Russian Chemical Reviews **65** (8) 657–661 (1996)
© 1996 Russian Academy of Sciences and Turpion Ltd

UDC 537.565

Methods for the measurement of ion mobilities and applications

G V Karachevtsev

Contents

I. Introduction	657
II. Ion mobilities	657
III. Mobility spectrometers and their applications	658
IV. Conclusion	660

Abstract. The results of studies of ion mobilities in gases, yielding information about ion-molecule interaction potentials, are surveyed. The principles of the operation and the characteristics of the ion mobility spectrometers are described. Examples of the applications of plasma chromatography in the study of ions are presented. The bibliography includes 70 references.

I. Introduction

The term mobility of ions is defined as the ratio of the rate of their directed uniform motion through a gas to the strength of the electric field inducing this motion. Ion mobilities in gases are widely used in both fundamental and applied branches of science. For example, the parameters of the interaction potentials have been determined and the bond dissociation energies, equilibrium bond lengths, and vibrational frequencies have been obtained from the mobilities of chromium, cobalt, and nickel ions in helium and neon at different temperatures.[1,2] Such information is of interest in the study of the physical and chemical characteristics of low-temperature plasma.

Analytical instruments based on measurements of ion mobilities have been developed in recent years. These instruments are known under different names: ion mobility spectrometers,[3] drift spectrometers, and plasma chromatographs.[4,5] The methods for the analysis of ions in these instruments consist in the study of the dependence of the mobilities of ions on their masses and, in a more general case, on the type of ions. Such devices do not require the creation of a high vacuum, which significantly simplifies their design compared with other analytical apparatus in which ionisation processes are employed (for example, mass spectrometers and electron spectrometers).

A schematic illustration of a drift spectrometer is presented in Fig. 1. A packet of ions with different mobilities is injected into the drift tube with a uniform electric field and an increased gas pressure. The initial packet is then divided into several packets in accordance with the number of different types of ions in the initial packet.

As in mass spectrometers, the ionisation in plasma chromatographs may be achieved by corpuscular radiation and photoradiation and by laser desorption as well as electro- and thermosputtering methods.[6–9]

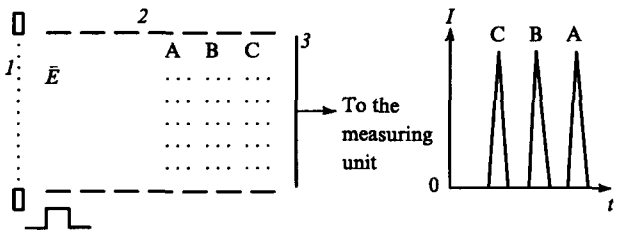


Figure 1. Schematic illustration of a drift spectrometer. (*1*) Ion shutter ensuring the passage of ions from the ion source to the drift tube (*2*); (*3*) ion detector; A, B, C — packets of ions with different mobilities.

G V Karachevtsev Department of Molecular Physics, Moscow Institute of Physics and Technology, Institutskii per. 9, 141700 Dolgoprudnyi, Moscow Region, Russian Federation. Fax (7-095) 408 68 69. Tel. (7-095) 408 55 27

Received 13 May 1995
Uspekhi Khimii **65** (8) 712–717 (1996); translated by A K Grzybowski

II. Ion mobilities

Data on ion mobilities in gases have been published in a series of communications.[10–24] The mobilities of ions depend on their masses, structures, and the effectiveness of energy exchange during their motion in an electric field in gases.

For electric fields usually employed in plasma chromatography at atmospheric pressure, the mobility coefficient K is independent of the electric field strength E. The mobility coefficient is linked by the Einstein relation to the ion diffusion coefficient D

$$K = 1.16 \times 10^4 \frac{D}{T},$$

where the dimensions are $cm^2\ V^{-1}\ s^{-1}$ for K, $cm^2\ s^{-1}$ for D, and K for T.

The average energy of the ions in the electric field is determined by the parameter E/N (N is the density of the gas) measured in townsends ($1\ Td = 10^{-17}\ V\ cm^2$). In plasma chromatography, the typical values of the quantities E/N are 1–2 Td.

Under these conditions, the elastic scattering of ions is determined by the polarisation capture occurring over distances appreciably greater than the geometrical dimensions of the molecule and ion. The mobility coefficient under standard conditions ($N = 2.69 \times 10^{19}$ molecules in $1\ cm^3$, $T = 273$ K) can be obtained by means of the following expression:

$$K = 13.85\left(\frac{1}{m} + \frac{1}{M}\right)^{0.5} \alpha^{-0.5},$$

where m is the mass of the ion in a.u., M the mass of the molecule in a.u., and α the polarisability of the molecules in $Å^3$.

The mobility is linked to the reduced mobility K_0 by the relation

$$K_0 = K \frac{273}{T} \frac{P}{760}.$$

Here P is the total pressure in mm Hg.

With increase in the energy of the relative motion of the ion and the molecule, the radius for the capture of the ion by the molecule diminishes and short-range exchange interactions begin to be manifested between the molecule and the ion. The mobility coefficient begins to depend on the electric field:

$$K = K_{(0)}\left[1 + \alpha_1\left(\frac{E}{N}\right)^2\right].$$

Here $K_{(0)}$ is the mobility in a zero electric field and α_1 is a coefficient which takes into account the deviation of the interaction potential from the polarisation potential. Over short distances, this deviation is responsible for the temperature dependence of the mobility coefficients. For example, with increase in temperature during the drift of Li^+ ions in helium, whereupon the short-range exchange forces become repulsive, the mobility coefficient increases, whereas in the drift of H^+ ions, where short-range attractive forces operate, it diminishes.[25]

We may note that the dependence of the average kinetic energy of the ion w on the temperature of the gas and the rate of drift v is determined by the Vanier formula

$$w = 1.5kT + 0.5mv^2 + 0.5Mv^2,$$

which is frequently employed in kinetic studies.

III. Mobility spectrometers and their applications

The spectrometers, the principle of the operation of which is based on the separation of ions in terms of their mobilities, can be used jointly with the usual high-vacuum mass spectrometers. Such combination requires the overcoming of appreciable technical difficulties, namely the mutual adjustment of the regions of the high and low gas pressures along the ion path,[26,27] but its advantage is that it ensures the possibility of solving problems inaccessible to each separate method. For example, an apparatus has been described[28,29] in which a quadrupole mass analyser is placed at the outlet from the plasma chromatograph (Fig. 2) Such devices make it possible to identify accurately the ions constituting a particular chromatographic peak.

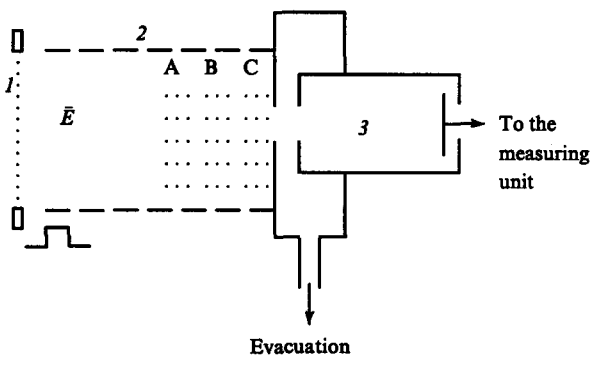


Figure 2. Schematic illustration of tandem drift spectrometer–mass spectrometer apparatus. (*1*), (*2*), A, B, C — as in Fig. 1, (*3*) quadrupole mass analyser.

Another version is possible where the plasma chromatograph is placed after the mass-spectrometric analyser (Fig. 3).[30] The carbon clusters C_n^+, obtained by evaporating graphite on exposure to laser radiation in a helium atmosphere with subsequent hypersonic expansion, have been investigated with the aid of such tandem apparatus.[2,31] The ions of the C_n^+ cluster were accelerated, passed through a mass analyser, retarded, and injected into a drift tube. In this case, it was possible to investigate the structure of ions having the same elemental composition. In particular, the drift times of the $C_3^+ - C_6^+$ clusters are the same for each particular C_n^+ ion. For the $C_7^+ - C_{10}^+$ ions, there are two resolved mobility

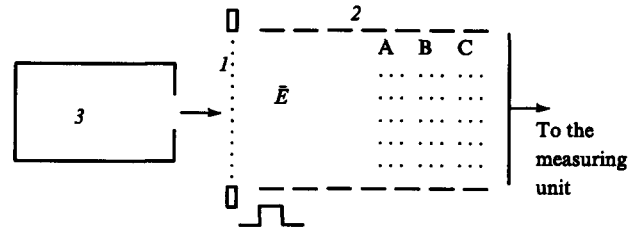


Figure 3. Schematic illustration of a tandem mass spectrometer–drift spectrometer apparatus. (*1*), (*2*), A, B, C — as in Fig. 1; (*3*) mass analyser.

peaks in each case, which corresponds to the presence of two isomeric forms of the clusters — cyclic and linear. The ions having the cyclic clusters have higher mobilities than the linear ones. For the C_{32}^+ cluster, it was found that the composition comprises 23% of monocycles, 71% of bicycles, 2.4% of open fullerenes, and 3.2% of fullerenes. Similar information is available for all the clusters up to C_{61}^+ (Fig. 4).[31]

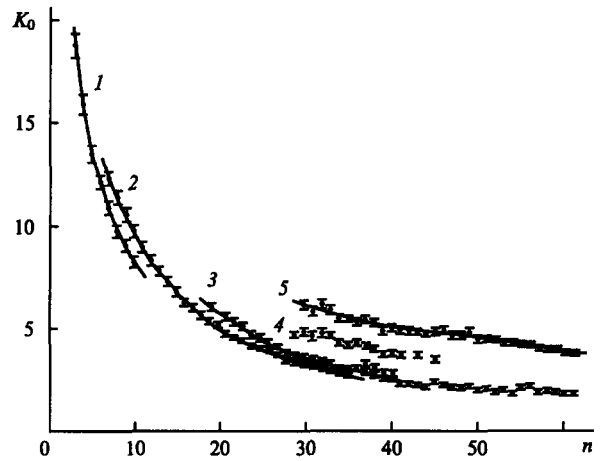


Figure 4. Dependence of the reduced mobility coefficients K_0 for the ions C_n^+ on n for different clusters. (*1*) Linear clusters; (*2*) monocyclic clusters; (*3*) planar polycyclic clusters; (*4*) open fullerenes; (*5*) fullerenes.

The theory of the mobility of carbon cluster ions taking into account the geometry and vibrational excitation of the clusters has been examined.[32] It was shown, for example, that the mobility increases with increase in the vibrational energy of the cluster. It was observed with the aid of ion mobility spectrometry that the protonation of aniline in the gas phase leads to two isomeric forms.[33] The addition of a proton to the nitrogen atom is most preferred. The addition of a proton to the benzene ring is less probable. Such ions have a higher mobility than the ions protonated at the nitrogen atom.

Other studies of the isomers with the aid of plasma chromatography have also been described.[34]

The plasma chromatograph can be used effectively as a highly sensitive selective detector in gas chromatography.[35] The design of the spectrometers, the method for the introduction of the specimens, and the interpretation of the spectra have been described in detail.[36] The plasma chromatograph usually consists of two consecutively arranged drift tubes. The first contains the source of radioactive radiation (a foil containing ^{63}Ni). This tube serves as the reactor for ion–molecule reactions, pure nitrogen, which can usually be obtained from liquid nitrogen, being normally used as the carrier gas. However, the water impurity remains even in highly purified nitrogen, leading, as a result of ion–molecule reactions, to the formation of stable positive ions of the type $H^+(H_2O)_n$ and $NO^+(H_2O)_n$. When purified air is used as the

carrier gas instead of nitrogen, the composition of the positive ions hardly changes, while the negative ions are of the type $O_2^-(H_2O)_n$.

The addition of trace amounts of organic substances to the carrier gas leads to reactions of the carrier gas ions with the impurity molecules; the products incorporate the impurity molecule. The second tube, fitted with a grid for the injection of ions, serves as an ion-drift spectrometer for the measurement of the spectrum of the ions in terms of their mobilities in the electric field. The spectrum is obtained by employing a weak electric field, which directs the ions formed in the reactor to the drift tube of the spectrometer. The packet of cluster ions moves in the inert pure nitrogen atmosphere, the directions of the streams of ions and nitrogen being opposed (in order to diminish the penetration of the carrier gas, containing the impurity, into the region of the analyser). During the motion of the ions through the drift tube, they are separated into packets with different mobilities. The heavier ions usually have smaller mobilities. The pulses of ions having different masses are recorded with the aid of an electrometer amplifier. The scan of a single spectrum in the mass range up to 400 a.m.u. takes 20 ms. Several hundreds of such spectra are usually summed and averaged in order to increase the accuracy of the experiment. A synchronous detector which integrates the signal during a short time interval moving slowly along the time axis relative to the pulse being injected, is used for this purpose.

The Fourier transformation has been used recently in ion mobility spectrometry.[37] The mobility interferogram is obtained with a single transfer of pulses to the modulating grids at the inlet to and outlet from the mobility spectrometer. The pulses are supplied from a rectangular pulse generator with a frequency scan. By applying the Fourier transformation to the interferogram, the usual ion mobility spectrum is obtained. The theory of the method has been described and examples of the measurement of the mobility spectra have been presented (Fig. 5).[37] This method may increase the rate of recording of the mobility spectrum and the sensitivity, which is particularly important when the mobility spectrometer is used as the detector for chromatographs.

The detectable amounts of impurities in 100 cm^3 of air are $10^{-9}-10^{-8}$ g for plasma chromatographs. The use of larger masses of the specimen (10^{-6} g and above) leads to the saturation of the response, the complete consumption of the reactant ions, and the formation of dimeric impurity ions. The interpretation of the mobility spectra then becomes difficult. The ion mobility spectra are also greatly distorted when a drift gas containing impurities which may enter into ion–molecule interactions with the test ions is employed. A discrepancy arises with the mobilities

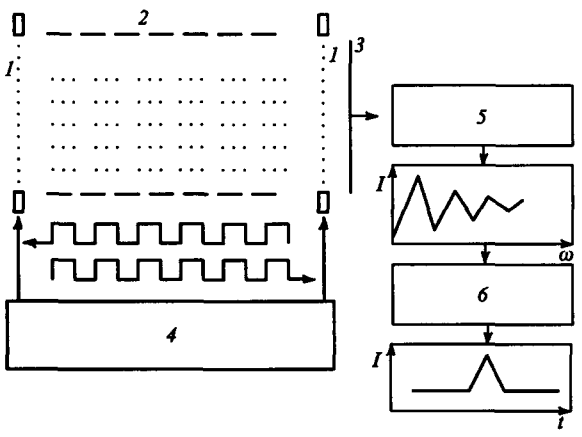


Figure 5. Schematic illustration of a mobility spectrometer with Fourier transformation. (*1*) and (*2*) as in Fig. 1; (*3*) ion collector; (*4*) generator of rectangular pulses with a variable frequency ω; (*5*) electrometer amplifier, analogue–digital transformer, and memory device ensuring the generation of the ion mobility interferogram; (*6*) Fourier transformation ensuring the generation of the ion mobility spectrum.

predicted by the classical theory when fast ion–molecule reactions take place in the system during a period shorter than the drift time. Typical examples of such reactions are the solvation and desolvation of ions by the water molecules present as an impurity in the drift gas.

A useful employment of the ion cluster formation process is also possible, for example, in order to increase the resolving power of plasma chromatographs.[38] If the sizes and masses of the ions are similar but the rates of formation of clusters are different, then the addition of cluster-forming gas to the carrier gas leads to an appreciable difference between the masses of the ions analysed and hence between their mobilities. The kinetic characteristics of the ion–molecule processes are similar in plasma chromatography and high pressure mass spectrometry.[39-42]

Reference data on the kinetic parameters of ion-molecule processes have been published.[43,44] The rate constants for exothermic bimolecular ion–molecule processes for low ion energies are determined by the long-range charge–induced dipole and charge–permanent dipole forces. These constants are usually of the order of 10^{-9} $cm^3\,s^{-1}$ and lower values have been found only in a few instances.[45]

The rate constants for termolecular ion–molecule association reactions are determined by the rate constants for the corresponding bimolecular processes and the lifetimes of the ion–molecule 'collision' complexes formed.

The rate constants for termolecular ion–molecule association processes are $10^{-32}-10^{-21}$ $cm^6\,s^{-1}$.[43,46]

We shall consider the typical conditions in the operation of plasma chromatograms. With the aid of a radioactive radiation source with an activity of ~ 10 μCi at atmospheric pressure, it is possible to obtain $\sim 10^{11}$ ions per second. At atmospheric pressure, the carrier gas flow rate is 100 ml min^{-1}, the electric field strength is 250 V cm^{-1}, the duration of the ion-injecting pulse is 0.2 ms, and the recording scanning pulse has the same duration. The spectra are usually obtained with a drift tube temperature of 100–150 °C and for a length of the drift region of 8 cm. For example, the mobility coefficient for the Cl^- ion at 150 °C is 4.7 $cm^2\,V^{-1}\,s^{-1}$. This yields a drift time of 8 ms. Watts and Wilders[47] made a detailed study of the resolving power of a plasma chromatograph. The formula obtained for the determination of the resolving power in the ideal case (when the resolving power is limited by diffusion) is

$$R = 2(EL)^{0.5},$$

where E is the electric field strength in V cm^{-1} and L the length of the drift tube in cm.

Watts and Wilders[47] studied the influence of the initial width of the ion packet and of the volume charge of the ions on the resolving power. For example, when account is taken of the finite duration of the ion packet, the formula for the resolving power assumes the following form:

$$R = \frac{L/\upsilon + t/2}{(48.4DL/\upsilon^3 + t^2)^{0.5}},$$

where t is the duration of the ion packet, υ the ion drift velocity, and D the diffusion coefficient.

For small electric field strengths

$$E < 4\pi eLn,$$

where n is the concentration of ions, a negative influence of the space charge of the ions on the resolving power may be observed. For example, when $E = 2$ V cm^{-1} and $L = 10$ cm, then appreciable distortion of E due to the space charge will occur for $n = 10^5$ cm^{-3}.

Mathematical methods for the reconstruction of poorly resolved peaks are widely used to increase the resolving power. For example, the spectra of chlorine and bromine isotopes have been resolved by this procedure.[48] Computers are used widely for the recording and treatment of spectra of different types.[49]

One of the principal elements of the design of plasma chromatographs is the grid ion filter. The filters may be of different types. The Tyndall filter consists of two wire grids close to one another and fixed at right angles to the axis of the drift tube. A potential is applied to the grids, i.e. there is a potential difference between them. As a result of this, the ions are not transmitted through the grid for most of the time. However, the potential difference changes sign periodically, which enables the ions to pass through the grid and enter the drift space.

It has been suggested [50] that the Tyndall filter be modified by employing microchannel plates. Such plates are beginning to be employed widely in various experimental techniques.[51] The design of the modified filter is convenient during assembly, ensures a parallel arrangement of the end faces, is mechanically stable, and is not short-circuited on contamination by conducting particles. The channels in such filters have diameters of 40–80 μm and are perpendicular to the surfaces of the plates (to ensure the effective transmission of ions).

The Bradbury–Nielson filter consists of a single grid made of wires arranged at short distances from one another. A sinusoidal potential is applied between the alternating wires of the grid, the average potential on each wire being equal to the potential of the uniform drift field in the plane of the grid. The ions which reach the grids at the moments when the instantaneous alternating potential is close to zero pass through the filter. A modification has been proposed also for this filter, in which foil strips are employed instead of wires.[52]

Ion mobility spectrometers in which the electric field vectors and the gas flow rates are directed to one side were examined above. Ion separators with the gas stream directed at right angles to the electric field in which the ions drift have been proposed (Fig. 6).[53] Such geometry leads to an increase in the resolving power. However, this requires a much greater stability of the gas flow rate compared with the usual geometry.

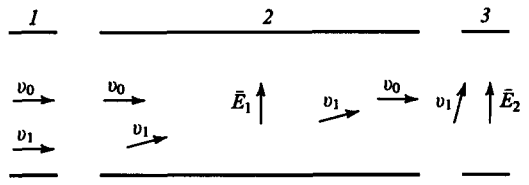


Figure 6. Schematic illustration of an ion mobility spectrometer with a perpendicular arrangement of the electric field and gas flow direction. (*1*) Ion source; (*2*) ion selector; (*3*) ion recorder; v_0 = gas flow rate; v_1 = velocity of ions; E_1, E_2 = electric field strengths.

Another probable advantage of this scheme is the measurement of the ion spectrum without employing a pulse technique — by recording constant ionic currents at different points in the plane of the collector. The ions are carried away by the gas stream at a steady rate and drift in the electric field at right angles to the stream at rates which depend on the mass of the ions. Heavy ions reach the plane of the collector at a long distance from the inlet, whilst light ions reach it at a short distance, since the drift velocity of light ions is usually greater than the drift velocity of heavy ones.

A procedure has been proposed [54–56] for the modification of the ion separation method with the gas flow rate and electric field strength vectors arranged at right angles, to one another. The method is based on subjecting the ions to constant and variable electric fields. When the ions are subjected to such an influence, there is an appreciable increase in the effectiveness of the separation, which is determined not only by the difference between the mobilities but also by the difference between the first derivatives of the mobilities with respect to the electric field. Spectrometers in which this modification procedure of the ion separation method is employed have been constructed by the Ekotek Company (Novosibirsk). The present author and Chentsov have estimated the resolving power of a spectrometer of this type.[57]

IV. Conclusion

The studies on ion mobilities in gases, initiated at the end of the last century by Thomson, Rutherford, Townsend, and Langevin, are still of interest both for fundamental science and for analytical techniques. In fundamental science, such studies make it possible to obtain data on the compositions, structures, and reactivities of ions, which permits a deeper understanding of the general problems of molecular structure and chemical reactivity. Data on gas-phase reactions are also of interest for high-energy chemistry, including radiation chemistry and the chemistry of low-temperature plasma. For example, the rate of recombination of positive and negative ions in plasma is determined directly by the mobilities of these ions.[58]

Definite progress has been noted recently in the improvement of the experimental methods for the study of ion mobilities. Experiments carried out at low temperatures [59–61] showed that at $T < 10$ K ion mobilities in helium diminish sharply and become lower than the polarisation limit, which may be a consequence of the manifestation of quantum effects. Further theoretical experimental studies are needed to elucidate the nature of the observed low-temperature effects. They may yield information about the mechanisms of low-temperature chemical processes.

The laser technique is being applied to an increasing extent in studies of ion mobilities and not only for the generation of the ions but also for the measurement of the velocity distribution of the drifting ions.[62] Systems in which the drift tube–laser combination is used may compete with the drift tube–mass spectrometer systems. One may probably expect an expansion of studies in this promising direction. Mobility spectrometers are being increasingly used for analytical purposes. Apart from the studies indicated above concerning their application in the investigation of carbon cluster isomers, there have been studies of the isomers of metallocarbon clusters.[63–65]

It has been shown that the metal atom may be both incorporated in the carbon network and accommodated in the cavity of fullerene. A further increase in the complexity of the objects investigated is also possible. Studies concerning the application of plasma chromatography for the identification of traces of vapours of drugs and explosives have been continued over many years. In the latest study on the detection of vapours of explosives by plasma chromatography, multiphoton laser ionisation was employed to generate the ions.[66] Studies on the drift of ions in gases in an electric field continue to develop vigorously.[67–70]

References

1. G Von Helden, P R Kemper, M T Hsu, M T Bowers *J. Chem. Phys.* **96** 6591 (1992)
2. M T Bowers, P R Kemper, G Von Helden, P A M van Koppen *Science* **260** 1446 (1993)
3. G A Eiceman, Z Karpas *Ion Mobility Spectrometry* (Boca Raton, FL: CRC Press, 1994)
4. T W Carr *Plasma Chromatography* (New York: Plenum, 1984)
5. R H St Louis, H H Hill, Jr *Crit. Rev. Anal. Chem.* **21** 321 (1990)
6. V E Skurat *Poluchenie i Issledovanie Ionov Neletuchikh Soedinenii v Gazovoi Faze [Radiatsionnaya Khimiya (Ser. Itogi Nauki i Tekhniki]* {The Generation and Study of the Ions of Non-volatile Compounds in the Gas Phase [Radiation Chemistry (Ser. Advances in Science and Engineering)]} (Moscow: Izd. VINITI, 1988)
7. *Proceedings of the NATO Advanced Research Workshop on Methods and Mechanisms for Producing Ions from Large Molecules* (Minaki, Canada: Plenum, 1990)
8. C Shumate *Trends Anal. Chem.* **13** 104 (1994)
9. G Von Helden, T Wyttenbach, M T Bowers *Science* **267** 1483 (1995)

10. E A Mason, E W McDaniel *The Mobility and Diffusion of Ions in Gases* (New York: Wiley, 1984)
11. E A Mason, E W McDaniel *Transport Properties of Ions in Gases* (New York: Wiley, 1984)
12. W Lindinger, T D Mark, F Howorka (Eds) *Swarms of Ions and Electrons in Gases* (Wien: Springer, 1984)
13. H W Ellis, R Y Pai, E W McDaniel, E A Mason, L A Vieland *At. Data Nucl. Data Tables* **17** 177 (1976)
14. H W Ellis, E W McDaniel, D L Albritton, L A Viehland, S L Lin, E A Mason *At. Data Nucl. Data Tables* **22** 179 (1978)
15. H W Ellis, E W McDaniel, M G Thackston, E A Mason *At. Data Nucl. Data Tables* **31** 113 (1984)
16. L A Viehland, E A Mason *At. Data Nucl. Data Tables* **41** 37 (1995)
17. F Celli, G Waddle, D P Ridge *J. Chem. Phys.* **73** 801 (1980)
18. J W Gallagher, D F Hadson, E E Kunhard, R J van Brunt (Eds) *Nonequilibrium Effects in Ion and Electron Transport* (New York: Plenum, 1990)
19. J Lin, T Su *J. Chem. Phys.* **95** 6471 (1991)
20. W A Wakeham, A S Dickinson, F R W McCourt, V Versovic (Eds) *Status and Future Developments in the Study of Transport Properties. NATO ASI Ser. C*, Vol. 361 (Dordrecht, Netherland: Kluwer Academic, 1992)
21. Z Berant, Z Karpas *J. Am. Chem. Soc.* **111** 3819 (1989)
22. K Giles, E P Crimrud *J. Phys. Chem.* **96** 6680 (1992)
23. E A Mason *Science* **260** 43 (1993)
24. N Ikvta, E Nishi, S Nakajiama *J. Phys. Soc. Jpn.* **61** 4425 (1992)
25. F Howorka, F C Fehsenfeld, D L Albritton *J. Phys. B, At. Mol. Phys.* **12** 4189 (1992)
26. D Smith, N D Adams, in *Gas Phase Ion Chemistry* Vol. 1 (Ed. M T Bowers) (New York: Academic Press, 1979) p. 2
27. S L Pozharov *Zh. Tekh. Fiz.* 2156 (1982)
28. Z Berant, O Shahal, Z Karpas *J. Phys. Chem.* **95** 7534 (1991)
29. US P. 36 211 240 (1971)
30. S H Kim, K R Betty, F W Karasek *Anal. Chem.* **50** 1784 (1978)
31. G Von Helden, M T Hsu, P R Kemper, M T Bowers *J. Chem. Phys.* **95** 3835 (1991)
32. L D Book, C Xu, G E Scuseria *Chem. Phys. Lett.* **222** 281 (1994)
33. Z Karpas, Z Berant, R M Stimac *Struct. Chem.* **1** 201 (1990)
34. D F Hagen *Science* **260** 115 (1993)
35. H H Hill, Jr, M A Baim *Science* **260** 143 (1993)
36. G E Spangler, M J Cohen *Science* **260** 1 (1993)
37. F J Knorr, R L Eaterton, W F Siems, H H Hill, Jr *Anal. Chem.* **57** 402 (1985)
38. USSR P. 1 627 984; *Byull. Izobret.* (6) 139 (1991)
39. A F Harrison *Chemical Ionization Mass Spectrometry* (Boca Raton, FL: CRC Press, 1983)
40. A A Polyakova, I A Revel'skii, M I Tokarev, L O Kogan, V L Tal'roze *Mass-Spektral'nyi Analiz Smesei s Primeneniem Ionno-Molekulyarnykh Reaktsii* (Mass-Spectrometric Analysis of Mixtures Using Ion-Molecule Reactions) (Ed. A A Polyakova) (Moscow: Khimiya, 1989)
41. M Sigel', V Fait, in *Kineticheskaya Mass-Spektrometriya i Ee Analiticheskie Primeneniya* (Kinetic Mass Spectrometry and Its Analytical Applications) (Moscow: Institute of Chemical Physics, 1979) p. 132
42. M W Siegel *Science* **260** 95 (1993)
43. L I Virin, R V Dzhagatspanyan, G V Karachevtsev, V K Potapov, V L Tal'roze *Ionno-Molekulyarnye Reaktsii v Gazakh* (Gas Phase Ion-Molecule Reactions) (Moscow: Nauka, 1979)
44. J Ikezoe, S Takebe, A Viggiano *Gas Phase Ion-Molecule Reactions Rate Constants Through 1986. Ion Reaction Research Group of the Mass Spectroscopy Society of Japan, Tokyo, 1987*
45. G V Karachevtsev, A Z Marutkin, V V Savkin *Usp. Khim.* **51** 1849 (1982) [*Russ. Chem. Rev.* **51** 1060 (1982)]
46. V M Smirnov *Iony i Vozbuzhdennye Atomy v Plazme* (Ions and Excited Atoms in Plasma) (Moscow: Atomizdat, 1974)
47. P Watts, A Wilders *Int. J. Mass Spectrom. Ion Process.* **112** 179 (1992)
48. F W Karasek, R J Laub, E de Decker *J. Chromotogr.* **93** 123 (1974)
49. V V Reznikov, M O Reznikova *Informatsionno-Analiticheskaya Mass-Spektrometriya* (Information Analytic Mass Spectrometry) (Moscow: Nauka. 1992)
50. USSR P. 1 737 770; *Byull. Izobret.* (20) 239 (1992)
51. B N Bragin, M M Butelov, A N Ivanova, V S Malysheva *Prib. Tekh. Eksp.* **1** 192 (1975)
52. K Iinuma, M Takebe *Aust. J. Phys.* **48** 491(1995)
53. US P. 3 668 388 (1972)
54. USSR P. 966 583; *Byull. Izobret.* (38) 208 (1982)
55. USSR P. 1 337 934; *Byull. Izobret.* (34) 210 (1987)
56. A S Avakumov, I A Buryakov, E V Krylov, in *Fizika Nizkotemperaturnoi Plazmy. Materialy 7-i Vsesoyuz. Konferentsii* (Physics of Low Temperature Plasma. Proceedings of the Seventh All-Union Conference) (Tashkent: Fan, 1987) Part 1, p. 21
57. G V Karachevtsev, A A Chentsov *Tr. MFTI. Ser. Fiz. Kvantovoi Elektron. (Moscow)* 1996 (in the press)
58. N L Aleksandrov, D A Novitskii *Pis'ma Zh. Tekh. Fiz.* **19** (13) 9 (1993)
59. J Sanderson, H Tanuma, N Kobayashi, Y Kaneko *J. Phys. B, At. Mol. Opt. Phys.* **26** L465 (1993)
60. J Sanderson, H Tanuma, N Kobayashi, Y Kaneko *J. Phys. B, At. Mol. Opt. Phys.* **27** L433 (1994)
61. N Saito, T M Kojima, N Kobayashi, Y Kaneko *J. Chem. Phys.* **100** 5726 (1994)
62. V M Bierbaum, in *SASP-94. Symposium on Atomic, Cluster and Surface Physics. Contributions.* (Eds T D Mark, R Schaittwieser, D Smith) (Maria Alm, Austria: Hintermoos, 1994) p. 29
63. G von Helden, N G Gotts, P Maitre, M T Bowers *Chem. Phys. Lett.* **227** 601(1994)
64. K B Shelimov, M F Jarrold *J. Am. Chem. Soc.* **117** 6404 (1995)
65. K B Shelimov, D E Clemmer, M F Jarrod *J. Phys. Chem.* **99** 11376 (1995)
66. A Clark, R M Deas, C Kosmidis, K W D Ledingham, A Marshall, R P Singhal, in *Proceedings of the 6th International Symposium on Advance Nucleus Energy Research 'Innovative Laser Technology in Nuclear Energy' 1994* Vol. 2, p. 521
67. K R Jennings (Ed.) *Fundamentals of Gas Phase Ion Chemistry. NATO ASI Ser.* (New York: Kluwer, 1991)
68. *Proceedings of the 1992 Workshop on Ion Mobility Spectrometry, Mescalere, NM, 1992*
69. *Proceedings of the 8th International Seminar on Electron and Ion Swarms, Trendheim, Norway, 1993*
70. G E Srangler *Anal. Chem.* **65** 3010 (1993)