# New Method for Ion Mobility Determination by Stability Threshold Measurement in Gas Filled Radio Frequency Quadrupoles

# A. V. Loboda<sup>1</sup>, V. I. Kozlovski<sup>1</sup>, E. V. Chardakova<sup>1</sup>, A. V. Tolmachev<sup>1</sup>, I. V. Sulimenkov<sup>1</sup>, A. F. Dodonov<sup>1</sup>\* and H. Wollnik<sup>2</sup>

<sup>1</sup>Institute of Energy Problem of Chemical Physics (Branch), R.A.C., 142432, Chernogolovka, Moscow Region, Russia <sup>2</sup>II.Physikalisches Institut Justus-Liebig Universitaet Giessen, Germany

SPONSOR REFEREE: Professor Victor Talrose, Russian Academy of Sciences, Moscow 117829, Russia.

A new method is proposed for determining ion mobility by use of a RF-only quadrupole equipped with a longitudinal electrical field along its axis (RFQLEF). This method is based on measuring the transmission threshold for the ions of interest as a function of the RF voltage and frequency. The method is based on the analysis of the equation of the motion of ions under the RF-only quadrupolar electrical field and the friction force due to collisions of the ions with the buffer gas molecules. The stability diagram for this equation was found numerically by a modified matrix method. According to the stability diagram the threshold values of the RF voltage and frequency determine the mobility coefficient for the ions of interest. Mobility coefficients for electrosprayed ions of several substances (bradykinin 2+, gramicidin S 2+ and 1+, multicharged ions of apomyoglobin and cytochrome c) were measured and compared with literature values.  $\bigcirc$  1998 John Wiley & Sons, Ltd.

Received 5 November 1997; Accepted 14 November 1997 Rapid Commun. Mass Spectrom. **12**, 45–49 (1998)

Vacuum RF only multipoles<sup>1</sup> are widely used as ion guides in mass spectrometry. As shown in Ref. 2, gas filled RFonly multipoles at a pressure of several mTorr have 'collisional focusing' properties. The theory of RF-only multipole ion guides is reviewed in Ref. 1. The theory describing collisional focusing and energy normalizing properties of gas-filled RF-only multipoles is reported in Ref. 3. One disadvantage of an RF-only multipole as an ion guide is the rejection of light-mass ions. For the vacuum RF-only quadrupole (RFQ) this is well known as Mathieu's light-mass instability.<sup>4</sup> The parameters of a vacuum RFQ at the instability threshold are determined by Mathieu's criterion. In the case of a gas filled RFQ the observed threshold  $^{5,6}$  differs from that for the vacuum case. The friction of the buffer gas damps the instability and decreases the threshold for light-mass ion rejection. In the present paper we describe the ion motion in an RFQ taking into account the friction force due to collisions of an ion under investigation with buffer gas molecules, and obtain the dependence of the RFQ threshold parameters on the friction force, i.e. a stability diagram. Thus an ion mobility coefficient, related to the friction force, can be obtained via the RFQ instability threshold.

These mobility coefficients, as measured in drift spectrometers directly via the dependence of the ion drift time on the electrical field strength, are of interest for many

\*Correspondence to: A. F. Dodonov, Institute of Energy Problem of Chemical Physics (Branch), R.A.C., 142432, Chernogolovka, Moscow Region, Russia.

Contract/grant sponsor: Russian Foundation for Basic Research; Contract/grant number: N96-03-343546.

Contract/grant sponsor: Volkswagen Stiftung; Contract/grant number: 70676.

applications such as ion chromatography, determination of ion cross sections and ion 'heating' (declustering and fragmentation) while moving through the buffer gas under an electrical field.

The method proposed here allows determination of the mobility coefficient  $\kappa$  of ions by measuring their instability threshold parameters.

## THEORY

Assuming that the mean velocity of the buffer gas molecules is zero before the collision with an ion and equal to the velocity of the ion after collision, one can obtain from the momentum conservation law for a time  $\delta t$ :

$$qE \cdot \delta t = M \cdot \delta u + m \cdot u \cdot k \cdot n \cdot \delta t \tag{1}$$

Here *E* is the electrical field strength; *M*, *u*, *q* are mass, velocity and charge of the ion; *m* is the mass of the buffer gas molecule, *n* the buffer gas density, and *k* the collisional rate constant. Note that  $k \cdot n$  is the number of collisions per unit time. In the limit  $\delta t \rightarrow O$  we have:

$$du/dt + u/\tau = (q/M)E$$
(2)

where  $\tau = M/(mkn)$  is a characteristic velocity relaxation time. Under a constant electrical field the steady-state ion velocity is proportional to the electrical field strength, as in ion mobility theory:

$$u = \kappa E = \tau(q/M)E \tag{3}$$

where

$$\kappa = \tau(q/M) \tag{4}$$

is the mobility coefficient. In the case of an RF-only quadrupole, E, is given by:

$$E = 2(x/R)^2 U_{RF} sin(\omega t) - 2(y/R)^2 U_{RF} sin(\omega t),$$
(5)

where  $\omega$  is the angular frequency and  $U_{RF}$  is the amplitude

of the RF voltage applied to the quadrupole rods. R is the distance between the axis of the RFQ and the rods. Eqn (2) for this case splits in two independent equations for the x and y directions:

$$d^{2}x/dt^{2} + dx/dt/\tau = q/M \cdot 2(x/R)^{2} U_{RF} sin(\omega t)$$
 (6a)

$$l^2 y/dt^2 + dy/dt/\tau = -q/M \cdot 2(y/R)^2 U_{RF} sin(\omega t)$$
 (6b)

Eqn (6b) is identical to Eqn (6a) exept for a time shift of half of a RF period. Substituting  $t^* = \omega \cdot t$  one can rewrite Eqn (6a) as

$$d^2x/dt^{*2} + dx/dt^* \cdot \gamma = (1/2 \cdot Q_M) \cdot x \cdot sin(t^*)$$
(7)

where  $\gamma = 1/(\omega/\tau)$  and  $Q_M = 4qU_{RF}/(M/\omega^2 R^2)$  is the so called Mathieu's parameter. Eqn (7) can have stable or unstable solutions depending on the values of  $\gamma$  and  $Q_M$ .

In the vacuum case ( $\gamma = 0$ ) the stability areas for  $Q_M$  are well known,<sup>4</sup> with the first one covering the range  $0 < Q_M < 0.906$ . For the gas filled RFQ with  $\gamma \ge 0$  we used the modified transfer matrix method<sup>4</sup> to obtain the boundaries of the stability areas. Stability conditions in terms of the transfer matrix method can be written as:

$$|\lambda_1, \lambda_2| \le 1,\tag{8}$$

where  $\lambda_1$ ,  $\lambda_2$  are eigenvalues of the transfer matrix for one RF period. This matrix, for particular values of  $\gamma$  and  $Q_M$ , was constructed from the values of  $(x; dx/dt^*)$  at  $t^* = 2\pi$  by numerically solving Eqn (7) with the initial conditions:

$$t^* = 0, x = 1, dx/dt^* = 0$$
 (9a)

$$t^* = 0, \ x = 0, \ dx/dt^* = 1$$
 (9b)

The boundaries of the stability area, in coordinates ( $\gamma$ ,  $Q_M$ ), for Eqn (7) are presented in Fig. 1.

The lower boundary of the first stability area is the most interesting one for mobility measurements. In order to determine the velocity relaxation time  $\tau$  we first determine experimentally  $Q_{Mexp}$  at the instability threshold. From this  $Q_{Mexp}$  we then obtain a corresponding  $\gamma_{exp}$  by locating the



**Figure 1.** The stability diagram for Eqn (7). ( $\Box$ ) lower boundary of the first instability region, (+) upper boundary of the first instability region, (×) lower boundary of the second instability region.

crossing point of the line  $Q_M = Q_{Mexp}$  and the boundary curve in Fig. 1. The velocity relaxation time  $\tau$  is:

$$\tau = I/(\gamma_{exp}\omega),\tag{10}$$

while the mobility coefficient is:

$$\kappa = \tau \ (q/M) = 1/(\gamma_{exp} \omega M/q). \tag{11}$$

and is determined from Eqns (4) and (10) using the M/q value measured by the mass spectrometer.

From Eqns (1)–(4) one can derive the dependence of the mobility coefficient:

$$\kappa = \kappa_0 \left( P_0 / P_{RFQ} \right) \left( T / T_0 \right)^{1/2}, \tag{12}$$

from the buffer gas parameters. Here  $\kappa_0$  is the reduced mobility coefficient,  $P_{RFQ}$  and T are pressure and temperature of the buffer gas in the RFQ while  $P_0 = 760$  Torr and  $T_0 = 273$ K are standard pressure and temperature.

There are some limitations of the proposed method. One of them arises from the discrete character of the friction force, while the friction force described by Eqn (1) is correct only if the mass of the ion is much greater than the mass of the buffer gas molecule, M >> m. The second limitation is due to the finite size of the RFQ and the finite number of RF cycles the ion spends in the RFQ. This problem can be partially avoided by modifying the stability criterion (8) taking into account the real number (N) of RF cycles and a reasonable estimated magnitude of the parameter I of the instability derivation, with:

$$|\lambda_I^N; \lambda_2^N| < \mathbf{I} \tag{13}$$

In our RFQLEF, which features a DC longitudinal electrical field additional to the lateral quadrupolar RF field, ions experience around 20–200 RF cycles, for which case the criterion (8) gives relatively good results. When the ion velocity becomes comparable to, or higher than, the mean velocity of the buffer gas molecules, we have a so called non-linear mobility in which case there can be deviations from the stability diagram obtained (Fig. 1).

It is interesting to compare the approach described so far with the direct numerical simulation of the multipole ion guide described previously,<sup>3</sup> which takes into account the random thermal forces. This approach allows taking into account the buffer gas temperature and estimation of the ion beam radius resulting from 'collisional focusing'. This algorithm allows a direct numerical solution for the ion trajectories. A corresponding PC-based program reported in Ref. 7 allows specification of various parameters of the system i.e., ion mass, charge, initial energy and position, RF frequency and amplitude, dimensions of the ion guide and, finally, the buffer gas parameters of pressure, temperature, molecular mass and flow speed. The model was used for the computation of the stability threshold  $Q_M$ as a function of  $\omega \tau$ . The resulting curve was compared with experimental data for the stability threshold of myoglobin ions.<sup>6</sup> Experimental points for 5 different pressure values agree well with the theoretical dependence. The cross section thus obtained for the 15+ myoglobin ion is in good agreement with the cross section measured previously<sup>8</sup> by an entirely different method. The results of this model and the approach suggested in this paper are in good agreement. Note that the stability regions in Fig. 1 were confirmed by numerical calculations using the program of Ref. 7.

At this point we would like to emphasise that the present approach allows one to consider stability conditions as a function of simple dimensionless variables  $\gamma$  and  $Q_M$ , disregarding various inessential parameters of the system.



**Figure 2.** The dependence of the intensity of doubly charged bradykinin ions  $[M + 2H]^{2+}$  on the value of  $U_{RF}$ , obtained for  $v_{RF} = 500$  kHz,  $P_{RFO} = 0.7$  Torr and T = 298 K.

# **EXPERIMENTAL**

Experiments were performed using a molecule–ion reactor (MIR), i.e. a gas filled RF-only quadrupole with a superimposed longitudinal electrical field<sup>5,10</sup>. This MIR was connected as the API interface to the orthogonal time-of-flight mass spectrometer (o-TOF-MS). The quadrupole aperture was 3.6 mm, the diameter of the quadrupole rod 4 mm and the quadrupole length 25 mm. The rods consisted of a number of metal rings divided by thin insulators. A fused silica capillary with an inner diameter of 0.05 mm was used in the electrospray ion source. Gramicidin S and bradykinin (Sigma) were dissolved in methanol to a concentration of  $10^{-6}$  M. The horse heart apomyoglobin (Sigma) and cytochrome c were dissolved in 80:20 water/ acetonitrile with 3% of acetic acid. (Sigma, St Louis, MO, USA).

### **RESULTS AND DISCUSSION**

A cut off of a selected ion peak was observed in the mass



**Figure 3.** Velocity relaxation time  $\tau$  values for bradykinin 2+ ions calculated from  $U_{\text{RF}}$  and  $v_{\text{RF}}$  by measuring the cut off as a function of  $U_{\text{RF}}$ .



**Figure 4.** Reduced mobility coefficient  $\kappa_0$  for singly and doubly charged gramicidin S ions, calculated from  $U_{\text{RF}}$  and  $v_{\text{RF}}$  by by measuring the cut off as a function of  $U_{\text{RF}}$ .

spectra if the amplitude of the RF-voltage  $U_{RF}$  was varied at constant RF frequency  $v_{RF} = \omega/2\pi$ . From such a pair of  $U_{RF}$  and  $v_{RF}$  values one can calculate the corresponding Mathieu's parameter  $Q_M$  and  $\tau$  values for the ions of interest, as described above in the theoretical part of this paper. In practice, the ion intensity near the instability threshold drops sharply by several orders of magnitude over a 1–5% variation of the RF amplitude or frequency.

The dependence of the intensity of doubly protonated bradykinin  $[M + 2H]^{2+}$  on  $U_{RF}$  is presented in Fig. 2. This



**Figure 5.** Reduced mobility coefficient values  $\kappa_0$  calculated from measured  $\tau$  values by eqns (4) and (12) for multicharged ions of apomyoglobin (+) and cytochrome  $c(\nabla)$ , dissolved in acetonitrile 80%/water 18%/acetic acid 3%, as a function of the charge number Z ( $\Box$ ). The reduced mobility coefficient values for apomyoglobin ( $\bigcirc$ ) are taken from Ref. 9.

Compound and charge state	m/z	Velocity relaxation time, $\tau$ [mks]	Mobility under experimental conditions, $\kappa$ [cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ]	Reduced mobility, $\kappa_0 [\text{cm}^2 \text{V}^{-1} \text{s}^{-1}]$	Reduced mobility from Ref.9. $\kappa_0 [\text{cm}^2 \text{V}^{-1} \text{s}^{-1}]$
Apomyoglobin 8+	2117			01 1	0.68
Apomyoglobin 9+	1882	0.76	389	0.45	0.71
Apomyoglobin 10+	1694	0.73	415	0.49	
Apomyoglobin 11+	1540	0.70	437	0.51	0.83
Apomyoglobin 12+	1411	0.69	467	0.55	
Apomyoglobin 13+	1303	0.67	496	0.58	0.86
Apomyoglobin 14+	1210	0.66	523	0.61	
Apomyoglobin 15+	1129	0.65	550	0.64	0.91
Apomyoglobin 16+	1058	0.64	577	0.67	
Apomyoglobin 17+	996	0.63	608	0.71	0.98
Apomyoglobin 18+	941	0.61	628	0.73	
Apomyoglobin 19+	891	0.62	664	0.78	
Apomyoglobin 20+	847	0.61	688	0.80	
Apomyoglobin 21+	807	0.62	738	0.86	
Apomyoglobin 22+	770	0.62	776	0.91	
Apomyoglobin 23+	736	0.63	825	0.96	
Apomyoglobin 24+	706	0.66	900	1.05	
Cytochrome c 8+	1545.1	0.54	336	0.40	
Cytochrome c 9+	1373.4	0.51	358	0.42	
Cytochrome c 10+	1236.0	0.50	385	0.45	
Cytochrome c 11+	1123.7	0.47	403	0.47	
Cytochrome c 12+	1030.0	0.47	436	0.51	
Cytochrome c 13+	950.8	0.45	456	0.54	
Cytochrome c 14+	882.9	0.44	483	0.57	
Cytochrome c 15+	824.0	0.44	517	0.61	
Cytochrome c 16+	772.6	0.44	553	0.65	
Cytochrome c 17+	727.1	0.44	580	0.68	
Bradykinin 2+	531	0.43	780	0.69	
Gramicidin S 2+	571	0.32	539	0.64	
Gramicidin S 1+	1142	0.51	429	0.51	

#### Table 1. The reduced mobility coefficients for the investigated ions

curve was constructed from a set of mass spectra recorded by varying the RF amplitude and keeping the RF frequency  $v_{RF}$  constant. The calculated values of  $\tau$  for a set of different  $U_{RF}$  values, for bradykinin  $[M + 2H]^{2+}$  ions, are presented in Fig. 3. The mean value of  $\tau$  is 0.43 + 0.01 µs for our experimental conditions (the pressure in the RFQ was 0.7 Torr and the temperature of the buffer gas 298K).

We have measured values of  $\tau$  for singly and doubly charged gramicidin S ions  $[M + H]^+$  and  $[M + 2H]^{2+}$ , for several frequencies and RF amplitudes. The calculated values of  $\kappa_0$  for different  $U_{\rm RF}$  voltages show a weak dependence on amplitudes and frequencies of the RFvoltage (see Fig. 4). This may be due to an inaccuracy of the measurement of that  $U_{\rm RF}$  which is really applied to the quadrupole rods, and to a nonlinearity of the RF amplifier used in the experiments. The mean values of  $\kappa_0$  are  $0.47 \pm 0.02 \,{\rm cm}^2/({\rm Vs})$  and  $0.85 \pm 0.02 \,{\rm cm}^2/({\rm Vs})$  for singly and doubly charged gramicidin S ions.

In Fig. 5 the  $\kappa_0$  values of multicharged apomyoglobin and cytochrome c ions are shown as functions of their charge states. These curves have been obtained by varying the amplitude  $U_{\rm RF}$  of the RF-voltage while the RFfrequency  $v_{\rm RF}$  was kept constant. In Fig. 5 and Table 1 we present  $\kappa_0$  values measured previously<sup>9</sup> for comparison. It can be seen that all three curves show very similar slopes. The shift between our result and the result of Ref. 9 for apomyoglobin is probably due to systematic errors in pressure measurements, and in slightly incorrect values of the RFQ geometric parameters (quadrupole rod diameter and distance between the rods) used for the calculation.

The accuracy of the velocity relaxation time  $\tau$  corre-

sponds to the accuracy of  $\gamma_{exp}$  which improves with an increased  $Q_{mexp}$  i.e. an increase of the friction force in Eqn (2). Under appropriate experimental conditions the inaccuracy of  $\kappa$  can be several percent. The reduced mobility coefficients  $\kappa_0$  were calculated using Eqn(12). The resulting values of  $\kappa_0$  for bradykinin 2+, gramicidin S 2+ and 1+, and of multicharged apomyoglobin and cytochrome c ions, as measured by the instability threshold method, are shown in Table 1.

#### Acknowledgements

The authors appreciate the support of this work by the Russian Foundation for Basic Research (N96-03-34254a) and the Volkswagen Stiftung (No. 70676).

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