Heating of Ions Moving in a Gas Under the Influence of a Uniform and Constant Electric Field

Valeri V. Raznikov*, Vyacheslav I. Kozlovsky, Alexander F. Dodonov and Marina O. Raznikova

Institute of Energy Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka Moscow region, Russia

SPONSOR REFEREE: Professor V. L. Talrose, Russian Academy of Sciences, Moscow

A simple model for estimation of the internal temperature of ions, moving in a monoatomic gas under the influence of an electric field, is considered. The basic assumption of the model is formation of ion-atom complexes in a quasi-equilibrium state for some of the ion-atom collisions, and other collisions are considered as elastic in which no energy is transferred to the internal energy of the ion. For Langevin collision cross sections, the model allows coinciding equations to be obtained for internal and translational or effective temperatures of ions, in cases where the polarization energy of the atom in the local electric field of the ion is not taken into account. The influence of this polarization energy leads, in the context of the model considered here, to an increase of internal ion temperature by a factor of 1.3–1.5 compared to its effective temperature (which coincides with the buffer gas temperature for zero external electric field). Using this result the significant discrepancies in activation energies for dissociation of protonated leucine enkephalin, measured by different methods, are qualitatively explained. Copyright © 1999 John Wiley & Sons, Ltd.

In a number of tandem mass spectrometry methods for structure investigations of gaseous polyatomic ions, 'slow heating' methods[1] seem to be among the most promising. The main advantage of these methods is the possibility for acquisition of ion dissociation rates as a function of internal ion temperature, thus giving information about dissociation energetics. Compared to relatively complicated methods in this field such as continuous wave infrared multiphoton dissociation (cwIRMPD),[2–5] or dissociation induced by blackbody radiation,[6–9] collisional activation in a quadrupole ion trap[10] seems to be much simpler and more suitable for wide use. In one sense a similar approach is realized in the molecular ion reactor (MIR) used in the MIR time-of-flight mass spectrometry (TOFMS) instrument.[11] The central question for approaches of this type is the estimation of the internal temperature of ions moving in a gas under the influence of some combination of electric fields. The first step for such an estimation is evaluation of ion heating in a constant and uniform electric field under steady state conditions.

Many studies in the literature devoted to ion transport under electric fields in gases that address ion 'temperature' are concerned with ion kinetic energy and not the internal energy. Two papers published recently by Goeringer and McLuckey[12,13] seem to be the most relevant to this problem. These authors proposed an approach for estimation of the internal temperature of ions moving in an atomic buffer gas under an electric field by calculation of their translational or effective temperature T_{eff}. Their basic assumption was coincidence of T_{eff} with T_i (the internal temperature of the ions) independent of differences between elastic and inelastic collisions, and for cases in which all possible ways of ion internal energy exchange other than ion-atom collisions could be neglected. In those cases in which this assumption is valid, the problem of estimation of ion internal temperature should be simplified significantly, as the corresponding formalism for calculation of ion effective temperature is in general much simpler than that for evaluation of excitation of internal degrees of freedom of ions by inelastic collisions. Unfortunately, practical use of this principle has proved to be not so successful, and the same authors in their most recent paper[14] used thermal heating of ions instead of field heating for kinetic measurement of fragmentation of ions derived from leucine enkephalin.

Nevertheless, it seemed to be of interest to try to find some evidence in support of this postulate, or to determine the conditions for it to be valid. In addition, such considerations are useful for simulation of ion dynamics in molecular ion reactors of the type used in our MIR-TOFMS instrument, and for interpretation of the corresponding experimental data.

LANGEVIN MODEL FOR ION-ATOM COLLISIONS

When the ion is small or its charge is large enough, the interaction of a colliding ion and atom is determined mainly by polarization of the atom in the local electric field of the

Correspondence to: V. V. Raznikov, Institute of Energy Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka Moscow region, Russia.
E-mail: raznikov@binep.ac.ru

ion with potential:

$$U(R_1, \ldots, R_n) = -\sum_{j=1}^{n} \frac{\beta e_0^2}{2R_j^4} \qquad (1)$$

where R_j is the distance between the atom and j-th charge location in the ion, n is the number of charges, β is the atom polarizability, and e_0 is the value of a single elementary charge. The process of ion-atom collisions determined by potential of this kind, for small ions with a single charge, was considered by Langevin at the beginning of this century.[15] It was found that the atom can be captured by the ion if the distance between them becomes less than some critical value, and the cross section for such collisions is inversely proportional to the relative ion-atom velocity. For potential functions given by Eqn 1 this property is only approximately valid but, for simplicity of analysis, it will be used further here with the understanding that the term 'Langevin collision cross section' is understood to be a cross section inversely proportional to the ion-atom relative velocity.

Such a property of collision cross sections was implicitly used in the derivation of the equation for T_{eff} (Eqn 5 in the paper of Goeringer and McLuckey[13]). For this purpose these authors used for the average kinetic energy of the colliding atom the value $3/2kT$, and for that of the ion a value $(mv_d^2/2 + 3/2kT_{eff})$. Here v_d is the average drift velocity of the ion, T is the buffer gas temperature, and k is the Boltzmann constant. It is known, however, that the velocity distribution of gas atoms colliding with the walls of a containing vessel is equal to the velocity distribution of the atoms inside the vessel multiplied by this velocity[16] (for a moving surface this multiplier should be the corresponding relative velocity). In other words, the probability density for atoms colliding with the walls to have the kinetic energy ε is proportional to $[\varepsilon. \exp(-\varepsilon/kT)]$, and the average kinetic energy of such atoms is:

$$\frac{\int_0^{\infty} \varepsilon^2 \exp(-\varepsilon/kT)d\varepsilon}{\int_0^{\infty} \varepsilon \exp(-\varepsilon/kT)d\varepsilon} = 2kT \qquad (2)$$

For ions large enough that they can be considered to be a 'wall', this result means that, for a constant cross section for ion-atom collisions, the average kinetic energy of atoms colliding with a very heavy ion without any external electric field should be $2kT$ and not $1.5kT$.

In the Langevin case where the ion-atom collision cross section is inversely proportional to their relative velocity, the velocity distribution function of colliding atoms becomes the same as that for the atoms inside the vessel. This means that the probability of a collision of an approaching ion and atom does not depend on their relative velocity as well as on their own velocities. In turn this means also that, independent of the ion drift velocity (or the field strength), the distribution in the direction of motion of atoms colliding with the ion should be uniform or isotropic in the laboratory system of reference, and the average momentum of colliding atoms would be zero. It also means that the average kinetic energy of colliding atoms would be $1.5kT$, and the averaged stochastic part of the kinetic energy of the colliding ions would be $1.5kT_{eff}$.

Another important property of the Langevin model of ion-atom collisions is that, at least for large polyatomic ions, the directions of motion of recoiling atoms after collision in the centre-of-mass reference system may be considered to

be isotropic and independent of the direction of this centre-of-mass motion as the atom should impact physically on some part of the randomly oriented ion with a complicated 'surface'. For this reason it is probable that some atoms will not leave the ion immediately after the initial impact. It is sufficient for this purpose to lose some part of the initial kinetic energy of the atom such that the remaining energy is less than the polarization energy of the atom at the point of impact. Thus the atom, after an unsuccessful attempt to escape, returns back to the ion, and such impacts continue up to the moment when appropriate energy fluctuations in the ion give the atom sufficient energy to be released. Thus long-lived ion-atom collision complex formation is possible, and a quasi-equilibrium state of this complex may be achieved. (As pointed out by Talrose[17] some time ago, formation of such complexes with lifetimes in the range of 10^{-8}–10^{-7} sec, and with a nearly uniform energy distribution for their internal degrees of freedom, is highly probable in ion-molecule collisions). Further, for simplicity, all ion-atom collisions can be divided into two cases: elastic collisions involving no energy transfers into internal energy of the ion, and collisions forming quasi-equilibrium ion-atom complexes but with lifetimes much less than the time between collisions. However, as will be concluded from the formalism developed below, the latter restriction is of no importance for ions which are sufficiently large.

The present considerations are based on more detailed analysis of the same two equations (Eqns 1 and 2 in Ref. 13) for momentum and energy gained from the uniform and constant electric field E_0 in unit time by atoms colliding with the ion, as in the steady state all averaged properties of the ion are unchanged. The remaining question concerns what average ion velocity before the collision should be used. One investigation[13] used the average ion drift velocity v_d, but this assumption seems to us to be not evident. Ions are accelerated in the uniform electric field between collisions, so that just before collision the velocity of the ion in the field direction is maximal compared to all other times between this and the preceding collision, and it is difficult to expect that in any case the average ion velocity just before collision v_{max} should be equal to the time-average (or drift velocity) of the ion v_d.

To investigate when this assumption[13] is valid, consider the consequences of the momentum conservation law for ion-atom collisions which are proved to be essentially the same for both types of collision mentioned above. For the velocity vector $\vec{v}_c$ of the ion-atom complex (their centre-of-mass) at the moment of collision, it is possible to write:

$$m\vec{v} + M\vec{V} = (m + M)\vec{v}_c,$$
$$\vec{v}_c = \frac{m\vec{v} + M\vec{V}}{m + M} \qquad (3)$$

where $\vec{v}$ is the ion velocity vector before collision, M is the atom mass and $\vec{V}$ is its velocity vector. (Here, and subsequently, all velocities of the ion and the atom 'before and after collision' are taken to refer to large enough ion-atom separations that the influence of the polarization potential can be ignored).

Let the field direction coincide with the x-axis. Denote the x-component of the velocity of the recoiling ion in the centre-of-mass reference system (the system which is moving with constant velocity vector $\vec{v}_c$) as g'_x. Denoting by v^k_{max} and v^k_{min} the ion velocity component in the x-

direction just before and after the k-th collision, and using Eqn 3, gives:

$$v_{min}^k = \frac{mv_{max}^k + MV_x}{m + M} + g_x' \qquad (4)$$

After averaging, with average values of V_x and of g_x' both zero, and with $v_{min} = \langle v_{min}^k \rangle$, gives:

$$v_{min} = \frac{mv_{max}}{m + M} \qquad (5)$$

The same expression applies to the average velocity of the atom after collision with the ion, and on average each such atom acquires momentum equal to Mv_{min}. The following equation, for momentum gained from the electric field E_0 in unit time, is then valid:

$$eE_0 = \mu v_{max} \nu \qquad (6)$$

where e is the ion charge, ν is the ion-neutral collision frequency, and $\mu = mM/(m + M)$ is the reduced mass.

To relate v_{max} to v_d it is necessary to have the distribution function for the duration of time intervals between collisions, which can be written in the form:

$$P(t) = \nu \exp(-\nu t) \qquad (7)$$

where $P(t)$ is the density of probability that the time between collisions of the ion with the atoms is equal to t. Such a distribution is valid for any series of independent events (or Poisson process[18]), and the series of ion-atom collisions closely approximates such processes. From Eqn 7 it is easy to derive for average values the obvious equality $\langle t \rangle = 1/\nu$, and also the not so evident one $\langle t^2 \rangle = 2/\nu^2$.

For v_d the following expression may be written:

$$v_d = \lim_{N \to \infty} \frac{1}{\theta_N - \theta_1} \sum_{k=1}^{N-1} \int_{\theta_k}^{\theta_{k+1}} [v_{min}^k + eE_0(\tau - \theta_k)/m]d\tau \quad (8)$$

where θ_k is the time of the k-th collision. After integrating and substituting $t_k = (\theta_{k+1} - \theta_k)$, this equation may be transformed to:

$$v_d = \lim_{N \to \infty} \frac{N-1}{\theta_N - \theta_1}$$

$$\times \left(\lim_{N \to \infty} \frac{1}{N-1} \sum_{k=1}^{N-1} v_{min}^k t_k + \lim_{N \to \infty} \frac{eE_0}{2m(N-1)} \sum_{k=1}^{N-1} t_k^2 \right) \quad (9)$$

If the random values v_{min}^k and t_k are independent, the first term in the brackets on the right side of Eqn 9 may be replaced by v_{min}/ν. This is exactly true when the probability of ion-atom collision is independent of the ion velocity, as is the case for Langevin collisions. For large ions this result is always approximately true for small electric fields and buffer gas temperatures which are not too large. For the second term in the brackets of Eqn 9 the average value $\langle t^2 \rangle = 2/\nu^2$, and Eqn 6 may be used:

$$v_d = \nu \left(\frac{v_{min}}{\nu} + \frac{\mu v_{max}}{m\nu} \right) \qquad (10)$$

After substitution using Eqn 5 and $\mu = mM/(m + M)$, the equality $v_d = v_{max}$ is derived, and the equation for momen-

tum may be written in the form of Eqn 1 from Ref. 13:

$$eE_0 = \mu v_d \nu \qquad (11)$$

ESTIMATION OF EFFECTIVE AND INTERNAL TEMPERATURES OF IONS; RESULTS AND DISCUSSION

To derive finally the expressions for effective and internal temperatures of the ion, we write down the equation for the energy gained from the field in unit time, which should be equal to the average energy acquired by the atom after each collision multiplied by the collision frequency:

$$eE_0 v_d = \frac{M}{2} \langle (\vec{V}', \vec{V}') - (\vec{V}, \vec{V}) \rangle \nu \qquad (12)$$

where $\vec{V}'$ is the atom velocity vector after collision. If we denote by $\vec{G}$ and $\vec{G}'$ the atom velocity vectors before and after collision, in the centre-of-mass reference system, which implies that $\vec{V} = \vec{v}_c + \vec{G}$ and $\vec{V}' = \vec{v}_c + \vec{G}'$, and use the notations $\vec{g}$ and $\vec{g}'$ for the corresponding velocity vectors of the ion, it is possible to write:

$$m\vec{g} + M\vec{G} = 0,$$
$$\vec{G} = -\frac{m}{M}\vec{g},$$
$$\vec{V} = \vec{v}_c - \frac{m}{M}\vec{g} \qquad (13)$$
$$\vec{g} = \vec{v} - \frac{m\vec{v} + M\vec{V}}{m + M} = \frac{M}{m + M}(\vec{v} - \vec{V}) \qquad (14)$$
$$m\vec{g}' + M\vec{G}' = 0,$$
$$\vec{G}' = -\frac{m}{M}\vec{g}$$
$$\vec{V}' = \vec{v}_c - \frac{m}{M}\vec{g}' \qquad (15)$$

After substituting Eqns 13 and 15 into 12, the following equations may be written:

$$eE_0 v_d = m \langle (\vec{v}_c, \vec{g}) - (\vec{v}_c, \vec{g}') + \frac{m}{2M}[(\vec{g}', \vec{g}') - (\vec{g}, \vec{g})] \rangle \nu \quad (16)$$

$$eE_0 v_d = \frac{\mu}{m + M} \langle m(\vec{v}, \vec{v}) - (m - M)(\vec{v}, \vec{V}) - M(\vec{V}, \vec{V}) \rangle \nu \quad (17)$$

$$\langle (\vec{g}', \vec{g}') - (\vec{g}, \vec{g}) \rangle = 0 \qquad (18)$$

Equation 18 is written only for inelastic collisions because, for each elastic collision, the last term in the averaging brackets of Eqn 16 is zero due to kinetic energy conservation. For inelastic collisions Eqn 18 describes the fact that, at steady state, on average the initial kinetic energy of the collision complex in the centre-of-mass reference system is equal to the kinetic energy of this complex after collision. Thus the last term in the averaging brackets of Eqn 16 disappears. For the second term in these brackets it should be noted that averaging of the product $(\vec{v}_c, \vec{g}')$ gives zero, as it can be postulated that the distribution of the vector $\vec{g}'$ is isotropic and independent of the direction of $\vec{v}_c$. After substituting Eqn 14 and the expression (Eqn 3) for the vector $\vec{v}_c$, Eqn 17 actually coincides with Eqn 2 from Ref. 13 if the distribution of the vector $\vec{V}$ is considered as isotropic (so that $\langle (\vec{v}, \vec{V}) \rangle$ is zero). As this equation considers only the velocities of ion and atom before collision, it is valid for all types of collisions, and not only for *atoms* colliding with the polyatomic ions.

This equation, after substituting Eqn 11 and replacing $\langle m(\vec{v}, \vec{v}) \rangle$ by $[mv_d^2 + 3kT_{eff}]$ and $\langle M(\vec{V}, \vec{V}) \rangle$ by $3kT$ gives:

$$\mu v_d^2 \nu = \frac{\mu}{m + M} \langle m(\vec{v}, \vec{v}) - M(\vec{V}, \vec{V}) \rangle \nu \qquad (19)$$

$$M v_d^2 = 3kT_{eff} - 3kT$$

$$T_{eff} = T + \frac{Mv_d^2}{3k} \qquad (20)$$

The last equation is actually the same as Eqn 5 in Ref. 13, given there for elastic collisions and a weak electric field.

To derive an equation for T_i (the internal temperature of the ions), transform Eqn 18 taking into account that:

$$\langle m(\vec{g}', \vec{g}') + M(\vec{G}', \vec{G}') \rangle = \langle (m + m^2/M)(\vec{g}', \vec{g}') \rangle = 3kT_i$$

in the equilibrium state if the polarization energy of the atoms is ignored, and if there are no energy preferences for inelastic collisions:

$$\langle (\vec{g}, \vec{g}) \rangle = \frac{M}{mM + m^2} 3kT_i,$$

$$\mu \langle (\vec{v}, \vec{v}) - 2(\vec{v}, \vec{V}) + (\vec{V}, \vec{V}) \rangle = 3kT_i, \qquad (21)$$

$$\frac{M}{(m + M)}(mv_d^2/3k + T_{eff}) + \frac{m}{(m + M)}T = T_i. \qquad (22)$$

Substituting Eqn 20 into this equation finally gives:

$$T_i = T + \frac{Mv_d^2}{3k}. \qquad (23)$$

Thus T_{eff} and T_i coincide at steady state for the conditions used above for deriving this equation.

Now assume that ion-atom collision cross sections can be considered to be constant. Suppose further for simplicity that the ion mass is large enough compared to that of the atom, and that the equality $v_d = v_{max}$ is valid. In this case the atoms colliding with the ion would have a negative average component of velocity $\langle V_x \rangle$ in the field direction, and Eqn 11 via accurate averaging of Eqn 4 and the new momentum balance, transforms to:

$$eE_o = \mu(v_d - \langle V_x \rangle)\nu$$

After substituting this equation into Eqn 17, and taking into account that $v_d V_x$ for large ions equals $\langle (\vec{v}, \vec{V}) \rangle$, the same result as Eqn 19 for calculation of T_{eff} is derived in the case considered here. At the same time the term $\langle -2(\vec{v}, \vec{V}) \rangle$ in Eqn 21 for T_i becomes positive, and therefore $T_i > T_{eff}$. Taking into account the increase of average kinetic energy of the colliding atom and ion for the condition of constant collision cross section stipulated at the beginning of this paragraph can only enhance this inequality.

Another possible reason for lack of coincidence of T_i and T_{eff}, at least for large enough ions, is significant polarization energy of the colliding atom in the local electric field of the ion for Langevin collisions. In this case Eqn 21 should have a term on the right side smaller than $3kT_i$. This decrease of this term is connected with the polarization energy loss of the recoiling atom, and may be estimated using the following simple considerations. In order to achieve thermal equilibrium in the ion-atom collision complex, its minimum lifetime should be about ten average time intervals between the ion-atom impacts within that complex. This implies that, assuming that the Arrhenius law for unimolecular decay is valid, $\exp(E_{pol}/kT_I) \approx 10$, and the polarization energy of the

atom E_{pol} should not be less than $2kT_i$. It means also that the atom recoiling from the ion can be released from the complex only if its initial kinetic energy is more than $E_{pol} = 2kT_I$, and the average kinetic energy of such atoms may be calculated as:

$$\frac{\bar{E}_{kin}|E_{kin} > E_{pol} = \int_{E_{pol}}^{\infty} \varepsilon \sqrt{\varepsilon} \exp(-\varepsilon/kT_i)d\varepsilon}{\int_{E_{pol}}^{\infty} \sqrt{\varepsilon} \exp(-\varepsilon/kT_i)d\varepsilon} \qquad (24)$$

Numerically the average initial kinetic energy of such atoms may be calculated to be about $(E_{pol} + 1.15\, kT_i)$. Therefore the right side of Eqn 21 becomes close to $2.3\, kT_i$ and T_i increases by a factor of about 1.3 in comparison with the case of zero polarization energy. In cases where the lifetime of the ion-atom complex is *not* less than 10^{-8} sec (see Ref. 17) the polarization energy is estimated to be more than $10\, kT_i$. It may be shown using Eqn 24 that, for such polarization energy, the average initial kinetic energy of atoms released from the complex is slightly more than $(E_{pol} + kT_I)$, and and T_i increases by a factor of about 1.43–1.5 in comparison to the case when polarization energy of the atom is not taken into account.

The possible objection, that the value of T_i used here may be higher than that corresponding to the time-averaged internal energy of the ion, because the present value corresponds to the moment just after collision, may be rejected at least for large ions. In this case the influence of a single collision on the ion's average internal energy per degree of freedom (proportional to the internal temperature) may be negligibly small. At the same time for Langevin collisions Eqn 20 would still be valid, and the inequality $T_I > T_{eff}$ follows.

As T_{eff} for zero external field is equal to the buffer gas temperature, we come to the following unexpected conclusion: in the context of the present model, the internal temperature of the ion is significantly greater than the temperature of a buffer gas in the state of thermal equilibrium. However, simple reasoning shows that it is also reasonable to expect some effect of this type in the case of no collision complex formation. If the atom has non-zero polarizability it has extra kinetic energy, equal to the energy of its polarization at the moment of ion-atom impact, in addition to its thermal kinetic energy. For the ion internal degrees of freedom this is almost the same as increasing the temperature of the buffer gas if no complex is formed. In cases of complex formation but for collision cross sections assumed to be constant rather than the Langevin values, the increase of ion internal temperature may be even greater than by the factor of 1.5, at least for large enough ions. It may be seen that the left side of Eqn 21 for large ions, in the case of zero external field and constant collision cross sections, is equal to $4kT$. The right side of this equation, for sufficiently long-lived complexes, is $2kT_i$. Thus the maximum factor for increase of ion internal temperature is 2.

As some kind of experimental confirmation of this conclusion, the results of investigations of dissociation of protonated leucine enkephalin from Refs. 14 and 19 can be considered. In Ref. 14 the kinetics of this process was measured in an ion trap. The buffer gas was helium, at a pressure of about 10^{-4} Torr. The temperature of the buffer gas was changed thermally in a relatively narrow interval around 200 °C. The Arrhenius plot for dissociation constants was quite good,[14] and gives for the activation energy

$E_a = 1.28 \pm 0.08$ eV, and for the preexponential factor log $A = 12.55 \pm 0.87$. In Ref. 19 the same kinetics were measured in a heated capillary in an electrospray ion source. The measurements were performed using air at about 0.1 atmospheres pressure. The temperature range was 360–400 °C. The Arrhenius plot for dissociation constants was also good,[19] and gave $E_a = 38.3$ kcal/mol $= 1.66$ eV, and for the pre-exponential factor log $A = 15.7$. Unfortunately, experimental uncertainties were not given.[19] In both papers[14,19] it was shown that conditions were close enough to the high-pressure limit to give a good approximation to the true Arrhenius parameters.

For the diatomic molecules of air, the expected maximum increase of internal temperature for large ions may be estimated in the same way as for a monoatomic gas on taking into account the following factors:

the average energy of the molecules approaching the ion has an additional contribution of rotational energy of kT;
the molecules recoiling from the quasi-equilibrium ion-molecule complex have, on average, an additional rotation energy kT_I which is not influenced noticeably by the local ion electric field;
excitation of the molecular vibrations of the diatomic molecules probably may be neglected since the temperatures were not very high;[19]
Eqn 21 should be treated as an averaged energy balance for the ion in the centre-of-mass reference system.

For Langevin collisions the left side of Eqn 21 for zero external field for large ions should be equal to $5kT$. The right side of this equation for long-lived complex formation is $4kT_i$. Thus the maximum factor for increase of the internal ion temperature T_I in this case is 5/4. For the case of constant collision cross sections and large ions, this equation transforms to: $6kT = 4kT_i$, and the maximum factor would be 3/2.

Using these considerations and the maximum factors for increase of T_i for a monoatomic buffer gas, it is possible to estimate the connection between measured activation energies in the two cases (Refs. 14 and 19) if it is supposed that these experiments involved the formation of long-lived ion-atom and ion-molecule collision complexes. For Langevin collision cross sections the apparent activation energy for a diatomic buffer gas should be 6/5 of that for a monoatomic gas. For constant collision cross sections this coefficient is 4/3. For $E_a = 1.28$ eV, measured for helium,[14] the expected values for air would be 1.54 eV for Langevin and 1.71 eV for constant collision cross sections, respectively. The measured value 1.66 eV[19] lies between these values. It is not so evident, but quite possible, that the difference in preexponential factors may be ascribed to the slow decrease of T_i/T_{eff} with temperature.

For estimation of the true activation energy it is sufficient to multiply the measured value by the corresponding ratio T_i/T_{eff}. For measurements in an ion trap with helium[14] this gives 1.92 and 2.56 eV for Langevin and constant collision cross sections, respectively. For a heated capillary with air[19] these values are 2.08 and 2.49 eV, which are the same to within the uncertainties of the measurements. As was pointed out[14] the main primary product of dissociation of protonated leucine enkephalin is the b_4 ion, which is produced by simple cleavage of the peptide bond adjacent to the C-terminus of this compound. Unfortunately we could not find in the literature any direct data for dissociation energy of peptide bonds in neutral molecules. Only two examples for dissociation energies of amide bonds measured by the electron impact method were found.[20] The energies for the following two reactions were given:

$$(CH_3)_2NCHO = N(CH_3)_2 + HCO - 59 \, \text{kcal/mol} = 2.56 \, \text{eV};$$

$$CH_3CON(CH_3)_2 = CH_3CO + N(CH_3)_2 - 75 \, \text{kcal/mol} = 3.26 \, \text{eV}.$$

Of course these data cannot be directly transferred to dissociation of peptide bonds in protonated peptides, but some relationship is possible as bonds of a type similar to peptide bonds dissociate in both of these cases.[20]

CONCLUSIONS

Using formalisms of classical mechanics and molecular physics, the following results were derived from analysis of ion heating in a gas under a constant and uniform electric field in the steady state:

1. the coinciding equations for effective and internal temperatures of ions moving in a monoatomic gas were derived for the case in which ion-atom collisions provide the single significant way for internal ion energy exchange, and where:
ion-atom collision cross sections are inversely proportional to the ion-atom relative velocity;
all collisions can be considered either as elastic collisions with no energy transfers to internal energy of the ion, or as fully inelastic collisions when ion-atom complexes in a quasi-equilibrium state are formed but with lifetimes much less than the average time between collisions;
there are no collision energy preferences for collision to be elastic or inelastic;
for both types of collision the velocity distributions of recoiling ion and atom after collision, in the centre-of-mass reference system, are isotropic;
the influence of the local electric field of the ion is not taken into account;

2. when collision cross sections are assumed to be constant, and the other properties of the collisions are as before, at least for large ions $T_I > T_{eff}$;

3. for the Langevin collision model, in which polarization energy of the colliding atom in the local electric field of the ion is taken into account, and when all other properties of the collisions are the same as in case 1, the inequality $T_I > T_{eff}$ is valid at least for large ions; it may be estimated that, in the context of the present model, T_i is increased by a factor of 1.3–1.5 compared to T_{eff};

4. because under these conditions for zero external field T_{eff} coincides with the buffer gas temperature T, it follows that $T_I > T$ in the thermal equilibrium state, and the T_i/T_{eff} ratios given above are valid for this case also;

5. for long-lived collision complex formation in zero external field, the following maximum factors for T_i/T_{eff} ratios were also derived:
for constant collision cross section and atomic buffer gas, 2;
for Langevin collision cross section and diatomic buffer gas, 1.25;
for constant collision cross section and diatomic buffer gas, 1.5;

6. using these theoretical results, the significant discrepancies between the experimental activation energies for

dissociation of protonated leucine enkephalin, measured by different methods,[14,19] were qualitatively explained.

Acknowledgements

REFERENCES

1. S. A. McLuckey and D. E. Goeringer, *J. Mass Spectrom.* **32**, 461 (1997).
2. R. C. Dunbar, in *Gas Phase Ion Chemistry*, M. T. Bowers (Ed.), Academic Press, New York Vol. **2**, Chap. 14 (1979).
3. R. C. Dunbar, in *Gas Phase Ion Chemistry*, M. T. Bowers (Ed.), Academic Press, New York Vol. **3**, Chap. 20 (1979).
4. L. R. Thorne and J. L. Beauchamp, in *Gas Phase Ion Chemistry*, M. T. Bowers (Ed.), Academic Press, New York Vol. **3**, Chap. 18 (1984).
5. G. T. Uechi and R. C. Dunbar, *J. Chem. Phys.* **98**, 7888 (1993).
6. D. Thölmann, D. S. Tonner and T. B. McMahon, *J. Phys. Chem.* **98**, 2002 (1994).
7. R. C. Dunbar, *J. Phys. Chem.* **98**, 8705 (1994).
8. W. D. Price, P. D. Shnier, R. A. Lockusch, E. F. Strittmatter and E. R. Williams, *J. Am. Chem. Soc.* **118**, 7178 (1996).
9. R. C. Dunbar and T. B. McMahon, *Science* **279**, 194 (1998).
10. J. N. Louris, R. G. Cooks, J. E. P. Syka, P. E. Kelley, G. C. Stafford Jr. and J. F. J. Todd, *Anal. Chem.* **59**, 1677 (1987).
11. A. Dodonov, V. Kozlovsky, A. Loboda, V. Raznikov, I. Sulimenkov, A. Tollmachev, H. Wollnik and A. Kraft, *Rapid Commun. Mass Spectrom.* **11**, 1649 (1997).
12. D. E. Goeringer and S. A. McLuckey, *Rapid Commun. Mass Spectrom.* **10**, 328 (1996).
13. D. E. Goeringer and S. A. McLuckey, *J. Chem. Phys.* **104**, 2214 (1996).
14. K. G. Asano, D. E. Goeringer and S. A. McLuckey, *Int. J. Mass Spectrom. Ion Processes* **179**, (1998) in press.
15. P. Langevin, *Ann. chim. et phys.* **5**, 245 (1905).
16. R. Feynman, *The Feynman Lectures on Physics: Exercises*. Addison-Wesley Publishing Company, Inc. Reading, MA, (1964–1965)
17. V. L. Talrose, *Pure Appl. Chem.* **5**, 455 (1962).
18. G. Korn and T. Korn, *Mathematical Handbook for Scientists and Engineers*, McGraw-Hill, New York (1961).
19. M. Meot-Ner, A. R. Dongré, Á. Somogyi, V. G. Wysocki, *Rapid Commun. Mass Spectrom.* **9**, 829 (1995).
20. V. N. Kondrat'ev, (Ed.), *Dissociation Energies of Chemical Bonds. Ionization potential and electron affinity data.* "Nauka", Moscow, 1974 (in Russian).