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A convenient method for calculation of ionic diffusion coefficients for accurate selected ion flow tube mass spectrometry, SIFT-MS

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Abstract

A method to calculate diffusion coefficients of ions important for the selected ion flow tube mass spectrometry, SIFT-MS, is presented. The ions, on which this method is demonstrated, include the SIFT-MS precursors $H_3O^+(H_2O)_{0,1,2,3}$, $NO\cdot^+(H_2O)_{0,1,2}$ and $O_2^{\bullet+}$ and the product ions relevant to analysis of breath trace metabolites ammonia ($NH_3^{\bullet+}(H_2O)_{0,1,2}$, $NH_4^+(H_2O)_{0,1,2}$), acetaldehyde ($C_2H_4OH^+(H_2O)_{0,1,2}$), acetone (CH_3CO^+, $(CH_3)_2CO^{\bullet+}$, $(CH_3)_2COH^+(H_2O)_{0,1}$, $(CH_3)_2CO\cdot NO^+$), ethanol ($C_2H_5OHH^+(H_2O)_{0,1,2}$) and isoprene ($C_5H_7^+$, $C_5H_8^{\bullet+}$, $C_5H_9^+$). Theoretical model of the (12, 4) potential for interaction between the ions and the helium atoms is used, with the repulsive part approximated by the mean hard-sphere cross section and the attractive part describing ion-induced dipole interactions. The reduced zero-field mobilities at 300 K are calculated using the Viehland and Mason theory [L.A. Viehland, S.L. Lin, E.A. Mason, At. Data Nucl. Data Tables, 60 (1995) 37–95], parameterised by a simple formula as a function of the mean hard-sphere cross section, and converted to diffusion coefficients using the Einstein relation. The method is tested on a set of experimental data for simple ions and cluster ions.

Keywords: Mobility; Diffusion; SIFT-MS; Ion geometry; Interaction potential

1. Introduction

Diffusion of ions through gases is a well-understood transport process closely related to the drift of ions through a gas in the presence of an electric field, which is characterized by the ionic mobility [1]. Recently, an accurate knowledge of diffusion coefficients for polyatomic and cluster ions has become important in the field of selected ion flow tube mass spectrometry, SIFT-MS [2,3]. Here, radial diffusion through inert helium carrier gas is the dominant loss process of ions in the analytical flow tube and the accuracy of the analysis [4] is directly influenced by the difference between the diffusion coefficients of the precursor (reagent) ions and the product ions characteristic of compounds present in trace amounts in the analysed air, liquid headspace or breath.

One of the most important applications of SIFT-MS is the trace gas analysis of exhaled breath that is currently attracting a great deal of attention because of its potential for the non-invasive study of metabolic processes and for clinical diagnosis and therapeutic monitoring [5]. Characteristic compounds are present in breath at concentrations typically near and below a part-per-million [2,3]. There is a considerable amount of data available on the mobilities of ions in various buffer gases [6–8], but these data do not include most of the ions of interest relating to SIFT-MS breath analysis [9]. The product ions involved in breath analysis range from small radical cations like NH_3^+ to large cluster ions like $C_2H_5OHH^+(H_2O)_2$ and their diffusion coefficients are generally different than those of the precursor ions. Therefore, differential diffusion occurs, which influences the magnitudes of the precursor and product ion signals. So it is important that the values of their diffusion coefficients are calculated consistently so that systematic errors are not amplified by the

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subtraction of two similar values. Thus, there is a need for a straightforward and reliable method to calculate diffusion coefficients for characteristic SIFT-MS product ions in the helium carrier gas.

Diffusion coefficients of ions are related to their near-zero-field mobilities via the Einstein relation [1]. The actual value of the near-zero-field mobility for a given ion drifting through a buffer gas is entirely dependent on the form of the interaction potential between the ion and the atoms of the buffer gas. The problem of calculating the value of mobility from the interaction potential becomes mathematically accessible when the interaction potential can be treated as spherically symmetrical, in other words when the interaction energy of the ion and the buffer gas atom depends only on their distance and not on the angular configuration. The first rigorous ion mobility kinetic theory for such a case was developed by Viehland and Mason [10], providing a very good theoretical approximation based on the concept the momentum-transfer collision integral. For practical applications of this theory the values of these collision integrals were tabulated for the (n, 6, 4) model of ion–neutral atom interactions as functions of the effective ion temperature [10,11]. Thus, it is possible to build upon this reliable and often verified Viehland and Mason theory, as long as the actual interaction potential can be reasonably approximated by the spherically symmetrical model. This approach was first used for carbon cluster ions, C_x^+, for x up to 84, by von Helden et al. [12], by effectively approximating the interaction potential by a rectangular repulsive wall in the so-called hard-sphere model. The radius of the hard-sphere barrier was estimated by Monte-Carlo calculations of the average geometrical cross sections over numerous angular orientations of the cluster ions, in which the sizes of the individual atoms of the cluster ions were taken as their van der Waals radii [12].

This approach was further refined by de Gouw and coworkers [13,14] using the (12, 4) model potential, see Eq. (1) later, which is much more realistic than the rectangular wall for medium-sized organic ions and cluster ions. The parameters of this interaction potential were determined from the polarisabilty of the neutral N_2 molecules in the cluster ion describing the attractive induced-dipole interaction, and from the hard-sphere cross section determining the radius of the repulsive barrier for collisions with mean thermal kinetic energy. This theory was very successful in explaining the observed trends in experimentally determined mobilities of cluster ions (including the hydrated hydronium ions $H_3O^+(H_2O)_{1,2,3}$) drifting in helium and nitrogen buffer gases.

The main objective of the present study was to use the Viehland and Mason theory combined with the de Gouw et al. approach to estimate the parameters of the (12, 4) interaction potential to calculate the ion mobilities and diffusion coefficients of about 50 ions in helium, including several important for breath analysis using SIFT-MS, those few specific cluster ions for which experimental mobility values are available and for two negative ions that are of current interest in electron attachment research [15]. To test the validity of the method of calculation we also reproduce the mobility calculations for the ions included in the original paper by de Gouw et al. [13]. An early report on our work on diffusion calculations relevant to SIFT-MS was presented at a small international conference [16] and caused some interest amongst researchers using SIFT-MS and related flow tube techniques to quantitative trace gas analysis.

2. Method of calculation

The calculation is carried out in several steps: first the geometry of the molecular ion is determined, then the mean geometrical cross section for hard-sphere collisions is calculated, and finally mobility and diffusion coefficient are obtained from the approximate interaction potential parameterised using this hard-sphere cross section. Details of these calculation steps are given below.

2.1. Determination of ion geometries

We have used the *PC Spartan Pro* molecular modelling application (Wavefunction, Inc, Irvine, CA) to calculate the cluster ion geometries by the semi-empirical PM3 and the ab initio methods MP2/6-31G** and MP2/6-311+G**. The semi-empirical PM3 method was used to quickly calculate geometries of the precursor and product ions including the hydrates (calculations took 1–20 min on a 2.5 GHz Intel Celeron CPU). Ab initio methods using the Spartan program were used to validate the accuracy of the geometry calculations for H_3O^+ and its hydrates (using about 1–5 h CPU time). Cross section calculation using these ab initio geometries reproduced the cross sections calculated using the semi-empirical PM3 geometries to better than 0.7% accuracy. Thus, we decided to consistently use the Spartan PM3 semi-empirical method in order to obtain a uniform set of numerical data for all the ion geometries involved in this study. We have also used Gaussian 98 [17] to demonstrate that even when using more advanced B3LYP and MP3 levels of theory, the cross sections do not differ by more than 1% from our quick semi-empirical calculations. Thus, the choice of the actual theory behind the construction of the molecular model and calculation of the ion geometry is not critical with respect to the diffusion coefficients, and any molecular modelling application can be used, as long as the data are exportable to a set of Cartesian coordinates of the atoms. Note that our application [18] can open Spartan and Gaussian output files directly.

2.2. Calculation of the mean geometrical hard-sphere collision cross section

The hard-sphere cross section is determined numerically by projecting the molecular model onto a plane. The cross section is then calculated as the integrated area of the coordinates of the incoming carrier gas atoms perpendicularly to the