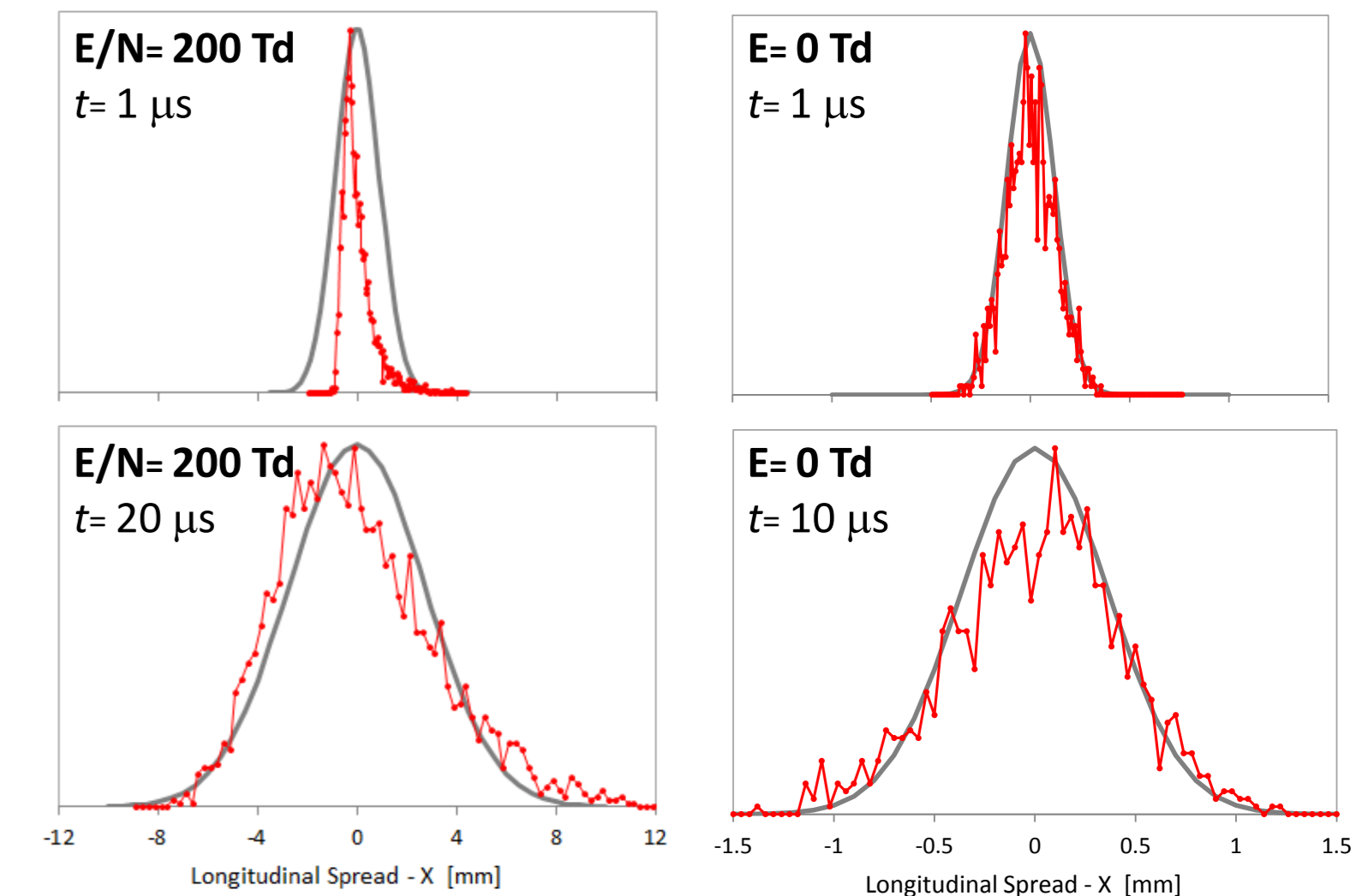


FIGURE 4. Simulated longitudinal spatial distribution of Na⁺ at 200 Td and in the absence of an electric field. Distributions obtained using the analytical expression and experimentally determined diffusion coefficients are also shown.

Diffusion of Na⁺ for the Langevin model matched experimental curves with high accuracy up to 100 Td and underestimated the longitudinal spread for the greater electric field intensities. Hard sphere collisions overestimated diffusion at low values of E/N while diffusion was underestimated at high E/N. A better fit is obtained throughout the range of E/N values examined in this work using the revised cross section determined based on ion mobility experimental data.

CONCLUSIONS

A revised collision model is proposed where the probability of a collision to occur is determined by higher order polynomials. The cross section dependence of the ions on the relative velocity of the collision partners is determined by matching the simulated ion mobility to experimental data. Simulation results in the absence of an external electric field and over a wide range of E/N values is performed to further validate the approach. It is shown that extrapolation of the higher-order cross section curves based on experimental ion mobility data allows also for diffusional effects to be predicted with sufficient accuracy.

REFERENCES

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