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Prior-expectation distribution functions for energy disposal and energy consumption in reactive molecular collisions*

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In a recent series of papers¹ we have applied the information-theoretic method to the analysis of energy requirements and energy disposal in reactive molecular collisions. The analysis is based on the concept of a "prior" expectation distribution which is the reference against which the actual observation is to be compared. In this Comment we reiterate the basic assumptions used in deriving the prior distribution. For utmost generality the prior distribution avoids making dynamical assumptions. Thus the prior distribution is not intended to predict the actual distribution of final states (or the different reactivities of initial states). The observed distributions often deviate markedly from the prior. The empirical and theoretical analysis of such deviations (or "surprisals") is an essential part of the method.

First, one recognizes that there are an infinite number of distributions, all of which satisfy the following two essential conditions: (a) energy disposal and energy requirements satisfy the conditions imposed by microscopic reversibility and (b) zero relevance, i.e., the product state distribution is independent of the different possible states of the reactants (at a given value of the energy and other good quantum numbers). These two conditions alone are only necessary but not sufficient to determine a unique "statistical" distribution. We have therefore imposed a further condition: *The prior distribution should be the most random one possible.* Among all conceivable distributions of quantum states (at a given energy) the prior distribution should have the least information content (i.e., the maximal entropy). We have been guided in this choice by the similar approach used in macroscopic statistical mechanics.¹ Hence, it is possible to tie the present results to those of conventional statistical thermodynamics.

For other purposes one may seek alternative definitions of a "statistical" distribution, particularly if the distribution is to have a predictive value. The RRKM approach² and the statistical theories of rates and cross sections³⁻⁵ illustrate an alternative choice.⁶ Note however, that all of these approaches are really *theories*; theories meant to agree with experiment! Toward that goal they incorporate as much dynamics as is essential and consistent with the first two conditions. These theories have had and will continue to have many useful applications. They are not in conflict with our prior distribution in the sense that no distribution is in such conflict. The prior distribution simply provides a reference for all possible distributions (often, however, the actual distributions predicted by these statistical theories are not markedly different from the prior).

The basic assumption used in deriving our prior distribution implies that, in the absence of information (and

for a given value of the energy and other good quantum numbers), all product quantum states are formed with the same rate.^{6,7} Invoking microscopic reversibility, this conclusion uniquely specifies the prior energy consumption.

We turn now to the details, consisting only of counting states. According to our condition all quantum states are formed with the same rate; the rate of formation of a group of states is then simply proportional to the number of states in that group. We illustrate the approach by considering energy disposal in an experiment where the total energy is in the range E to $E + dE$. We specify a group of product states by their relative translational energy being in the range E_T to $E_T + dE_T$ and the scattering (solid) angle being in the range Ω to $\Omega + d\Omega$. Since both E and E_T are specified, the allowed internal states of the products are uniquely determined. (All have the same $(E - E_T = E_n)$ internal energy.) The set of internal quantum states of energy E_n is the internal level n of degeneracy g_n . The number of translational states in the specified range is^{1,7} $\rho_T(E_T)dE_T(d\Omega/4\pi)$. Here $\rho_T(E_T) = A_T E_T^{1/2}$ is the translational density of states. A_T is a (unit bearing) constant.

According to our assumption, the rate of formation of the previously specified group of product states is $Rg_n\rho_T(E_T)dE_T(d\Omega/4\pi)$. R is the rate which we take⁸ to be the same for all product states. The total rate of product formation is $R\rho(E)dE$ where $\rho(E)$ is the total density of states: $\rho(E) = \sum_n g_n\rho_T(E - E_n)$ and $dE = dE_T$. Hence the prior fraction of products in the specified group is $P^0(n\Omega)d\Omega = g_n\rho_T(E - E_n)(d\Omega/4\pi)/\rho(E)$. We define $P^0(\Omega|n)$ (the prior angular distribution of products in the internal level n) by $P^0(n\Omega) = P^0(\Omega|n)P^0(n)$ such that $\int P^0(\Omega|n)d\Omega = 1$. Then $P^0(\Omega|n) = (4\pi)^{-1}$, i.e., the prior angular distribution of the products is isotropic. Also $P^0(n) = g_n\rho_T(E - E_n)/\rho(E)$. This is the prior distribution of the products internal levels (at a given total energy E).

For the case when the products are an atom and a diatomic molecule in a definite electronic state (in the absence of fields) $n = v, J$ and $g_n = 2J + 1$. If one collects products into wider "bins", say the group of products in the vibrational state v , then $P^0(v) = \sum_{J=0}^{J^*(v)} P^0(v, J) = \sum_{J=0}^{J^*(v)} (2J + 1)\rho_T(E - E_{vJ})/\rho(E)$, where $J^*(v)$ is the highest value of J allowed for given v and E . Approximate forms for $P^0(v)$ and other priors are available,¹ but the exact procedure is to use the summation above.

The considerations above are evidently limited to the distribution of states, i.e., to the relative magnitude of the rate constants into (or out of) a specified group of states. There is, of course, a more fundamental question, namely the absolute magnitude of the rates, and it

is this question that is the primary one for the statistical theories previously mentioned.

An extensive discussion of the origins and applications of the prior distribution is in preparation.

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¹(a) A. Ben-Shaul, R. D. Levine, and R. B. Bernstein, *J. Chem. Phys.* **57**, 5427 (1972); (b) R. D. Levine and R. B. Bernstein, *Acc. Chem. Res.* (to be published), and references therein.

²R. A. Marcus, *Chem. Soc. Faraday Discuss.* **55**, 9 (1973) and references therein.

³P. Pechukas and J. C. Light, *J. Chem. Phys.* **42**, 3281 (1965).

⁴E. E. Nikitin, *Theor. Exp. Chem.* **1**, 83, 90 (1965).

⁵(a) B. C. Eu and J. Ross, *J. Chem. Phys.* **44**, 2467 (1966); (b) W. H. Miller, *J. Chem. Phys.* **52**, 543 (1970); (c) R. D. Levine and R. B. Bernstein, *J. Chem. Phys.* **53**, 688 (1970); (d) T. F. George and J. Ross, *J. Chem. Phys.* **56**, 5786 (1972).

⁶The essential assumption of these other theories (in a simplified form) is that the number density of all product states formed in the collision is the same. We assume equal flux density into all final states. Note however, that it is the flux density (i.e., the rate) of the nascent products that is proportional to the bulk concentration of the products (provided that collisional relaxation of the internal states is arrested).

⁷J. L. Kinsey, *J. Chem. Phys.* **54**, 1206 (1971).

⁸Corresponding to the alternative⁶ assumption, $R \propto v$, where v is the final relative velocity.

ERRATA

Erratum: Calculation of the pressure-broadening of HCl and DCI infrared and Raman lines [*J. Chem. Phys.* **61**, 418 (1974)]

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Section II, paragraph 4: The sentence beginning "radiating molecules . . ." should read "radiating molecules with $J \sim 3$ collide most often with perturbing molecules that are in the correct level for a resonant collision to occur."