

Effect of Carrier Gas Nature on Collision-Induced Dissociation of Large Molecular Ions in Mass-Selective Detector with Atmospheric Pressure Chemical Ionization

A.S. Kudryavtsev¹, A.L. Makas¹, A.K. Rebrov², P.A. Skovorodko², M.L. Troshkov¹

¹*Design-Technological Institute of Instrument Engineering for Geophysics and Ecology, Siberian Branch of Russian Acad. Sci., 3/6, Acad. Koptug Ave., 630090 Novosibirsk, Russia*

²*Institute of Thermophysics, Siberian Branch of Russian Acad. Sci., 1, Acad. Lavrentyev Ave., 630090 Novosibirsk, Russia*

Abstract. To clarify the operating mechanism of mass-selective detector with atmospheric pressure chemical ionization a model of collision-induced dissociation of large molecular ions based on test particle Monte Carlo method is developed. The model was found to provide a good description of experimental dissociation curves including the effect of carrier gas nature.

Keywords: Mass-selective detector; collision-induced dissociation; Monte Carlo simulation; carrier gas nature;

PACS: 47.45.-n; 52.65.Pp; 82.20.-w; 82.80.Ms

INTRODUCTION

The atmospheric pressure chemical ionization (APCI) is one of the promising ion sources techniques in mass spectrometry (MS) [1]. Classical design of APCI interface has a two-stage differentially pumped system consisting of ionization region at atmospheric pressure, intermediate pressure region (IPR) at pressures about 1÷10 torr, and mass analyzer region [2, 3]. An electric field is applied in IPR to achieve collision-induced dissociation (CID) of the ions. Due to the complex character of ion-molecular processes determining the performances of APCI MS detector the optimization of such devices till now was performed mainly empirically. In our previous paper [4] the model of collision-induced dissociation of large polyatomic ions seeded in carrier gas flow in the presence of electric field was developed on the basis of linear Boltzmann equation solution by test particle Monte Carlo method. In spite of its simplicity and approximate nature the developed model was found to provide a good description of experimental results concerning dissociation of organophosphorus compounds when air was used as carrier gas [4]. In this paper the developed model is tested to describe the effect of carrier gas nature on the process.

EXPERIMENT

The experiments were carried out using APCI MS described in [5]. It has a two-stage differentially pumping system consisting of IPR pumped by a rotary pump and a mass analyzer region pumped by a high vacuum turbomolecular pump.

The ions were produced by using corona discharge in positive mode. Both the carrier gas and generated ions are flowing through the nozzle into IPR. The voltage U_{N-SK} is applied between the diaphragm with nozzle and the skimmer. Under the effect of the electric field the ions start to drift with respect to the gas flow and their internal energy may increase due to the collisions with carrier gas molecules. The ions dissociate on neutral and charged products when its internal energy exceeds a certain threshold value. This process is named a collision-induced

dissociation [2]. Some of the ions may enter the mass analyzer region through the skimmer orifice. Finally, the ions enter the mass analyzer through the orifice of diaphragm, which is grounded.

The experiments were performed for three organophosphorus compounds: dimethyl methylphosphonate (DMMP), diisopropyl methylphosphonate (DIMP) and tributylphosphate (TBP) with molecular masses 124, 180 and 266 a.m.u., respectively. The purified laboratory air and argon were used as carrier gases.

In the experimental study of CID processes the main results were the dissociation curves: the dependence of molecular ion and its fragments intensities versus potential difference U_{N-SK} .

At fixed corona discharge current and voltage U_{N-SK} the mass spectrum of compounds was recorded. By comparing it with the background mass spectrum, the fragments ions intensity was obtained, the procedure being repeated for all values of voltage U_{N-SK} . The dissociation curves were normalized on the total current of molecular ion and its fragments, because the transmission through the skimmer depends on the mass of ion and the voltage U_{N-SK} . Typical values of experimental parameters were as follows: $I_{C.D.} = 0.04 \mu A$, $U_{N-SK} = 10 \div 210 V$.

The experimental dissociation curves of TBP in air are shown by symbols in Fig. 1. Based on the analysis of the data available in literature [6, 7] the chemical structure of the fragments was recognized. These structures are also shown in Fig. 1.

The analysis of presented dissociation curves allows one to suppose that the collision-induced dissociation of TBP in air is of sequential character, which will be used while developing the corresponding model.

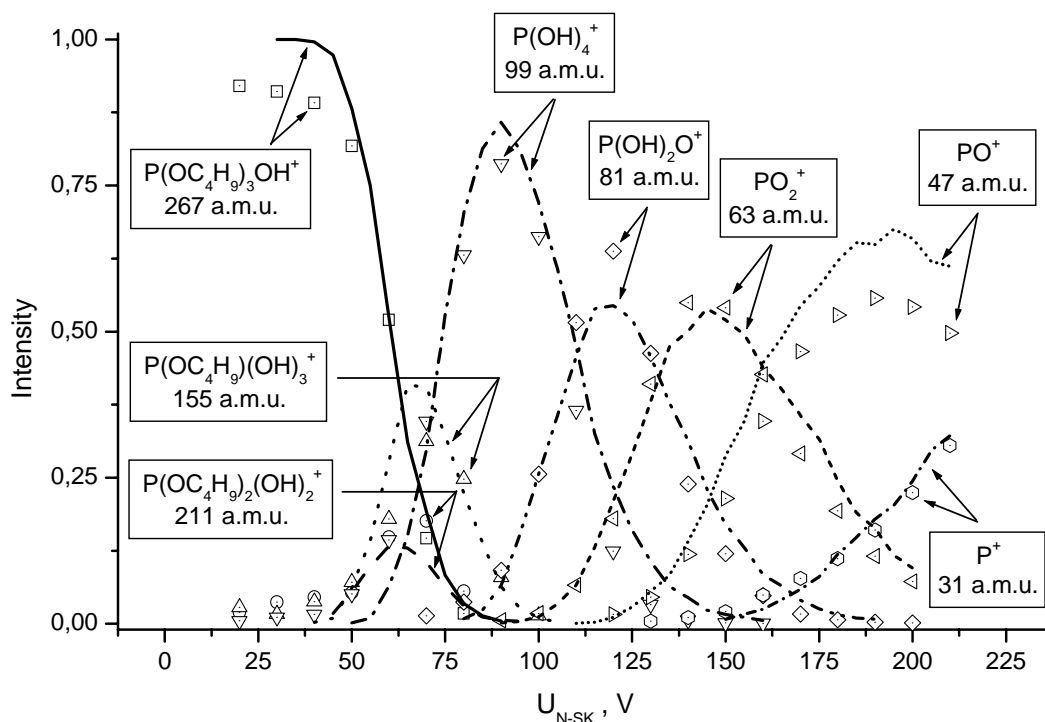


FIGURE 1. Experimental and Modeling Dissociation Curves of TBP in Air.

MODEL

In accordance with the recent concepts about the nature of collision-induced dissociation the phenomenon is caused by excitation of internal degrees of freedom of polyatomic ions due to their acceleration in the electric field and further transformation of translational energy into internal one at the collisions of ions with neutral molecules [2]. At some level of internal energy the ion may break into two or more fragments. The model of CID should take into account these peculiarities of the phenomenon and hence should be based on the Boltzmann equation.

An effective tool for solving the linear Boltzmann equation (neglecting the effect of the ions on the main flow due to small ions concentration under typical experimental conditions) is test particle Monte Carlo method [8]. To apply this method the molecular model of collision of ion with neutral molecule as well as the distribution of gas dynamic parameters of the main flow and the distribution of the electric field should be specified.

The representative set of the fragments under sequential dissociation of initial molecular ion was chosen based on the experimental results. In our previous paper [4] two molecular models determining the local mean free path of probe ion as well as the velocity components of neutral gas molecule – partner for collision were tested: solid spheres (SS) and Maxwell molecules (MM) models. From the comparison between experimental and numerical results it was concluded, that the real potential should have a core [9] restricting the mean free path of high-speed ion. The simplest model of potential with a core is the model of solid spheres. For SS molecular model to close the problem for each of the considered fragments four parameters should be specified: the cross-section σ , the number of internal degrees of freedom j , the portion of inelastic collisions $1/Z$ and the threshold energy E_t , determining the moment of transition of a given fragment into a further one if its internal energy exceeds this value. The evolution of internal energy of the fragment along the trajectory was described in the frames of the known Larsen-Borgnakke model [10]. From the above listed four parameters the values of j and σ were estimated on the basis of the chemical structure of the fragments and the available data on mobility of similar ions [9], the parameter Z was fixed at minimum level $Z = 1$, thus considering all the collisions as inelastic [4] while the value of threshold energy E_t was considered as fitting ones [4].

The distribution of gas dynamic parameters of the underexpanded free jet flow of air and argon under experimental conditions was obtained by numerical solution of the full set of Navier-Stokes equations by recently developed original algorithm [11]. The algorithm is based on the staggered grid and is characterized by low implicit artificial viscosity. The simulation was made for the whole flow field including the subsonic part of the nozzle representing the capillary of 0.08 mm in diameter and 0.2 mm in length. The discharge coefficient of the nozzle in the considered case ($p_0 = 760$ torr, $T_0 = T_\infty = 345$ K) is 0.78 for air flow and 0.765 for argon flow. The pressure in the flooded space p_∞ determined by volume flow rate of carrier gas and pumping speed of rotary pump was 5.5 torr for air flow and 4.87 torr for argon flow. The disturbances of the flow field caused by the presence of skimmer were not taken into account.

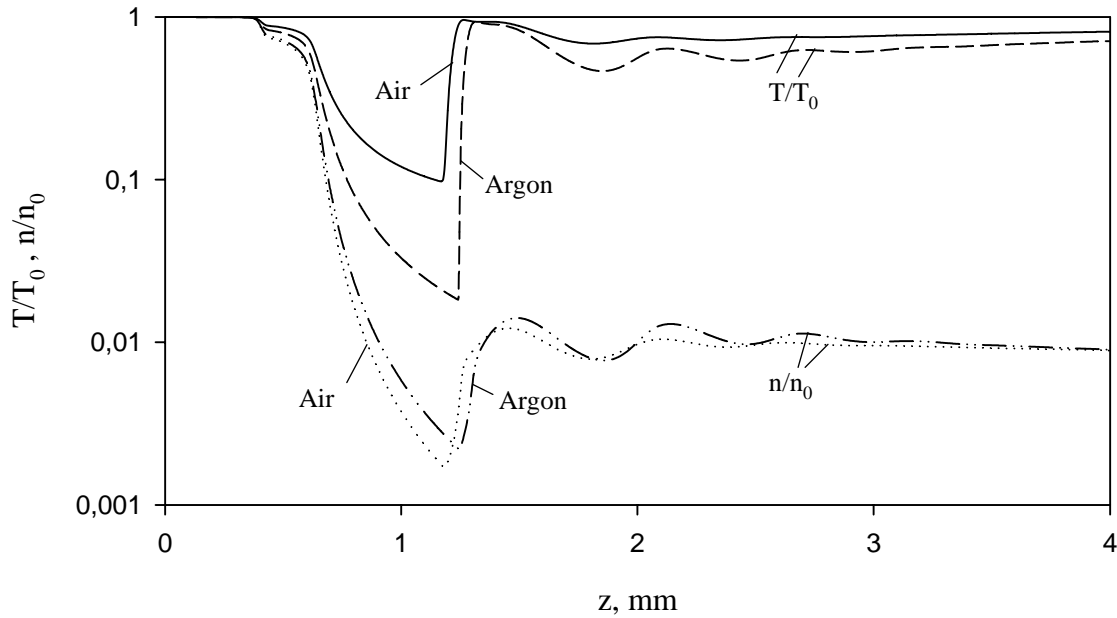


FIGURE 2. Axial Distributions of Density and Temperature in Underexpanded Free Jet of Air and Argon.

Fig. 2 illustrates the axial distributions of density n/n_0 and temperature T/T_0 (both for air and argon) normalized by corresponding values in the stagnation chamber, which reveal the behaviour typical of the flow in

underexpanded free jet with multicycle structure. The axial coordinate in Fig. 2 is accounted from the beginning of the domain placed 0.6 mm upstream the nozzle exit, the skimmer orifice being placed at $z = 3.6$ mm. In the skimmer vicinity the pressure is equal to pressure in the flooded space p_∞ with high accuracy, while the flow is transonic.

The procedure of obtaining the distributions of electric field necessary for simulation of motion of probe ions in the intermediate pressure region (between the nozzle and the skimmer) and in the mass analyzer region (between the skimmer and the inlet diaphragm of monopole mass analyzer) was described in Ref. 4.

The injection of initial molecular ion in the domain of simulation was performed from the nozzle exit assuming that the concentration of ions does not depend on radius and the translational and internal degrees of freedom of ion are in equilibrium with carrier gas. The position of point where the ion should collide with carrier gas molecule was determined through the relation $\int dl/\lambda(l) = -\ln(R)$, where $\lambda(l)$ - local mean free path of probe ion, R - random number uniformly distributed on the interval (0, 1), with the integration being performed along the trajectory of the ion. It should be noted that due to the effect of electric field the trajectory of free motion of the ion is not a straight line. Further details concerning the simulation procedure can be found in Ref. 4.

For each value of potential difference U_{N-SK} the evolution of sufficiently large number of probe ions (usually 10000) was traced. The normalization of the number of ions of each type reaching the diaphragm orifice by their sum allows one to obtain the theoretical dissociation curves, which were compared with experimental ones.

RESULTS AND DISCUSSION

We will illustrate here only the results obtained for TBP, the peculiarities of CID of DIMP and DMMP are similar to those typical of TBP.

The fitted values of parameter E_t for fragments of dissociation of TBP in air as well as parameters σ and j (the chemical formulas of fragments and their molecular masses are shown in Fig. 1) were reported in Ref. [4]. The parameter j was determined as $j = 3N - 3$, where N is the number of atoms in the fragment. The air was treated as a simple gas with molecular mass 28.96 a. m. u. and 2 internal degrees of freedom. The parameter E_t for each fragment was fitted from the condition that the predicted position of maximum of corresponding dissociation curve was the same as in the experiment.

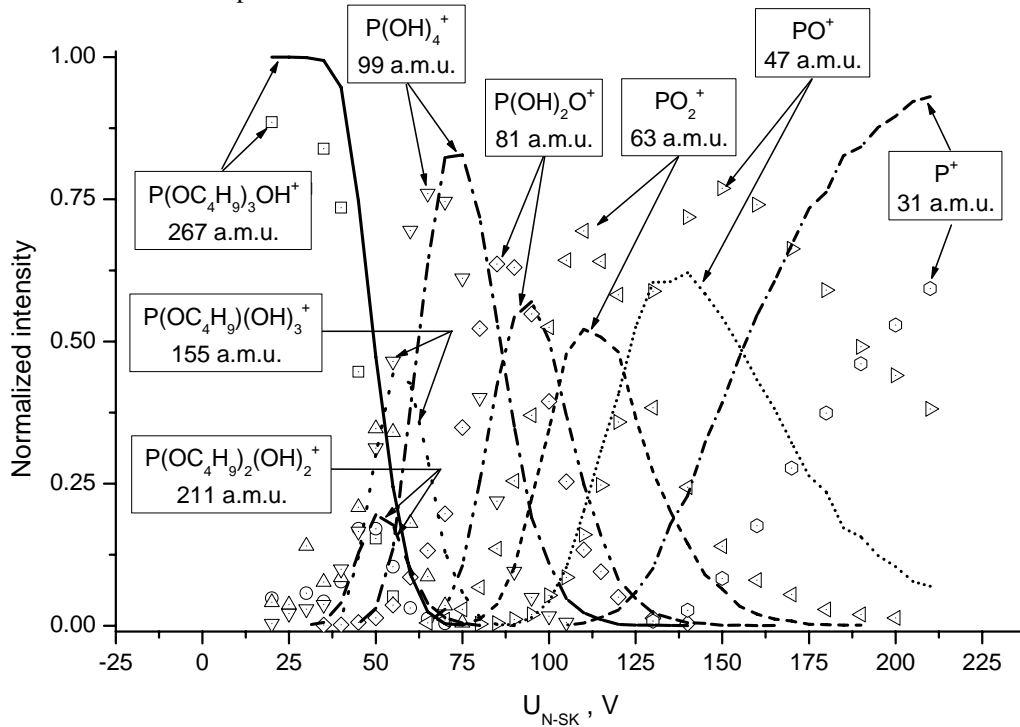


FIGURE 3. Experimental and Modeling Dissociation Curves of TBP in Argon.

The calculations show that the dissociation of ions takes place in relatively small vicinity of skimmer inlet orifice that is connected with gas dynamic and electric fields distributions. The typical axial dimension of dissociation region depends on potential difference U_{N-SK} and is ~ 0.2 mm for $U_{N-SK} = 90$ V, ~ 0.3 mm for $U_{N-SK} = 120$ V and ~ 0.8 mm for $U_{N-SK} = 210$ V. The radius of this region depends on U_{N-SK} only slowly and is ~ 0.15 mm. The mentioned above focusing action of the electric field results in significant portions of injected ions that passes the skimmer orifice and reaches the diaphragm orifice. At $U_{N-SK} = 160$ V this portion is maximum and is equal to 0.33.

The typical velocity of ions in the skimmer orifice plane increases from ~ 1 km/s at $U_{N-SK} = 30$ V to ~ 6 km/s at $U_{N-SK} = 210$ V. Behind the skimmer further acceleration of the ions by the electric field formed by potentials U_A and U_F takes place.

The model predictions for fragmentation of TBP in air, corresponding to experimental results shown in Fig. 1 by symbols, are shown in the same Figure by lines. As it is seen from Fig. 1, a good agreement between the experiment and the model is observed not only for the positions of maximum of fragments intensities, that is not surprising, but also for maximum values themselves as well as for the intensities profiles, that indicates adequate description of the main features of CID by the model.

Figure 3 represents the comparison between experimental (symbols) and modeling (solid lines) dissociation curves of TBP in argon. The simulation of TBP dissociation in argon flow field was performed by using the same parameters of the model as in the case of TBP dissociation in air [4]. The parameters M , j and E_t should not depend on the carrier gas nature while the values of σ were conserved since the solid sphere molecular diameters of air and argon molecules are quite similar [10]. The parameter Z was also fixed at minimum level $Z = 1$, thus again all the collisions were treated as inelastic. No internal degrees of freedom were taken into account for monatomic argon.

As it is seen from Figs. 1 and 3 the dissociation curves of TBP in argon are quite similar to those in air with noticeably lower values of voltage between the nozzle and the skimmer. The decrease of voltage for the locations of peaks of main fragments is reproduced by the model in spite of some noticeable difference between experimental and modeling profiles in Fig. 3 that indicates the necessity of further refining of the model. Nevertheless, the analysis of calculated results allows one to explain the observed shift of dissociation curves while replacing air by argon. The main reason for such a shift is connected with the absence of the internal degrees of freedom in argon that leads to higher values of internal energy collected by the fragment during its collision with monatomic molecule. At the collision of fragment with polyatomic molecule some portion of total internal energy is transferred to internal degrees of freedom of carrier gas molecules.

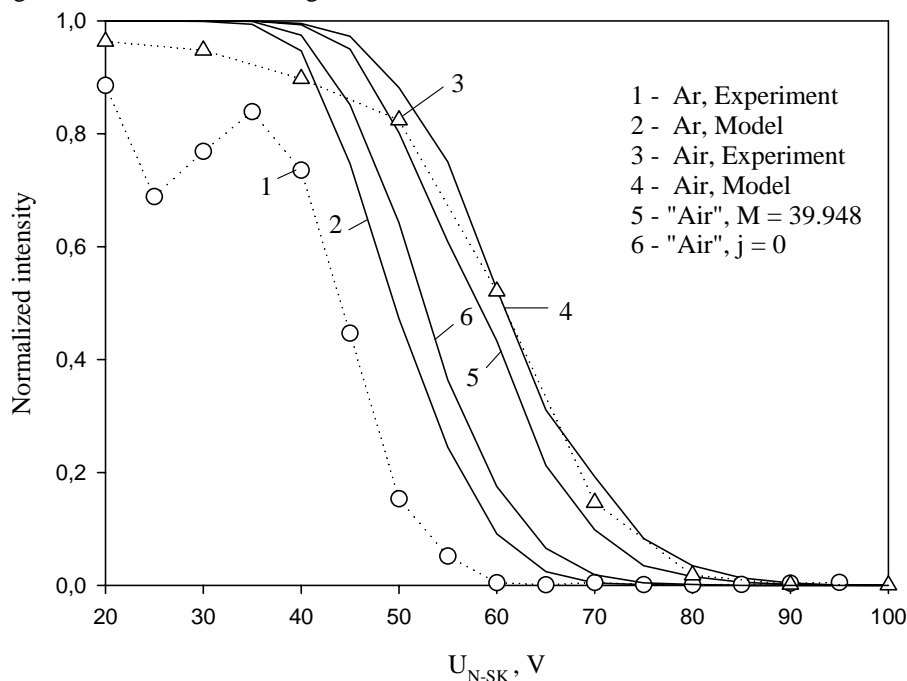


FIGURE 4. The effect of carrier gas nature on dissociation curve of molecular ion of TBP.

The stated conclusion is well illustrated in Fig. 4 where the effect of carrier gas nature on dissociation curve of molecular ion $\text{P}(\text{OC}_4\text{H}_9)_3\text{OH}^+$ of TBP is analyzed. Experimental (1, 3) and modeling (2, 4) curves are the same as presented in Figs. 1, 3. The curve 5 was obtained for artificial case of “air” molecules with molecular mass 39.948 (as for argon), while curve 6 was obtained neglecting the internal degrees of freedom of “air” molecules ($j = 0$). The latter curve was obtained using the flow field of argon reducing its molecular mass to 28.96 (as for air). As it is seen the effect of molecular mass on CID is similar for monatomic and diatomic molecules (cf. the curves 4, 5 and the curves 6, 2) and is considerably lower than the effect of the number of internal degrees of freedom for carrier gases with the same molecular mass (cf. the curves 4, 6 and curves 5, 2).

In papers [12, 13] semi-quantitative model of collision-induced dissociation of polyatomic ions in different carrier gases is proposed. In this model the only effect of carrier gas (N_2 , Ar, Kr) molecular mass is qualitatively accounted for, while the effect of internal degrees of freedom is ignored. As it is seen from the above illustrated results in the case of carrier gases with different atomicity the effect of molecular mass on CID may have a smaller value compared to the effect of the number of internal degrees of freedom. In any case the Larsen-Borgnakke description of translational and internal energy division between colliding unlike polyatomic molecules seems to be quite adequate and is preferable to any semi-quantitative model of the collisional process.

CONCLUSION

1. The dissociation curves of organophosphorus molecules DMMP, DIMP and TBP in air and argon are measured by APCI MS detector.

2. The model of collision-induced dissociation of large polyatomic ions seeded in carrier gas flow is developed on the basis of linear Boltzmann equation solution by test particle Monte Carlo method. In spite of its simplicity and approximate nature the developed model provides a good description of experimental dissociation curves including the effect of carrier gas nature.

3. The main reason for lower voltages in argon for the same dissociation degree as in air is connected with the absence of internal degrees of freedom in argon that leads to higher values of internal energy collected by the fragment during its collision with carrier gas molecule.

4. The effect of carrier gas molecular mass on CID, the only one accounted for in literature, may have a smaller value as compared to the effect of the number of internal degrees of freedom.

ACKNOWLEDGMENTS

The work was supported by the grant of Leading Scientific School (N 02.445.11.7293).

REFERENCES

1. Bruins A.P., *Mass Spec. Rev.*, 10, 53-77 (1991).
2. Kambara H., and Kanomata I., *Int. J. Mass. Spectrom. Ion Phys.*, 25, 129-136 (1977).
3. Fenn J.B., *Int. J. Mass. Spectrom.* 65, 459-478 (2000).
4. Kudryavtsev A.S., Makas A.L., Rebrov A.K., Skovorodko P.A., and Troshkov M.L., *Rarefied Gas Dynamics, Proc. 24th Intern. Symp.*, edited by M. Capitelli, AIP Conference Proceedings, Vol. 762, New York, 2005, pp. 337-342.
5. Makas A.L., Troshkov M.L., Kudryavtsev A.S., and Lunin V.M., *J. Chromatogr. B*, 800, 63-67 (2004).
6. Wensing M.W., Snyder A.P. and Harden C.S., *Rapid Commun. Mass Spectrom.*, 10, 1259-1265 (1996).
7. Lesage D. et al., *Rapid Commun. Mass Spectrom.*, 15, 1947-1956 (2001).
8. Perlmutter M., “Analysis of Couette Flow and Heat Transfer between Parallel Plates Enclosing Rarefied Gas by Monte Carlo”, *Rarefied Gas Dynamics, Proc. 5th Intern. Symp.*, edited by C. L. Brundin, Academic Press, London, 1967, Vol. 1, pp. 455-480.
9. McDaniel E. W., and Mason E. A., *The Mobility and Diffusion of Ions in Gases*, Wiley, New York, 1973.
10. Bird G.A., *Molecular Gas Dynamics and the Direct Simulation of Gas Flows*, Clarendon, Oxford, 1994.
11. Broc A., De Benedictis S., Dilecce G., Vigliotti M., Sharafutdinov R.G., and Skovorodko P.A., *J. Fluid Mech.*, 500, 211-237 (2004).
12. Schneider Bradley B., and Chen David D. Y., *Analytical Chemistry*, 72, No 4, 791-799 (2000).
13. Schneider Bradley B., Douglas D. J., and Chen David D. Y., *Rapid Commun. Mass Spectrom.*, 15, 249-257 (2001).