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Unimolecular Reaction Dynamics from Kinetic Energy Release Distributions. 7. Average Translational Energy Release

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The relationship between the average translational energy $\langle\epsilon\rangle$ released in a unimolecular reaction and the internal energy E measured in excess of the dissociation threshold is not necessarily linear. In a purely statistical situation, it reflects the shape of the function $N(E)$ which expresses the way the density of vibrational−rotational states of the pair of fragments increases with E. In fact, $\langle\epsilon\rangle$ is seen to vary as a function of E in exactly the same way as $\{\mathrm{d}\ln[N(E)]/\mathrm{d}E^{-1}$. The most important feature of $N(E)$ is a dimensionless parameter $\gamma = E\{\mathrm{d}\log_{10}[N(E)]/\mathrm{d}E\}$ evaluated at the internal energy at which the measurement of $\langle\epsilon\rangle$ is made. The ratio $\langle\epsilon\rangle/E$ also depends on nonstatistical effects. An "ergodicity index" $\mathrm{e}^{-\mathrm{DS}}$, where DS denotes the so-called entropy deficiency associated with incomplete energy randomization, can be extracted from experiments. It measures the efficiency of phase space sampling by the pair of fragments. In the case of unimolecular reactions that proceed without any reverse activation barrier, simple relationships can be derived to relate the value of $\mathrm{e}^{-\mathrm{DS}}$ to that of γ and $\langle\epsilon\rangle/E$. When the average energy release is measured for a metastable dissociation in a two-sector mass spectrometer, the ratio $\langle\epsilon\rangle/E$ also depends in principle on the transmission efficiency function $T(E)$. However, the necessary correction is small and often negligible. Applications to the halogen loss reactions from $C_2H_5I^+$, $C_6H_5Br^+$, and $C_6H_5I^+$ are presented. Phase space appears to be sampled with an efficiency close to 100% both at very low and very high values of the internal energy. For intermediate values of E, the minimal efficiency is of the order of 75%. At higher values of the internal energy, numerous surface crossings bring about chaotic dynamics and efficient phase space sampling.

I. Introduction

A matter of considerable interest, both for its intrinsic importance in the study of the dynamics of unimolecular reactions and for its practical usefulness in the derivation of correct thermodynamic data, concerns the partitioning of the excess energy of a dissociation process among the translational, rotational, and vibrational degrees of freedom of the products. Mass spectrometric experimentation[1−11] is able to provide a so-called kinetic energy release distribution (KERD), denoted $P(\epsilon|E)$, giving the probability of generating fragments with a relative translational energy equal to ϵ if E denotes the internal energy, measured in excess of the dissociation threshold. This function is required to be normalized:

$$\int_0^E P(\epsilon|E)\,\mathrm{d}\epsilon = 1 \tag{1}$$

Average translational energy releases $\langle\epsilon\rangle$ are defined by

$$\langle\epsilon\rangle = \int_0^E \epsilon P(\epsilon|E)\,\mathrm{d}\epsilon \tag{2}$$

In the present paper, attention will be focused on the proportion of the excess energy released as translation $\langle\epsilon\rangle/E$. Furthermore, the discussion will be restricted to reactions that proceed without any reverse activation barrier.

Early attempts to rationalize this ratio[12−17] were based on the RRKM-QET theory.[1,12,18] Assuming (i) a fully statistical situation and (ii) that the kinetic energy in the reaction coordinate at the transition state is entirely converted into translational energy of the pair of fragments (thus neglecting exit channel effects), and (iii) ignoring the rotational degrees of freedom, the following equation can be derived:

$$P(\epsilon|E) = N^{\ddagger}(E-\epsilon)/\int_0^E N^{\ddagger}(E')\,\mathrm{d}E' \tag{3}$$

where $N^{\ddagger}(E)$ denotes the density of vibrational states of the transition state.

Assuming further that $N^{\ddagger}(E)$ increases with E as predicted by the classical approximation,[1,12,18] that is, assuming that

$$N^{\ddagger}(E) \propto E^{N_{\mathrm{react}}-2} \tag{4}$$

where N_{react} is the number of vibrational degrees of freedom in the reactant, one obtains an expression of the KERD:

$$P(\epsilon|E) = \left[\frac{N_{\mathrm{react}}-1}{E}\right]\left(1-\frac{\epsilon}{E}\right)^{N_{\mathrm{react}}-2} \tag{5}$$

The substitution of eq 5 into eq 2 leads to the simple equipartition limit $\langle\epsilon\rangle = E/N_{\mathrm{react}}$. Klots,[13] Franklin and co-workers,[14−16] and Carter[17] made various attempts to replace the classical density of states by a more accurate expression (e.g., the Whitten-Rabinovitch approximation).[1,12,18,19] Nevertheless, most authors have adopted the simple, but purely empirical correction proposed by Haney and Franklin,[14] which involves an effective number of oscillators in the transition state and which leads to the linear relationship $\langle\epsilon\rangle = E/0.44N_{\mathrm{react}}$.

However, the classical approximation (4) is known to be inaccurate, especially at low internal energies,[1,12,18] and its use is always somewhat suspicious. We note first that if it is replaced

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by an alternative empirical parametrization

$$N^{\ddagger}(E) \propto \exp(\alpha E) \tag{6}$$

which is still reasonable, although it somewhat overestimates the rate of increase of the density of states, then the conclusions change completely.

$$P(\epsilon|E) = [\alpha/(1 - e^{-\alpha E})]e^{-\alpha\epsilon} \approx \alpha e^{-\alpha\epsilon} \tag{7}$$

One has which, in practice, is apparently very close to eq 5. However, when eq 7 is substituted into eq 2, one gets simply $\langle\epsilon\rangle \approx \alpha^{-1}$, i.e., a constant energy release, independent of the internal energy!

Another possible parametrization of the density of states has been previously found[20] to be quite appropriate in a number of cases:

$$N^{\ddagger}(E) \propto \exp(\beta E^{1/2}) \tag{8}$$

However, when introduced into eqs 3 and 2, it predicts that the average translational energy release $\langle\epsilon\rangle$ should approximately increase as the square root of the available internal energy:

$$\langle\epsilon\rangle = (2/\beta)E^{1/2}[1 - 3/(2\beta E^{1/2}) \ldots] \tag{9}$$

Clearly, these observations call for further investigation into the matter.

A new impetus to the theory was given when Klots applied the principle of microscopic reversibility to the fragmentation and its reverse association reaction.[21−23] It follows that the relevant density of states is that of the pair of fragments and no longer that of the reactant or of the transition state. A major development in the study of translational energy releases resulted when various versions of phase space theory were introduced[1,3−6,9] in order to ensure conservation of angular momentum. Additionally, Klots assumed canonical equilibrium among translational, rotational, and vibrational degrees of freedom. The usual laws of statistical thermodynamics predict progressive excitation of vibrational levels as the temperature increases. This leads to a nonlinear, transcendental yet very simple equation between $\langle\epsilon\rangle$ and E.[1,24,25]

It will be argued in the present paper that the nonlinear relationship between $\langle\epsilon\rangle$ and E has a double origin. First, it reflects the distribution of energy levels of the pair of fragments, i.e., the way densities of states increase with E, represented by the function $N(E)$. Second, the relationship is also influenced by nonstatistical effects, i.e., by incomplete energy randomization.

II. Maximum Entropy Method

What is the dynamical significance of the translational energy at an infinite value of the reaction coordinate? There exists a method, called the maximum entropy analysis,[26−31] which addresses this problem. This theory is based on a new concept, denoted the *entropy deficiency* DS, which is directly related to the amount of vibrational energy not being randomized. More properly, any constraint acting on the dynamics along the reaction path (and thus leading to nonstatistical behavior) brings about a nonzero value of DS. In that approach, the concept of effective degrees of freedom is elaborated upon and replaced by an *effective number of phase space cells* sampled by the products. This number of cells is known[32] to be equal to the number of the vibrational−rotational states to which the fragments are effectively excited. In the maximum entropy approach, the fraction of states effectively populated with respect to its maximum value is measured by the quantity e^{-DS}.[33,34] Therefore, this quantity measures the efficiency of the randomization process. It can also be referred to as an "*ergodicity index*", with $e^{-DS} = 1$ corresponding to a complete exploration of the available phase space whereas small values of e^{-DS} indicate inefficient energy randomization. In previous papers of this series[20,35−38] it has been shown how the value of e^{-DS} can be extracted from an analysis of the entire KERD. Values of the order of 80% have been commonly obtained in the fragmentation of various ions like those of the halogenobenzenes,[35,36] pyridine,[37] and vinyl bromide,[38] while the dissociation of ionized iodopropane is found to proceed nearly statistically.[20] The variation with energy of the efficiency of phase space sampling has also been studied.[38]

The maximum entropy method starts by considering a hypothetical situation where the dynamics would proceed without any constraint other than energy conservation (thus disregarding the requirement that angular momentum be conserved). If this were the case, then all accessible quantum states of the pair of fragments would be populated with the same probability. The corresponding distribution of translational energies is called the *prior distribution.*[1,26−30,39] It is simply proportional to the total density of states and will be denoted by $P^0(\epsilon|E)$.

At a given total energy E, let us denote by ϵ the amount of energy that has flowed into the reaction coordinate with the remainder $(E - \epsilon)$ appearing as vibrational−rotational energy of the pair of fragments. Denoting as $N(E - \epsilon)$ the density of vibrational−rotational states of the pair of fragments, one has simply

$$P^0(\epsilon|E) \propto \epsilon^{1/2}N(E - \epsilon) \tag{10}$$

since the density of translational states in a three-dimensional space[1,26−30,32] is proportional to $\epsilon^{1/2}$. The prior distribution is normalized according to eq 1.

As explained in previous papers of this series,[20,35−38] a maximum entropy analysis reveals that, in all cases studied so far, the actual KERD is related to the prior distribution in the following way:

$$P(\epsilon|E) = e^{-\lambda_0}e^{-\lambda_1\epsilon^{1/2}}P^0(\epsilon|E) \tag{11}$$

The physical meaning of this equation is that the unimolecular distribution of ions is not completely statistical. It is subject to a dynamical constraint which is directly related to the square root of the translational energy ϵ, i.e., to the linear momentum of the separating fragments. The factor $\exp(-\lambda_1\epsilon^{1/2})$ which occurs in eq 11 results from this dynamical constraint. The constraint can be identified with the so-called momentum gap law[30,40−43] which is known to operate in molecular predissociation processes, and whose role will be discussed in section IX. The factor $\exp(-\lambda_0)$ is simply a normalization factor to be calculated by substituting eq 11 into eq 1. The entropy deficiency is then given by

$$\mathrm{DS} = \int_0^E P(\epsilon|E)\ln\left[\frac{P(\epsilon|E)}{P^0(\epsilon|E)}\right]\mathrm{d}E = -\lambda_0 - \lambda_1\int_0^E \epsilon^{1/2}P(\epsilon|E)\,\mathrm{d}E = -\lambda_0 - \lambda_1\langle\epsilon^{1/2}\rangle \tag{12}$$

III. Parametrization

Since the density of states is best calculated by a direct count method such as the Beyer−Swinehart algorithm,[1,18,44] the function $N(E)$ is known as a numerical table only. Therefore, there is no loss of generality in fitting the computed sequence of data to an empirical equation. For well-chosen functions, it may then be possible to carry out analytically the integrations required in eqs 1, 2, and 12, and to derive equations in closed form for the translational energy release. Three possible parametrizations for the function $N(E)$ will be examined in the present paper:

$$N(E) = C \exp(\alpha E) \tag{13}$$

$$N(E) = CE^{s} \tag{14}$$

$$N(E) = C \exp(\beta E^{1/2}) \tag{15}$$

The rate of increase of $N(E)$ is directly related to the parameters α, s, or β.

The first two equations are considered for their mathematical simplicity. From past experience, the third one is believed to often be very realistic.

With each possible parametrization of the density of states is associated a particular expression of the prior distribution, which can be normalized via standard calculations.[45,46]

If the density of states increases exponentially with the internal energy (eq 13), one finds

$$P^{0}(\epsilon) = (2/\pi^{1/2})\alpha^{3/2}\epsilon^{1/2}e^{-\alpha\epsilon} \tag{16}$$

Note that this distribution depends on ϵ alone. All reference to the total energy E has vanished because of the property of the exponential function which splits $N(E-\epsilon)$ (occurring in eqs 10 and hence 11) into the product $\exp(\alpha E)\exp(-\alpha\epsilon)$. The first factor $\exp(\alpha E)$, which contains all reference to the total energy E, vanishes in the normalization procedure. The physical consequences of this mathematical property will be discussed later on.

If $N(E)$ increases as the sth power of E (eq 14), then

$$P^{0}(\epsilon|E) = \frac{\Gamma(s + {}^{5}/_{2})}{\Gamma(3/2)\Gamma(s+1)}E^{-s-3/2}\epsilon^{1/2}(E-\epsilon)^{s} \tag{17}$$

where $\Gamma(x)$ denotes the gamma function.[45-47]

Equation 15 has been observed to provide an adequate parametrization of $N(E)$. Then

$$P^{0}(\epsilon|E) = A(E)\epsilon^{1/2}\exp(\beta\sqrt{E-\epsilon}) \tag{18}$$

with

$$A(E)^{-1} = (2/3)E^{3/2} + (\pi/\beta)E[I_2(\beta E^{1/2}) + L_2(\beta E^{1/2})] \tag{19}$$

where $I_2(x)$ and $L_2(x)$ denote the hyperbolic Bessel and Struve functions, respectively.[45-47]

IV. Energy-Resolved Measurements

As already mentioned, the purpose of the present paper is to show that the magnitude of the ratio $\langle\epsilon\rangle/E$ is determined by two factors: the density of states $N(E)$ and the efficiency of phase space sampling e^{-DS}.

If $N(E)$ increases as the sth power of E (eq 14), then the function that results from eqs 11 and 17 is equal to

$$P(\epsilon|E) = \frac{\Gamma(s + {}^{5}/_{2})}{\Gamma({}^{3}/_{2})\Gamma(s+1)}\exp(-\lambda_0)E^{-s-3/2}\epsilon^{1/2}(E-\epsilon)^{s}\exp(-\lambda_1\sqrt{\epsilon}) \tag{20}$$

The factor $\exp(-\lambda_0)$ is a normalization coefficient which can be calculated by substitution into eq 1. The factor $\exp(-\lambda_1\epsilon^{1/2})$ expresses the fact that the actual distribution may be dynamically constrained. The value of the Lagrange multiplier λ_1 is a priori unknown and varies from case to case. It is advantageous to replace it by the more physically transparent ergodicity index $\exp(-DS)$. Substituting eq 20 into eq 2 leads to integrations that can be carried out analytically.[45] It turns out that the quantities $\langle\epsilon\rangle$ and e^{-DS} can both be expressed in terms of hypergeometric functions[46] of the reduced parameter $\sigma \equiv (\lambda_1\sqrt{E}/2)$. Explicitly, one has

$$e^{\lambda_0} = {}_1F_2\left(\frac{3}{2};\frac{1}{2},s+\frac{5}{2};\sigma^2\right) - \frac{2\Gamma(s + {}^{5}/_{2})}{\Gamma({}^{3}/_{2})\Gamma(s+3)}\,{}_1F_2\left(2;\frac{3}{2},s+3;\sigma^2\right)\sigma \tag{21}$$

$$\lambda_1\langle\epsilon^{1/2}\rangle = 2e^{-\lambda_0}\sigma\left[\frac{\Gamma(s + {}^{5}/_{2})}{\Gamma({}^{3}/_{2})\Gamma(s+3)}\,{}_1F_2\left(2;\frac{1}{2},s+3;\sigma^2\right) - \frac{3}{(s + {}^{5}/_{2})}\,{}_1F_2\left(\frac{5}{2};\frac{3}{2},s+\frac{7}{2};\sigma^2\right)\sigma\right] \tag{22}$$

$$\frac{\langle\epsilon\rangle}{E} = e^{-\lambda_0}\left[\frac{({}^{3}/_{2})}{(s + {}^{5}/_{2})}\,{}_1F_2\left(\frac{5}{2};\frac{1}{2},s+\frac{7}{2};\sigma^2\right) - \frac{4\Gamma(s + {}^{5}/_{2})}{\Gamma({}^{3}/_{2})\Gamma(s+4)}\,{}_1F_2\left(3;\frac{3}{2},s+4;\sigma^2\right)\sigma\right] \tag{23}$$

Equations 21 and 22 are then substituted into eq 12. The quantities $\exp(-DS) = \exp(\lambda_0)\exp(\lambda_1\langle\epsilon^{1/2}\rangle)$ and $\langle\epsilon\rangle/E$ are seen to both depend on parameter s and on the reduced variable σ only. The latter can be numerically eliminated by substitution and the result fitted to a simple expression. This leads to a surprisingly simple yet accurate equation:

$$\langle\epsilon\rangle/E = [0.13/(s+2.5)]\,(1 + 2.0e^{-DS})^2 \tag{24}$$

The quality of the fit is excellent for any value of s when $0.2 \le \exp(-DS) \le 0.9$. In that range, the joint value of the pair $\langle\epsilon\rangle/E$ and $\exp(-DS)$ is very close to that obtained by the much more laborious solution of eqs 21, 22, and 23. Equation 24 implies that, as commonly expected, $\langle\epsilon\rangle$ increases proportionally to E in the entire energy range where eq 14 is realistic, i.e., in the range where the exponent s remains constant.

The same procedure can be repeated when the density of states $N(E)$ increases exponentially with energy (as in eq 13). The distribution that satisfies eqs 1, 11, and 16 is given by

$$P(\epsilon) = (2/\pi^{1/2})\alpha^{3/2}e^{-\lambda_0}\,\epsilon^{1/2}e^{-\lambda_1\epsilon^{1/2}}e^{-\alpha\epsilon} \tag{25}$$

Note again that, just as for eq 16, this result is independent of the internal energy E as a result of the factorization properties of the exponential function.

Substituting it into eqs 1 and 2 leads to integrations that can be carried out analytically.[45] The results are

$$e^{-\lambda_0} = 2(2/\pi)^{1/2}\exp(\lambda_1{}^2/8\alpha)D_{-3}(\lambda_1/\sqrt{2\alpha}) \tag{26}$$

$$\langle\epsilon\rangle = (6/\alpha)D_{-5}(\lambda_1/\sqrt{2\alpha})/D_{-3}(\lambda_1/\sqrt{2\alpha}) \tag{27}$$

where $D_\nu(x)$ denotes[45,46] the parabolic cylinder function of order ν and argument x.

In a similar way

$$\lambda_1\langle\epsilon^{1/2}\rangle = 3(\lambda_1/\sqrt{2\alpha})D_{-4}(\lambda_1/\sqrt{2\alpha})/D_{-3}(\lambda_1/\sqrt{2\alpha}) \quad (28)$$

Since both $\langle\epsilon\rangle$ and e^{-DS} are functions of the same reduced parameter $(\lambda_1/\sqrt{2\alpha})$ alone, it is possible to eliminate the latter by substitution, and to fit the result to a simple expression. This leads to

$$\langle\epsilon\rangle = (0.11/\alpha)(1 + 2.18e^{-DS})^2 \quad (29)$$

Here again the very simple eq 29 leads to results that are practically equivalent to those obtained by the solution of eqs 26−28 when $0.2 \le \exp(-DS) \le 0.9$.

Thus, strange as it may seem but just as in the case of eq 7, the average translational kinetic energy release is seen to be independent of the value of E when $N(E)$ increases exponentially with E. This result may seem unrealistic and unphysical, but it should be viewed as a limiting case that reveals tendencies. The steeper the density of states increases with internal energy, the less sensitively the average translational energy depends on E.

If $N(E)$ now increases as the exponential of $E^{1/2}$ (eq 15) (i.e., the more realistic parametrization), one obtains, after similar but more complicated calculations:

$$\langle\epsilon\rangle/E = [0.27/(\beta E^{1/2} + 2.2)](1 + 1.85e^{-DS})^2 \quad (30)$$

$$\langle\epsilon\rangle = (0.27/\beta)(1 + 1.85e^{-DS})^2[E^{1/2} - 2.2/\beta + (4.84/\beta^2)E^{-1/2} - ...] \; (31) \quad (31)$$

The average energy release now increases approximately as the square root of E.

Equations 24, 29, 30, and 31 are quantitatively valid in the range $0.2 \le e^{-DS} \le 0.9$. They underestimate $\langle\epsilon\rangle/E$ when $e^{-DS} \ge 0.9$ and overestimate it when $e^{-DS} \le 0.2$. Simple analytical expressions are also available in the limiting case where $e^{-DS} = 1$:

$$\langle\epsilon\rangle/E = 1.5/\alpha E \quad (32)$$

$$= 1.5/(s + 2.5) \quad (33)$$

$$= 3/(\beta E^{1/2} + 2.5) \quad (34)$$

The latter equation is valid provided that $\beta E^{1/2} > 5$.

The significance and the relationships which exist among eqs 24, 29, 30, and 31, as well as among eqs 32−34 will be analyzed in sections VI and IX.

V. Energy-Averaged Measurements

Unfortunately, eqs 24 and 29−31 cannot be expected to remain directly valid when the measurement generates a value of $\langle\epsilon\rangle/E$ averaged over a certain energy range, as in the study of metastable transitions in sector instruments. In these experiments, only dissociations that occur in a time window defined by the entry and exit times in the field-free region (denoted τ_1 and τ_2) are registered. A bell-shaped transmission function $T(E)$ can be defined,[7] which depends on the rate constant $k(E)$ of the dissociation process

$$T(E) = B\{\exp[-k(E)\,\tau_1] - \exp[-k(E)\tau_2]\} \quad (35)$$

where B is determined by the normalization condition

$$\int_0^\infty T(E)\,dE = 1 \quad (36)$$

The function $T(E)$ thus represents the distribution of internal energies of those ions that dissociate in the metastable time window. The experimentally determined KERD is therefore given by the average

$$\tilde{P}(\epsilon) = \int_0^\infty P(\epsilon|E)\,T(E)\,dE \quad (37)$$

However, the correction resulting from imperfect energy selection of the metastable ion is, in the worst cases, of the order of 2% or 3% at most. In practice, this is smaller than the experimental uncertainties on $\langle\epsilon\rangle$ and on the average internal energy. A demonstration is given in the Appendix.

VI. Unified Presentation

So far, the rate of increase of the density of vib-rotational states of the pair of fragments has been measured by the parameters α, s, or β. It is also possible to express it in terms of the logarithmic derivative of $N(E)$ [i.e., the slope of $N(E)$ when plotted on a logarithmic scale]. Let us define the dimensionless quantity

$$\gamma = E\{d\log_{10}[N(E')]/dE'\}|_E \quad (38)$$

evaluated at the internal energy E at which the measurement of $\langle\epsilon\rangle$ is made.

Being derived from a logarithmic derivative, γ does not depend on the energy units used to measure E and $N(E)$. Calculating γ for the densities of states given by eqs 13 to 15 leads to

$$2.3026\gamma = s \quad \text{or } \alpha E \quad \text{or } 0.5\beta E^{1/2} \quad (39)$$

Replacing the original parameters by γ unifies the description and leads to strikingly similar equations.

If $N(E)$ increases exponentially with energy (eq 13), one has, by substitution into eq 29

$$\langle\epsilon\rangle/E = (0.049/\gamma)(1 + 2.18e^{-DS})^2 \quad (40)$$

If $N(E)$ increases as the sth power of E (eq 14), one has, from eq 24

$$\langle\epsilon\rangle/E = [0.057/(\gamma + 1.09)](1 + 2.0e^{-DS})^2 \quad (41)$$

If $N(E)$ increases as the exponential of $E^{1/2}$ (eq 15), then, from eq 30

$$\langle\epsilon\rangle/E = [0.059/(\gamma + 0.48)](1 + 1.85e^{-DS})^2 \quad (42)$$

Equations 40−42 are remarkably similar. They are valid in the range $0.2 \le e^{-DS} \le 0.9$. The predicted behavior is even more similar in the limiting case where $e^{-DS} = 1$ (i.e., in a fully statistical situation). Considering the parametrizations expressed by eqs 13, 14, and 15, one has, respectively:

$$\langle\epsilon\rangle/E = 0.65/\gamma \quad (43)$$

$$= 0.65/(\gamma + 1.09) \quad (44)$$

$$= 0.65/(\gamma + 0.54) \quad (45)$$

VII. Ethyl Iodide

The average translational energy released in the reaction $C_2H_5I^+ \rightarrow C_2H_5^+ + I$ for energy-selected ethyl iodide ions has been measured by Baer et al.[48] up to an internal energy of 2.4 eV by the photoion−photoelectron coincidence (PIPECO)

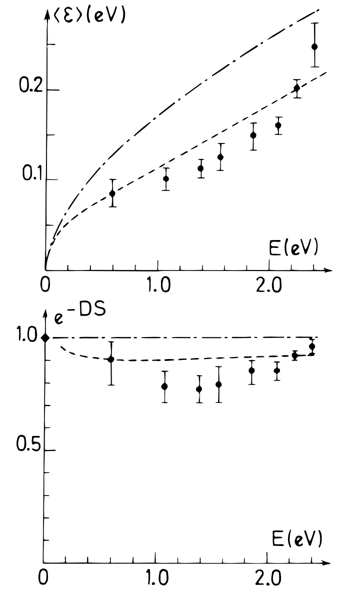

Figure 1. Upper part: average translational energy release $\langle\epsilon\rangle$ as a function of the excess internal energy E for $C_2H_5^+ + I$ formation from ethyl iodide. Filled symbols with error bars: experimental PIPECO measurements of ref 48. Dashed−dotted line: prior distribution. Dashed line: predictions of Klots' model. Lower part: ergodicity index exp(−DS) obtained by applying eqs 42 and 45 to these data.

technique. In order to interpret the results obtained by these authors, the vibrational frequencies and rotational constants of the $C_2H_5^+$ fragment ion have been calculated[49] by the B3LYP/6-31G(d) method and scaled afterward by a factor of 0.9806, as recommended by Scott and Radom.[50] In its most stable conformation, the $C_2H_5^+$ ion adopts the nonclassical bridged structure, belonging to the C_{2v} point group. However, there also exists a classical isomer, which provides a shallow secondary minimum or a saddle point a few kcal/mol above the nonclassical minimum.[51,52] Therefore, the potential energy surface is certainly anharmonic. Just as in the case of the $C_2H_3^+$ ion,[38] the hydrogen atoms of the ethyl ion can be expected to undergo large-amplitude motions when isomerization becomes possible. The lowest b_2 vibrational bending mode at 509 cm^{-1} (which certainly connects the two structures) has been treated as an anharmonic oscillator that converges to an energy of 2500 cm^{-1} and transforms above into a one-dimensional internal rotor. The vibrational−rotational density of states of the $C_2H_5^+$ ion has been calculated by a direct count algorithm,[1,18,44] modified to account for this transformation. In the energy range between 900 and 20 000 cm^{-1}, the resulting vibrational−rotational density of states is found to be nicely fitted by eq 15:

$$N(E) = \exp(0.164E^{1/2}) \tag{46}$$

when E is expressed in wavenumber units.

Therefore, eqs 42 and 45 can be applied to the experimental results obtained by Baer et al.[48] to estimate the efficiency of phase space sampling as a function of the internal energy E. The results are plotted in Figure 1. First, it follows from a simple logical argument that e^{-DS} must be equal to 1 at $E = 0$. The reason is that phase space is completely sampled when, at threshold, it is reduced to a single cell. This situation is represented by the filled diamond in the lower part of Figure 1. As the energy increases, the ergodicity index can only decrease. It is found to reach a minimum value of 0.77 ± 0.06 at $E = 1.38$ eV. More surprising is the fact that e^{-DS} increases again and is observed to approach an efficiency of 100% at high internal energies. The overall picture is very similar to that recently obtained (by a variety of experimental techniques) in the case of the $C_2H_3Br^+ \rightarrow C_2H_3^+ + Br$ reaction.[38] This is totally unexpected because, as the internal energy increases, the volume of phase space to be sampled increases enormously whereas the lifetime decreases. As discussed in more detail in ref 38, we ascribe this behavior to the strong vibronic interactions that result from the numerous surface crossings that bring about internal conversion to the ground state of the molecular ion. These surfaces cross along seams and strong nonadiabatic interactions are known to arise in the neighborhood of these seams.[53−56] The higher the internal energy E, the more extended and complicated the network of seams, especially in the case of open-shell molecular ions.[57,58] As a result, chaos is introduced into the nuclear dynamics.

Baer et al. have also calculated[48] the KERD predicted by Klots' theory,[1,23] which is based on the assumption that the Langevin model can be used to calculate the forces between separating fragments. The agreement between the predictions based on this model and the experimental results is good both at low and at high internal energies. However, in the intermediate range, the experimental $\langle\epsilon\rangle/E$ ratios are slightly lower than the predicted ones.

It is instructive to compare the KERD resulting from Klots' model to the prior distribution in order to derive the corresponding ergodicity index. Klots' model is found to describe a slightly constrained situation where approximately 91% of the available phase space is effectively sampled. In the range of internal energies where e^{-DS} drops down to its minimal value of 77%, the experimental average energy release is lower than that predicted by Klots.

In summary, the joint examination of the two parts of Figure 1 provides insight into the problem. Its lower part can be regarded as the image of the upper part, with a mapping function defined by eqs 42 and 45. It shows that the prior distribution is a reference and not a mediocre first approximation.

VIII. Bromo- and Iodobenzene

The translational energy released in the reaction $C_6H_5X^+ \rightarrow C_6H_5^+ + X$ (where X is either Br or I) in the metastable time window has been previously[36] determined in a two-sector mass spectrometer in both field-free regions with different amounts of internal energy. For example, when bromobenzene ions dissociate in the first field-free region with a fragment ion translational energy equal to 4 keV in the laboratory frame, the most probable internal energy E_S is equal to 0.85 eV and the measured average kinetic energy $\langle\epsilon\rangle$ is found to be equal to 0.060 eV. In that energy range, the rate constant varies as the 6-th power of energy (eq A2), and the rovibrational density of states of the $C_6H_5^+$ fragment can be fitted to eq 15 with a value of γ equal to 4.62. When these values are introduced into eq 42, one gets $e^{-DS} = 0.79$, whereas the tedious integration process carried out by Urbain et al [36] gives 0.77 ± 0.03.

In practice, neither the exponential parametrization (eq 13) nor the power law (eq 14) provides a very good representation of a genuine rovibrational density of states. However, they are still useful because they are found to bracket the actual $N(E)$ function, so that eqs 40 (column a of Table 1) and 41 (column b of Table 1), which are deduced from them, provide a lower and an upper bound to be compared with the correct value of e^{-DS} which is reported in column d of Table 1. By contrast, eq 42, deduced from the more realistic parametrization (15),

TABLE 1: Most Probable Internal Energy E_S and Average Internal Energy $\langle\epsilon\rangle$ Measured for the Halogen Loss Reaction of the Bromo- and Iodobenzene Cations [Ref 36][a]

molecular ion	E_S (eV)	$\langle\epsilon\rangle_{exp}$ (eV)	ν	γ	e^{-DS}			
					a	b	c	d
$C_6H_5I^+$	0.47	0.046	5.40	3.46	0.75	0.92	0.84	0.86
$C_6H_5I^+$	0.55	0.045	4.80	3.73	0.69	0.83	0.77	0.79
$C_6H_5I^+$	0.62	0.051	4.50	3.97	0.73	0.87	0.81	0.81
$C_6H_5Br^+$	0.67	0.059	6.30	4.13	0.79	0.94	0.88	0.85
$C_6H_5Br^+$	0.75	0.060	6.05	4.36	0.77	0.90	0.84	0.80
$C_6H_5Br^+$	0.85	0.060	6.00	4.62	0.73	0.85	0.79	0.77

[a] The exponent ν fits the increase of the rate constant with the internal energy E (eqs A2 and A4). Parameter γ describes the increase of $N(E)$ with the internal energy (eq 38). Column a: lower bound to the ergodicity index e^{-DS} deduced from eq 40 (exponential parametrization of $N(E)$). Column b: upper bound to e^{-DS} deduced from eq 41 (power law for $N(E)$). Column c: value of e^{-DS} deduced from eq 42 (more realistic parametrization of $N(E)$). Column d: ergodicity index deduced (with an uncertainty equal to ± 0.03) in ref 36 from a full numerical integration based on eq 37.

provides right away a better approximation (reported in column c of Table 1).

IX. Discussion

The ratio between the average translational energy $\langle\epsilon\rangle$ divided by the internal energy E is seen to depend both on the way the density of vib-rotational states of the pair of fragments increases with energy, represented by the function $N(E)$, and on the fraction of phase space sampled by the pair of fragments, e^{-DS}. We discuss the role played by these two functions in turn.

1. Density of States $N(E)$. (a) The most important feature of $N(E)$ is the dimensionless parameter γ defined in eq 38. Now, the logarithmic derivative appearing in γ contains E raised to a particular power. Hence, the behavior predicted by eqs 40−45 as a function of the internal energy E is different and depends on the shape of $N(E)$: $\langle\epsilon\rangle$ is independent of E for the exponential parametrization, but increases linearly with E if the power law is adopted; $\langle\epsilon\rangle$ is found to increase approximately as $E^{1/2}$ in the intermediate case (when $N(E)$ is parametrized as in eq 15). In fact, $\langle\epsilon\rangle$ is seen to vary as a function of E in exactly the same way as $\{d\ln[N(E)]/dE\}^{-1}$.

We note in this respect that the latter quantity as well as γ have a simple interpretation in the canonical description of KERDs. One has[59]

$$\{d\ln[N(E)]/dE\}^{-1} = k_B T^{\ddagger} \qquad (47)$$

where $T^{\ddagger}$ is an effective temperature defined by Klots.

(b) Why are eqs 40−45 so strikingly similar, in spite of the different shapes considered for the functions $N(E)$?

A partial answer to that question is provided by elementary mathematics. Consider the identity

$$\lim_{x\to 0}(1-x)^{1/x} = e^{-1}$$

from which one easily deduces

$$\lim_{\epsilon/E\to 0}(1-\epsilon/E)^{\alpha E} = e^{-\alpha\epsilon} \qquad (48)$$

Substituting, from eq 39, $s = \alpha E$ into eq 48 accounts for the similarity between eqs 40 and 41, at least in the range $\epsilon \ll E$.

As to the third parametrization, let us expand the square root in eq 18:

$$\exp(\beta\sqrt{E-\epsilon}) = \exp(\beta E^{1/2})\exp[-(0.5\beta E^{1/2})(\epsilon/E)]\exp[-(\beta E^{1/2}/8)(\epsilon/E)^2] = \exp(\beta E^{1/2})[1 - 0.5\beta E^{1/2}(\epsilon/E) + (1/2)0.5\beta E^{1/2}(0.5\beta E^{1/2} - 0.5)(\epsilon/E)^2 \ldots] \qquad (49)$$

The factor $\exp(\beta E^{1/2})$ can be shifted into the normalization constant. Substituting, from eq 39, $0.5\beta E^{1/2}$ by s into the second factor leads to

$$1 - s(\epsilon/E) + (1/2)s(s-0.5)(\epsilon/E)^2 \approx 1 - s(\epsilon/E) + (1/2)s(s-1)(\epsilon/E)^2 \approx (1-\epsilon/E)^s \qquad (50)$$

Substituting $0.5\beta E^{1/2}$ by αE leads to

$$1 - \alpha\epsilon + (1/2)\alpha^2(1 - 0.5/\alpha E)\epsilon^2 \approx 1 - \alpha\epsilon + (1/2)(\alpha\epsilon)^2 \approx \exp(-\alpha\epsilon) \qquad (51)$$

In summary, the three parametrizations are expected to lead to similar results when $\epsilon \ll E$, and parameter γ, as defined in eq 38, appears to be the most important feature of $N(E)$.

2. "Ergodicity Index" exp(−DS). Because phase space exploration is sometimes incomplete as a result of dynamical constraints, the ratio $\langle\epsilon\rangle/E$ is also influenced by the value of e^{-DS}. A case is made out in the present paper to replace the vague concept of "subset of active degrees of freedom" by that of "ergodicity index measuring the extent of phase space sampling", e^{-DS}.

Equations 40−45 allow us to extract the value of this index in a straightforward way from energy-selected measurements provided that the value of γ is known. The procedure is also possible in a study of metastable ions, but meets with the difficulty that the value of E_S (the most probable energy sampled in a two-sector instrument), i.e., the kinetic shift, should be known. Ideally, this requires either a knowledge of the function $k(E)$ extrapolated to its origin, or time-resolved measurements both in the micro- and in the millisecond range.[60] The fact that energy is not strictly selected in metastable ion studies is not in practice a major problem.

It results from previous papers of this series[20,35−38] that incomplete phase space sampling can be surprisingly well accounted for by the momentum gap law. This law directly addresses the efficiency of the energy flow between the reaction coordinate and the remaining degrees of freedom during the separation of the products. According to this law, there exists a systematic bias against energy release in the reaction coordinate as translational motion of the separating fragments. This reluctance can be understood if the dissociation process is analyzed as a vibrational predissociation.[61] Quantum-mechanically, predissociation involves an interaction between two wave functions: that of the bound state and that of the translational motion of the pair of fragments. The latter oscillates rapidly as a function of the reaction coordinate. The larger the amount of energy released in the reaction coordinate, the more rapidly the translational wave function oscillates and the smaller the efficiency of the predissociation process.[36,37,40−42] The analysis is also possible in classical mechanics.[30] Vibrational predissociations are controlled by the Franck−Condon principle, which prevents large changes in the nuclear momenta. Here again, large translational energy releases are disfavored with respect to a purely statistical partitioning. The energy in excess of the dissociation asymptote is preferentially released as rotational or vibrational energy of the fragments.

Equations 40−45 are in line with these views for the following reasons.

(a) It follows from these equations that the larger the efficiency of phase space sampling, the larger the ratio $\langle\epsilon\rangle/E$. In other words, when nonstatistical effects show up, they lead to a reduction of the translational energy released in the reaction coordinate, as exemplified in Figure 1.

(b) The linear relationship between e^{-DS} and the square root of $\langle\epsilon\rangle/E$ that exists in eqs 40−45 may be related to eq 11, which specifies that the constraint which operates on the dynamics is related to the momentum, and not to the translational energy.

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Appendix

The average translational energy release measured in metastable ion studies does not correspond to a well-defined energy, but to a distribution represented by the function $T(E)$ defined in eq 35. Substituting eqs 35 and 37 into eq 2 and changing the order of integration,[45] one obtains

$$\begin{aligned}\langle\epsilon\rangle &= \int_0^\infty \epsilon\,\tilde{P}(\epsilon)\,d\epsilon = \int_0^\infty d\epsilon\,\epsilon \int_\epsilon^\infty dE\,T(E)\,P(\epsilon|E)\\ &= \int_0^\infty dE\,T(E)\int_0^E d\epsilon\,\epsilon\,P(\epsilon|E) = \int_0^\infty dE\,T(E)\,\langle\epsilon\rangle_E\end{aligned} \tag{A1}$$

where $\langle\epsilon\rangle_E$ denotes the average translational energy that would have been released if all the decaying ions had strictly the internal energy E, i.e., the quantity defined in eq 2 and calculated in section IV.

Assume now that, in the energy range where $T(E)$ is nonzero, the rate constant can be fitted to the following empirical equation[35−37]

$$k(E) = k_{opt}(E/E_S)^\nu \tag{A2}$$

where E_S is the energy at which $T(E)$ reaches its maximum and where

$$k_{opt} = k(E_S) = [\ln(\tau_2/\tau_1)]/(\tau_2 - \tau_1) \tag{A3}$$

is the rate constant that is sampled with the highest probability. The empirical exponent ν is related to the rate of increase with energy of the rate coefficient $k(E)$:

$$\nu = 2.3026E[d\log_{10}\{k(E)\}/dE]_{E=E_s} \tag{A4}$$

In practice, ν is commonly found to range between about 4 and 10.[35−37]

With this parametrization, the calculation of average translational energies via eq A1 is readily carried out.

(1) If $N(E)$ increases exponentially with E [as expressed in eq 13], then $\langle\epsilon\rangle$ is independent of E and eqs 29 and 32 remain valid. The imperfect energy selection achieved in metastable ion studies has then no effect on the translational energy release.

(2) If $N(E)$ rises as the sth power of E, one finds, from eqs 14, 24, 35, 36, A2, A3, and after a bit of algebra[45]

$$\langle\epsilon\rangle \approx E_S\frac{\Gamma(1+2/\nu)}{\Gamma(1+1/\nu)}\left[1+\left(\frac{1}{2\nu}\right)\left(\frac{1}{\nu}+\frac{1}{3}\right)\left(\frac{\tau_2-\tau_1}{\tau_1+\tau_2}\right)^2\right][0.13/(s+2.5)](1+2.0e^{-DS})^2 \tag{A5}$$

In the limiting case where $e^{-DS} = 1$, one has, from eq 33:

$$\langle\epsilon\rangle \approx E_S\frac{\Gamma(1+2/\nu)}{\Gamma(1+1/\nu)}\left[1+\left(\frac{1}{2\nu}\right)\left(\frac{1}{\nu}+\frac{1}{3}\right)\left(\frac{\tau_2-\tau_1}{\tau_1+\tau_2}\right)^2\right][1.5/(s+2.5)] \tag{A6}$$

The imperfect energy selection achieved in metastable ion studies leads to a very slight underestimate of the average translational energy but the distortion is very small. For example, in the case of metastable bromobenzene ions,[35,36] $\tau_1 = 1.74$ μs, $\tau_2 = 3.77$ μs. The correcting factor

$$\frac{\Gamma(1+2/\nu)}{\Gamma(1+1/\nu)}\left[1+\left(\frac{1}{2\nu}\right)\left(\frac{1}{\nu}+\frac{1}{3}\right)\left(\frac{\tau_2-\tau_1}{\tau_1+\tau_2}\right)^2\right] \tag{A7}$$

is equal to 1.03 when $\nu = 3$. It drops down to its minimum value of 0.97 when $\nu = 8$ and approaches 1 at still higher values of ν.

(3) If, finally, $N(E)$ is parametrized as expressed in eq 15, then the relationship between $\langle\epsilon\rangle$ and E becomes more complicated. With respect to the energy-selected case, it involves correction factors which, however, are in practice even smaller than in case (2).

$$\begin{aligned}\langle\epsilon\rangle \approx (0.27/\beta)\,(1+1.85\,e^{-DS})^2\Bigg\{&E_S^{1/2}\frac{\Gamma(1+3/2\nu)}{\Gamma(1+1/\nu)}\Bigg[1+ (1/12\nu)\left(\frac{5}{2\nu}+1\right)\left(\frac{\tau_2-\tau_1}{\tau_1+\tau_2}\right)^2\Bigg] - 2.2/\beta + E_S^{-1/2}\times\\ &(4.84/\beta^2)\frac{\Gamma(1+1/2\nu)}{\Gamma(1+1/\nu)}\left[1-(1/2\nu)\left(\frac{1}{\nu}+\frac{1}{3}\right)\left(\frac{\tau_2-\tau_1}{\tau_1+\tau_2}\right)^2\right] - \ldots\Bigg\}\end{aligned} \tag{A8}$$

In the limiting case where $e^{-DS} = 1$, one has, from eq 34:

$$\begin{aligned}\langle\epsilon\rangle \approx\ &E_S^{1/2}(3/\beta)\frac{\Gamma(1+3/2\nu)}{\Gamma(1+1/\nu)}\left[1+(1/12\nu)\left(\frac{5}{2\nu}+1\right)\times\left(\frac{\tau_2-\tau_1}{\tau_1+\tau_2}\right)^2\right] - 7.5/\beta^2 + E_S^{-1/2}(18.75/\beta^3)\frac{\Gamma(1+1/2\nu)}{\Gamma(1+1/\nu)}\Bigg[1-\\ &(1/2\nu)\left(\frac{1}{\nu}+\frac{1}{3}\right)\left(\frac{\tau_2-\tau_1}{\tau_1+\tau_2}\right)^2\Bigg] - \ldots\end{aligned} \tag{A9}$$

For $\tau_1 = 1.74$ μs and $\tau_2 = 3.77$ μs, the main correcting factor is equal to 1.00 when $\nu = 3$. It admits its minimum value of 0.98 when $\nu = 6$ and approaches 1 at still higher values of ν. The correction resulting from imperfect energy selection of the metastable ion is thus in practice smaller than the experimental uncertainties on $\langle\epsilon\rangle$ and E_S.

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