Chemical Physics Letters 693 (2018) 66-71

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper Tunneling and reflection in unimolecular reaction kinetic energy release distributions

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ARTICLE INFO

Article history: Received 17 November 2017 In final form 30 December 2017 Available online 6 January 2018

Keywords: Kinetic energy release distributions RRKM Spherical potentials Detailed balance

ABSTRACT

The kinetic energy release distributions in unimolecular reactions is calculated with detailed balance theory, taking into account the tunneling and the reflection coefficient in three different types of transition states; (i) a saddle point corresponding to a standard RRKM-type theory, (ii) an attachment Langevin cross section, and (iii) an absorbing sphere potential at short range, without long range interactions. Corrections are significant in the one dimensional saddle point states. Very light and lightly bound absorbing systems will show measurable effects in decays from the absorbing sphere, whereas the Langevin cross section is essentially unchanged.

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1. Introduction

The utility of unimolecular reactions in physical chemistry can hardly be overstated. The theory of the phenomenon comes in several varieties that can be classified by the nature of the transition state that separates the precursor and the product in phase space. The description of the situation where the reaction coordinate has a saddle point shape, with the reaction bound to occur along a local minimum on all but one direction in phase space where it passes through a maximum, is one of the simplest to describe theoretically, and has been widely used to model the dynamics and thermodynamics of dissociating molecules, including kinetic energy release distributions, in the context of the RRKM version of transition state theory [1-3]. The shape of the potential along the reaction coordinate determines both the shape of the distribution of the kinetic energy released in the asymptotically separated states which are the ones measured and, by integration over this kinetic energy, the total dissociation rate constant.

With the presence of a barrier, the idea of tunneling trough this barrier appears naturally, with the concomitant consequences for the rate constants that involve such a transition state. The effects on the total (kinetic energy-integrated) rate constant was derived in [4]. The connection of this type of transition state to the detailed balance expression for the rate constant seems not to have been formulated previously explicitly. Such a result will be relevant

for the interpretation of experimental data of the type presented in e.g. [5–9], where kinetic energy release distributions show finite energy gaps, indicating the presence of reverse barriers of varying magnitudes. As the parameters of the saddle point determine whether or not the transverse motion is thermally activated, i.e. corresponding to a tight or loose transition states, an interpretation of KER data must involve these parameters. Here, however, the discussion of the saddle point transition state will be restricted to tight transition states only, corresponding to a truly onedimensional motion along a uniquely defined reaction coordinate with no vibrational excitation of the transverse motion.

This is one extreme in the space of possible transition states. Another extreme, a transition state entirely without a reverse activation energy, will also be considered. A large number of experimental data rule out a reverse activation barrier and favor this type of barrier-less transition state, see e.g. [10-30]. The tunneling effects in the kinetic energy release distributions seem to have been mainly ignored in these cases, although they were included in a few cases [31,4,32,33,34].

The absence of a saddle point in the traditional sense presents a situation for which detailed balance is well suited. The formulation of detailed balance theory was pioneered by Weisskopf to describe the emission of neutrons from highly, incoherently excited nuclei [42]. Like for neutrons impinging on a nucleus, there is by assumption no intrinsic barrier for the reverse process in the problem. However, even in the absence of a static barrier, a barrier will arise in the radial motion as the combination of the long range angular momentum repulsion and the short range attraction of the cohesive forces in the system, and there are therefore obvious







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advantages to be able also to treat a saddle point transition state with detailed balance.

The purpose of the present work is to provide results for the quantum corrections to kinetic energy release distributions in a few situations where the calculations are tractable. The RRKM situation is fairly straightforward but the derivation of the result will serve to shed light on the connection between the saddle point transition state theory and detailed balance theory, which then will be used for the non-barrier calculation.

The quantization of the rotational motion of the parent and product will be ignored on the grounds of relative unimportance. Moments of inertia are assumed so large and rotational levels consequently so closely spaced that angular momenta can be treated as continuous variables. Angular momentum conservation is automatic in capture processes in spherical potentials and need not be implemented explicitly [35]. Also the changes in angular momentum of the large fragment due to the removal of the orbital angular momentum is ignored. With the mass of the evaporated small fragment, assumed a monomer, denoted by μ , its kinetic energy by ε , the linear dimension of the decaying particle by r_0 and its rotational energy by $E_{rot,N}$, the ratio of the orbital and molecule/cluster angular momentum is on the order of

$$\frac{L_o}{L_N} \sim \frac{r_0 \sqrt{2\mu\varepsilon}}{r_0 \sqrt{2\mu N E_{rot,N}}} = \sqrt{\frac{\varepsilon}{N E_{rot,N}}},\tag{1}$$

which is usually small and means that the changes in rotational density of states of the product can be ignored [36].

2. RRKM-KER

The kinetic energy release distributions of the decay channel for a saddle point transition state is determined by the RRKM rate constant

$$k(E) = \frac{N_t(E - E_t)}{h\rho_r(E)},\tag{2}$$

where *E* is the excitation energy, E_t the activation energy required to reach the transition state, N_t is the integrated level density of the transition state,

$$N_t \equiv \int_0^{E-E_t} \rho_t(E') dE' = \int_0^{E-E_t} \rho_t(E-E_t-\varepsilon) d\varepsilon,$$
(3)

where ε is the kinetic energy released in the process, and ρ_r is the level density of the reactant. *h* is Planck's constant. The energy-specified rate constant which gives the kinetic energy release distributions is

$$k(E;\varepsilon)\mathrm{d}\varepsilon = \frac{\rho_t(E - E_t - \varepsilon)}{h\rho_r(E)}\mathrm{d}\varepsilon. \tag{4}$$

It is convenient to express the dependence of the product level density on ε with a simple exponential expression based on the leading order expansion of the logarithm:

$$\rho_t(E - E_t - \varepsilon) \approx e^{\ln(\rho_t(E - E_t)) - \varepsilon^{\frac{\partial \ln(\rho_t(E - E_t))}{\partial E}}} \equiv e^{-\varepsilon/k_B T_t} \rho_t(E - E_t),$$
(5)

where T_t is the effective temperature of the transition state. This expansion has been discussed at a number of places (see e.g. [37]) and will be used here without any further justification. The kinetic energy release distribution at the top of the barrier becomes

$$k(E,\varepsilon)\mathrm{d}\varepsilon \propto \mathrm{e}^{-\varepsilon/T_t}\mathrm{d}\varepsilon. \tag{6}$$

Boltzmann's constant, k_{B} , is set equal to unity here and in the following, i.e. temperatures are measured in energy units or vice versa. Asymptotically separated species will have kinetic energy release distributions shifted by the barrier height $V_{max} - V(r \rightarrow \infty) \equiv \Delta E$:

$$k(E,\varepsilon)\mathbf{d}(\varepsilon) \propto \begin{cases} \mathbf{e}^{-(\varepsilon - \Delta E)/T_t} \mathbf{d}\varepsilon, & (\varepsilon \ge \Delta E) \\ \mathbf{0}, & (\varepsilon < \Delta E) \end{cases}$$
(7)

Apart from this offset, the distributions are uniquely characterized by the transition state temperature.

The many applications RRKM rate constants have found in the past notwithstanding, the derivation of the energy distributions seems not entirely satisfactory, as it is based on a constant potential for the calculation of its semiclassical level density of the reaction coordinate. This step occurs in Eq. (3), where the integration over the decaying states, weighted by the flux factor given by the speed, v, and the concentration, 1/L, gives the differential

$$\frac{v}{L}\frac{1}{h}\mathrm{d}x\mathrm{d}p = \frac{1}{L}\frac{1}{h}\mathrm{d}x\mathrm{d}E',\tag{8}$$

where *L* is the arbitrary length over which one calculates the semiclassical free particle density of states given by the differential on the left hand side of the equation, and where $E' \equiv vp/2$ is the kinetic energy. The flat potential that gives rise to the specific expression in Eq. (8) is causing the potential conflict with the assumed parabolic parametrization of the barrier.

To examine the point where this inconsistency has quantitative consequences, the range of applicability of the approximation needs to be examined. A necessary criterion for the use of the density of states derived from a flat potential is that the de Broglie wavelength, λ of the quasi-particle, as calculated point-wise from the kinetic energy, does not change significantly over one wavelength. With the potential, centered at x = 0,

$$V = -\frac{1}{2}\mu\omega^2 x^2,\tag{9}$$

and a kinetic energy $\boldsymbol{\epsilon}$ at the top of the barrier, the criterion becomes

$$\frac{h}{p(0)} - \frac{h}{p(\lambda(0))} \ll \frac{h}{p(0)} \Rightarrow \varepsilon \gg h\omega/2.$$
(10)

With typical kinetic energies of $\varepsilon \sim T_t/2$ this becomes

$$\Gamma_t \gg 2\pi\hbar\omega.$$
 (11)

With $\hbar\omega$ on the order of typical vibrational frequencies, this inequality is not trivially fulfilled. It is therefore necessary to evaluate the corrections to Eq. (6) arising from this approximation.

One may attempt to calculate the corrections with an improved single degree level density for the reaction coordinate. Attempts to do so tend to introduce ambiguities, because the inverted parabola does not have a natural quantization due to the absence of classical turning points, and boundary conditions will then have to be introduced by hand in an ad hoc fashion.

The application of the requirement of detailed balance to the reaction solves this problem. Detailed balance is based on the identity of the product of the level density of one of the states and the rate constant out of this state to the analogous product for the inverse process. In unimolecular decay this leads to the rate constants

$$k(E;\varepsilon)\mathrm{d}\varepsilon = \frac{g\mu}{\pi^2\hbar^3}\sigma(\varepsilon)\varepsilon\frac{\rho_t(E-E_a-\varepsilon)}{\rho_r(E)}\mathrm{d}\varepsilon,\tag{12}$$

where *E* is the excitation energy, ε the kinetic energy, *g* the small fragment electronic degeneracy, or more generally electronic partition function [38], μ the reduced mass of the channel, $\sigma(\varepsilon)$ the energy dependent capture cross section for the inverse process, and *E*_a the activation energy, which in this case is the energy of the transition state minus the ground state energy of the reactant.

The similarity with the RRKM equation is obvious and would become even more after integration over the kinetic energy of the channel. For the purpose of this discussion, the salient point in the equation is the presence of the capture cross section and the absence of a reaction coordinate translational motion level density. The equation is general, as written, and the connection to the one-dimensional RRKM problem is established by considering the steps that lead to Eq. (12). Apart from the electronic degeneracy factor, which will be ignored for this calculation, the factor multiplying the ratio of level densities is the three dimensional analogue to Eq. (8). It arises as the product of the fragment concentration, the speed v, and the capture cross section, σ ;

$$v\frac{1}{V}\frac{\mathrm{d}^{3}p\int\mathrm{d}^{3}x}{h^{3}}\sigma(\varepsilon) = v\frac{\mathrm{d}^{3}p}{h^{3}}\sigma(\varepsilon), \tag{13}$$

where the cancelled quantity V is the volume of the container where the reaction takes place. When the reaction proceeds onedimensionally, along the *z*-axis, say, the cross section can be expressed as

$$\sigma(\varepsilon) = |T(\varepsilon)|^2 h^2 \delta(p_x) \delta(p_y), \tag{14}$$

where *T* is a dimensionless transmission coefficient which is a function of the kinetic energy, and hence $|T|^2$ the transmission probability.

It is implicit in the calculation here and in standard RRKM theory that the shape of the saddle point does not change during passage. A periodic variation of the transition state potential has been found to influence the tunneling rate [39]. Such corrections will not be discussed here.

Inserting the cross section in Eq. (14) into the equation for the prefactor, Eq. (13), and integrating out the two momenta p_x, p_y gives

$$\int dp_x dp_y \frac{\nu dp_z}{h^3} \sigma(\varepsilon) = \frac{\nu_z}{h} |T(\varepsilon)|^2 dp_z = |T(\varepsilon)|^2 \frac{d\varepsilon}{h}.$$
(15)

This result should be compared with the prefactor in Eq. (2). We see that these are identical when the transmission coefficient is a step-function with the step at zero energy,

$$|T(\varepsilon)|^2 = \Theta(\varepsilon),$$
 (classical motion). (16)

Generally, however, this classical value is insufficient. Two (related) effects will make it so. The first is the quantum mechanical tunneling of atoms through the top of the barrier. This will allow transmission of particles with energy below the saddle point through the barrier. The other effect, also of quantum mechanical origin, is the fact that impinging particles will be reflected with non-zero probability also above the barrier. The effective density of states of the reaction coordinate is then the free particle values multiplied by the transmission coefficient.

Both tunneling and reflection can be accounted for by a single calculation, as was already shown in [4], where the consequences for the total unimolecular rate constants were derived. The potential around the saddle point was assumed to be of the form [40]

$$V = \Delta E \cosh^{-2} \left(\frac{\mu}{\Delta E} \omega z \right)$$

$$\approx \Delta E - \frac{1}{2} \mu \omega^2 z^2 + \mathcal{O} \left(\frac{1}{24} \frac{\mu^3 \omega^6 z^6}{\Delta E^2} \right),$$
(17)

centered at z = 0. The transmission coefficient of this potential is calculated in [41]. It is, with higher order exponentially suppressed terms left out, equal to

$$|T|^{2} = \frac{e^{4\pi\frac{\hbar E}{\hbar bo}}(\sqrt{1+\frac{E}{\Delta E}-1})}{e^{4\pi\frac{\hbar E}{\hbar bo}}(\sqrt{1+\frac{E}{\Delta E}-1})+1},$$
(18)

which also includes cases of negative kinetic energies, as measured from the top of the saddle point. With Eq. (7) this gives the distributions far from the saddle point, shifted by ΔE ;

$$k(E,\varepsilon)\mathbf{d}(\varepsilon) \propto e^{-(\varepsilon - \Delta E)/T_t} \frac{e^{4\pi \frac{\Delta E}{\hbar\omega}(\sqrt{\frac{\varepsilon}{\Delta E}} - 1)}}{e^{4\pi \frac{\Delta E}{\hbar\omega}(\sqrt{\frac{\varepsilon}{\Delta E}} - 1)} + 1} d\varepsilon,$$
(19)

where $\varepsilon \ge 0$. If ΔE is much larger than the typical thermal energy, which can be verified in the experimental kinetic energy release spectra, the arguments of the exponentials can be expanded to first order in $\varepsilon - \Delta E$ to give

$$k(E,\varepsilon)\mathbf{d}(\varepsilon) \propto e^{-(\varepsilon - \Delta E)/T_t} \frac{e^{\frac{2\pi(\varepsilon - \Delta E)}{\hbar\omega}}}{e^{\frac{2\pi(\varepsilon - \Delta E)}{\hbar\omega}} + 1} \mathbf{d}\varepsilon.$$
 (20)

This covers $\varepsilon < \Delta E$, as well as above-the-barrier situations. As also observed in [4], this energy dependence allows for situations where the kinetic energy release distribution is peaked at an energy corresponding to tunneling. This will occur when (see Fig. 1)

$$\hbar \omega > \pi T. \tag{21}$$

3. Spherical potentials

As mentioned previously, a significant part of measured kinetic energy release distributions show no appreciable gap, $\Delta E \approx 0$. However, the equations of motion for the radial coordinate still contains the centrifugal barrier. With the static potential V(r), the total (effective) radial potential is

$$V_e(r) = V(r) + \frac{L^2}{2\mu r^2},$$
 (22)

where *L* is the magnitude of the (conserved) angular momentum vector, μ is the reduced mass of the channel and *r* the center-ofmass distance between the two fragments. The barrier for this potential is fairly asymmetric, with a short range attractive part and a long repulsive tail.

A general solution to this problem in closed form is not feasible because of the number of different possible functional forms of the potentials. We will here treat only the two special cases of (i) the potential arising from the interaction of a small, polarizable fragment and a larger ionic fragment, and (ii) two neutral species with no interaction beyond a contact distance, at which they fuse. Case (i) has been considered in [44], but with a tunneling matrix element based on Coulomb repulsion, i.e. a 1/r vs. the relevant $1/r^2$ repulsive potential. The question therefore deserves a second view.



Fig. 1. The transmission coefficient (dotted line), the uncorrected kinetic energy distribution (dashed line), and the corrected kinetic energy release distribution according to Eq. (20) (full line), all for a model system with $\Delta E = 1 \text{ eV}$, $\hbar \omega = T_t = 0.1 \text{ eV}$. The curves for Eqs. (19) and (20) are indistinguishable on the scale of the figure.

3.1. Langevin cross section corrections

For case (i), the classical cross section is the one given by Langevin;

$$\sigma_L = \pi \left(\frac{2\alpha''}{\varepsilon}\right)^{1/2},\tag{23}$$

where $\alpha'' \equiv \alpha e^2/4\pi\epsilon_0$ and α is the polarizability. The dimension of α'' is energy times length to the fourth power. The derivation of this cross section is based on conservation of angular momentum and energy which combine to give the equation of motion for the radial coordinate:

$$\varepsilon = -\frac{1}{2}\frac{\alpha''}{r^4} + \frac{1}{2}\mu\dot{r}^2 + \varepsilon\frac{b^2}{r^2},$$
(24)

when the angular momentum is expressed in terms of the impact parameter *b*. For the point where the time derivative of the radial coordinate is zero, $\dot{r} = 0$, there is a highest value of b, b_m , for which this equation has a solution. The cross section equals πb_m^2 . The radial distance corresponding to \dot{r} is located at the maximum of the effective radial potential

$$V_e = -\frac{1}{2}\frac{\alpha''}{r^4} + \frac{L^2}{2\mu r^2}.$$
 (25)

The magnitude of the angular momentum is

$$L = b\sqrt{2\mu\varepsilon}.$$
 (26)

Expanding the potential to second order in r at the maximum gives

$$V_e \approx \frac{L^4}{8\mu^2 \alpha''} - \frac{1}{4} \frac{L^6}{\mu^3 \alpha''^2} \left(r - \frac{\sqrt{2\mu\alpha''}}{L} \right)^2.$$
(27)

Identification of the terms with those of Eq. (17) and representing the barrier with Eckart's function, disregarding the asymmetry of the barrier, we have the correspondences

$$\Delta E \leftrightarrow \frac{L^4}{8\mu^2 \alpha''},\tag{28}$$
$$\omega \leftrightarrow \frac{L^3}{\sqrt{2\mu^2 \alpha''}}.$$

The modified capture cross section is then calculated as

$$\sigma(\varepsilon) = \int_0^\infty 2\pi |T|^2 b db, \tag{29}$$

with the transmission coefficient given in Eq. (18). Expressed with the parameters

$$\Delta E = \frac{\varepsilon^2}{2\alpha''} b^4 \equiv ab^4, \tag{30}$$
$$\hbar \omega = \hbar \frac{2\varepsilon^{3/2}}{\sqrt{\mu}\alpha''} b^3 \equiv cb^3,$$

the cross section becomes

$$\sigma = 2\pi \int_0^\infty \frac{e^{\frac{2\pi(e-ab^4)}{cb^3}}}{e^{\frac{2\pi(e-ab^4)}{cb^3}} + 1} b \, db.$$
(31)

With typical values of parameters, $\varepsilon = 0.1$ eV and μ some tens of Dalton, the numerator of the argument of the exponential varies much faster than the denominator. With an expansion to first order in *b* around the critical impact parameter where the fraction vanishes, we then get

$$\sigma = 2\pi \int_0^\infty \frac{e^{\frac{8\pi a}{c} \left(b - \left(\frac{a}{a}\right)^{1/4}\right)}}{e^{-\frac{8\pi a}{c} \left(b - \left(\frac{a}{a}\right)^{1/4}\right)} + 1} b \, db.$$
(32)

The expansion of the argument of the exponential, retaining only the first order term is not very accurate. However, as numerical examples below will show, the effects are small for this potential, and approximations do not need to be extremely good at this point.

Continuing therefore with this approximation, we note that the derivative of the argument of the exponential is typically 10^{12} m⁻¹ at the expansion point. The expression can therefore be calculated with the Sommerfeld expansion [45] with *b* in the role of energy, $c/8\pi a$ as temperature and $(\varepsilon/a)^{1/4}$ acting as the chemical potential. The result is

$$\sigma = \pi \left(\frac{2\alpha''}{\varepsilon}\right)^{1/2} + \frac{\pi}{24} \frac{\hbar^2}{\mu\varepsilon}.$$
(33)

The first term is the Langevin cross section, and the second the quantum correction. For masses of a few tens of Dalton and kinetic energies of 0.1 eV, the correction is small. For the specific example of C₂ loss from an idealized point-like C₆₀, using the parameter values $\alpha'' = 72 \text{ eV} \text{ Å}^4$ [46], $\mu = 24 \text{ u}$, and the energy 0.4 eV, gives the negligible correction of $2 \cdot 10^{-4} \text{ Å}^2$. For atoms evaporating from helium droplets, with T = 0.4 K, the correction is 4 Å^2 , which is comparable to the surface diffuseness squared in these systems.

3.2. Absorbing sphere

The Langevin cross section describes an idealized situation where the interacting particles are point-like. To account for the size of the involved molecules, the simplest step is to introduce a finite radius, r_0 , at which the two particles fuse. The general solutions of the classical equations of motion in that case are easily obtained for attractive potentials by an extension of the reasoning used to derive the Langevin cross section (see for example section 5 of chapter 5 in [35]). Including the finite capture radius into the Langevin cross section will, however, introduce a new parameter in the problem, viz. the position of the barrier relative to the capture radius. This will change the shape of the barrier maximum from a rounded shape to a strongly peaked one, and all possible combinations of these in between. This makes a solution very unwieldy, requiring the patching together of several approximate solutions. We will here consider the simpler case of vanishing long range interactions. This corresponds to calculating the quantum corrections to the capture cross section of two neutral particles with no appreciable product of polarizabilities.

The absence of a long range potential renders the radial potential that of the angular momentum barrier with a sharp cutoff at the absorbing sphere radius;

$$V_e = \begin{cases} \frac{L^2}{2\mu r^2} & (r \ge r_0), \\ -\infty & (r < r_0). \end{cases}$$
(34)

The potential is reminiscent of the emission of electrons from a surface in an electric field [47]. The known exact solutions [48,43] for that problem are unfortunately only marginally relevant here, because the differences in the potentials are still too large. Furthermore, we note that the identification of the flat potential in the interior of a solid surface, relevant for thermionic emission from the quasi-free electron gas in metals, with the absorbing potential relevant here may be a questionable proposition.

The reflection requires special consideration in the absence of a long range potential. Physically, the reflection corresponds to scattering from regions where there is no potential and none has been encountered. It is not reasonable to expect such an effect to appear in a semiclassical calculation. The same conclusion is also reached if one considers the motion around an arbitrarily chosen point in the absence of any potential. Clearly, this will not lead to any reflection. The reflection will therefore be set to zero, and the tunneling through the barrier will be the only effect that will be considered.

The square modulus of the Wenzel-Brillouin-Kramers tunnel matrix element is given by

$$|T|^{2} = \exp\left(-\frac{\sqrt{2\mu}}{\hbar}\int_{r_{0}}^{r_{t}}\left(\frac{L^{2}}{2\mu r^{2}}-\varepsilon\right)^{1/2}\mathrm{d}r\right)$$
$$= \exp\left(-\frac{r_{0}\sqrt{2\mu\varepsilon}}{\hbar}\frac{b}{r_{0}}\int_{1}^{b/r_{0}}x^{-2}\sqrt{x^{2}-1}\,\mathrm{d}x\right),\tag{35}$$

where $r_t = b$ is the classical turning point (there are two, the outer is the relevant one here). This predicts complete transmission at the top of the barrier and above, corresponding to our case.

The integral in Eq. (35) has no solution in terms of known functions [49]. Instead it was found numerically that in the interval $10^{-2} \le b/r_0 - 1 \le 1$, the product of the integral and the prefactor b/r_0 is well approximated by the function $0.93(b/r_0 - 1)^{1.5}$. With this, the cross section can be calculated in terms of the gamma function. The result is:

$$\sigma(\varepsilon) = \pi r_0^2 \left(1 + 1.31 \left(\frac{\hbar}{r_0 \sqrt{2\mu\varepsilon}} \right)^{4/3} + 1.89 \left(\frac{\hbar}{r_0 \sqrt{2\mu\varepsilon}} \right)^{2/3} \right).$$
(36)

With the abbreviation

$$\varepsilon_0 \equiv \frac{\hbar^2}{2\mu r_0^2},\tag{37}$$

the corresponding kinetic energy release distributions are then

$$P(\varepsilon)d\varepsilon \propto \varepsilon \left(1 + 1.31 \left(\frac{\varepsilon_0}{\varepsilon}\right)^{2/3} + 1.89 \left(\frac{\varepsilon_0}{\varepsilon}\right)^{1/3}\right) e^{-\varepsilon/T} d\varepsilon.$$
(38)

The corrections have the largest consequences for light species with low binding energies. The average kinetic energy is calculated to

$$\langle \varepsilon \rangle = T \frac{2 + 1.56 \left(\frac{\varepsilon_0}{T}\right)^{2/3} + 5.63 \left(\frac{\varepsilon_0}{T}\right)^{1/3}}{1 + 1.17 \left(\frac{\varepsilon_0}{T}\right)^{2/3} + 3.38 \left(\frac{\varepsilon_0}{T}\right)^{1/3}}.$$
(39)

Fig. 2 shows the calculated values for a helium droplet with radius 1 nm at a product temperature of 0.4 K, which is the expected value for such droplets. The average energy in the tunneling-corrected spectrum is 0.71 K, vs. the 0.8 K for the uncorrected spectrum. Fig. 3 shows the average values as a function of the dimensionless parameter $\hbar/r_0\sqrt{2\mu T}$. The integrated spectra differ by a factor of 2.2, i.e. the averaged cross section increases



Fig. 2. The kinetic energy release distributions for a helium droplet of radius 1 nm with the quantum corrected capture cross section of Eq. (36) (full line) and uncorrected (dotted line). The curves are normalized to the same area.



Fig. 3. The average kinetic energy vs. the parameter $\hbar/r_0\sqrt{2\mu T}$.

by this factor when tunneling is taken into account. This factor also gives the increase in total rate constant due to tunneling. The width is less affected; The standard deviation is reduced from 0.57 K to 0.54 K.

4. Summary

The kinetic energy release distributions gains considerable corrections in saddle point transition states. For the two spherical systems investigated, only the absorbing sphere leads to a measurable change in the KER distributions, most pronounced for light fragments and small effective product temperatures.

Declarations of conflicting interest

None.

References

- Wendell Forst, 'Theory of Unimolecular Reactions', Academic Press, New York and London, 1973.
- [2] Thomas Baer, William L. Hase, 'Unimolecular Reaction Dynamics', Oxford University Press, New York, Oxford, 1996.
- [3] J. Laskin, C. Lifshitz, J. Mass Spectrom. 36 (2001) 459-478.
- [4] W.H. Miller, J. Am. Chem. Soc. 101 (1979) 6810.
- [5] J.F. Elder Jr., R.G. Cooks, J.H. Beynon, Org. Mass Spectrom. 11 (1976) 423–428.
- [6] In Chul Yeh, Myung Soo Kim, Rapid Commun. Mass Spectrom. 6 (1992) 293-297.
- [7] Tae Geol Lee, Seung C. Park, Myung Soo Kim, J. Chem. Phys. 104 (1996) 4517.
- [8] D.Y. Kim, J.C. Choe, M.S. Kim, J. Phys. Chem. A 103 (1999) 4602–4608.
- [9] B. Manil, L. Maunoury, J. Jensen, H. Cederquist, H.T. Schmidt, H. Zettergren, P. Hvelplund, S. Tomita, B.A. Huber, Nucl. Instr. Meth. Phys. Res. B 235 (2005) 419–424.
- [10] D.M. Mintz, T. Baer, Int. J. Mass Spectrom. Ion Phys. 25 (1977) 39.
- [11] C. Lifshitz, E. Tzidony, Int. J. Mass Spectrom. Ion Phys. 39 (1981) 181-195.
- [12] C. Lifshitz, P. Berger, E. Tzidony, Chem. Phys. Lett. 95 (1983) 109.
- [13] W. Brand, T. Baer, Chem. Phys. 76 (1983) 111.
- [14] C. Lifshitz, S. Gefen, R. Arakawat, J. Phys. Chem. 88 (1984) 4242-4246.
- [15] B.E. Miller, T. Baer, Chem. Phys. 85 (1984) 39-45.
- [16] D.V. Dearden, J.L. Beauchamp, P.A.M. van Koppen, M.T. Bowers, J. Am. Chem. Soc. 112 (1990) 9372.
- [17] P.A.M. van Koppen, M.T. Bowers, J.L. Beauchamp, Organometallics 9 (1990) 625-630.
- [18] Seung Il Cho, Joong Chul Choet, Myung Soo Kim, Rapid Commun. Mass Spectrom. 7 (1993) 594.
- [19] I.C. Yeh, Y.H. Kim, M.S. Kim, Chem. Phys. Lett. 207 (1993) 487.
- [20] J.C. Lorquet, B. Leyht, Org. Mass Spectrom. 28 (1993) 1225-1228.
- [21] J. Gidden, P.A.M. van Koppen, M.T. Bowers, J. Am. Chem. Soc. 119 (1997) 3935– 3941.
- [22] F. Gu1the, R. Locht, B. Leyh, H. Baumgärtel, K.-M. Weitzel, J. Phys. Chem. A 103 (1999) 8404–8412.
- [23] P. Urbain, B. Leyh, F. Remacle, A.J. Lorquet, R. Flammang, J.C. Lorquet, J. Chem. Phys. 110 (1999) 2911.
- [24] P. Urbain, B. Leyh, F. Remacle, J.C. Lorquet, Int. J. Mass Spectrom. 185/186/187 (1999) 155–163.

- [25] J.C. Lorquet, Int. J. Mass Spectrom. 201 (2000) 59-67.
- [26] S. Matt, O. Echt, A. Stamatovic, T.D. Märk, J. Chem. Phys. 113 (2000) 616.
- [27] J.J. Hache, J. Laskin, J.H. Futrell, J. Phys. Chem. A 106 (2002) 12051–12057. [28] S. Matt-Leubner, A. Stamatovic, R. Parajuli, P. Scheier, T.D. Märk, O. Echt, C.
- Lifshitz, Int. J. Mass Spectrom. 222 (2003) 213–219. [29] J.J. Hache, J.H. Futrell, J. Laskin, Int. J. Mass Spectrom. 233 (2004) 223–231.
- [30] K. Głuch, S. Matt-Leubner, O. Echt, R. Deng, J.U. Andersen, P. Scheier, T.D. Märk, Chem. Phys. Lett. 385 (2004) 449-455.
- [31] B.H. Solka, J.H. Beynon, R.G. Cooks, J. Phys. Chem. 79 (1975) 859.
- [32] A.J. Illies, M.F. Jarrold, M.T. Bowers, J. Am. Chem. Soc. 104 (1982) 3587.
- [33] J.A. Booze, K.-M. Weitzel, T. Baer, J. Chem. Phys. 94 (1991) 3649-3656.
- [34] D.S. Won, J.C. Choe, M.S. Kim, Rapid Commun. Mass Spectrom. 14 (2000) 1110-1115.
- [35] K. Hansen, Statistical Physics of Nanoparticles in the Gas Phase, Springer, Dordrecht, 2013.
- [36] K. Hansen, Chem. Phys. Lett. 383 (3-4) (2004) 270.
- [37] J.U. Andersen, E. Bonderup, K. Hansen, J. Chem. Phys. 114 (2001) 6518-6525.

- [38] K. Hansen, M. Manninen, J. Chem. Phys. 101 (1994) 10481.
- [39] Jiu-Yuan Ge, John Z.H. Zhang, J. Chem. Phys. 105 (1996) 8628.
- [40] C. Eckart, Phys. Rev. 35 (1930) 1303.
- [41] L.D. Landau, E.M. Lifshitz, Quantum Mechanics, Non-relativistic Theory, Pergamon Press, Oxford, 1976.
- [42] V. Weisskopf, Phys. Rev. 52 (1937) 295-303.
- [43] R.G. Forbes, J.H.B. Deane, Proc. Roy. Soc. A 467 (2011) 2927–2947.
- [44] C.E. Klots, Chem. Phys. Lett. 10 (1971) 422.
- [45] N.W. Ashcroft, N.D. Mermin, Solid State Physics, Saunders College Publishing, Fort Worth, 1976.
- [46] C. Kamal, A. Banerjee, T.K. Ghanty, A. Chakrabarti, Int. J. Quant. Chem. 112 (2012) 1097-1106.
- [47] R.H. Fowler, L. Nordheim, Proc. Roy. Soc. Lond. Ser. A 119 (1928) 173-181. [48] D.N. Christodoulides, A.G. Andreou, R.I. Joseph, C.R. Westgate, Solid State
- Electron. 28 (1985) 821-822. [49] I.S. Gradshteyn, I.M. Ryzhik, Table of Integrals, Series and Products, Academic
- Press, San Diego, 1994.