ON THE THEORY OF THE STATE DISTRIBUTION OF THE REACTION PRODUCTS AND RATES OF UNIMOLECULAR DISSOCIATIONS

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A recent variational implementation of RRKM theory, plus an additional dynamical assumption, is used to calculate the distribution of quantum states of reaction products of unimolecular dissociations. It is assumed that the "conserved" modes of the molecule are vibrationally adiabatic after passage through the transition state region, but that the "transitional modes" are nonadiabatic until the "loose transition state" region is reached. The rate constants k_{EJ} themselves are those of RRKM theory, but, for energies below those needed to yield vibrationally excited products, the phase space theory expression (PST) is obtained for the distribution of rotational states of the products. The product state distribution differs from that of PST when the energy is sufficient to permit product vibrational excitation. The unimolecular reactions considered are those for which there is no potential energy barrier for the reverse reaction (recombination).

1. Introduction

Of particular interest in the study of the unimolecular dissociations of molecules having a given vibrational–rotational energy E are the rate of dissociation and the distribution of quantum states of the resulting reaction products. Various theories exist in the literature which attempt to predict both. They include phase space theory [1], which has had a number of successes in predicting the products' rotational state distribution, at least at low energies. Usually, on the other hand, its predicted reaction rates appear to be too high, because of the neglect of any hindrance to internal rotation of the separating fragments in the transition state [2]. Alternative models, which allow for steric hindrance and have been used to calculate the products' distribution of quantum states, include the adiabatic channel model (ACM) [3,4] and a statistical-adiabatic model [5]. The ACM assumes a vibrational adiabaticity for all coordinates during the motion of the fragments from the transition state region to infinity. Additional assumptions, including a universal interpolation formula for the energy levels, are typically added to simplify the calculation [3,4]. A statistical-adiabatic model [5] assumes adiabaticity for the "conserved modes" and a "statistical adiabaticity" for the others.

In the present paper a theoretical approach is described which contains any steric hindrance present in the transition state (RRKM theory) and which adds a dynamical postulate for the motions along the exit channel, a new postulate, for predicting the products' state distribution. To calculate the rate constants k_{EJ} for the unimolecular dissociation of an isolated molecule of energy E and total angular momentum quantum number J, the recently described variational implementation of RRKM theory is used [6–8], in which the number of states $N_{EJ}(R)$ is calculated along a reaction coordinate R, using a quantum count of certain modes and a Monte Carlo count of the classical-like modes (section 2). (Cf. refs. [4,9] for earlier usage of the variational criterion itself.) We next introduce a dynamical approximation for motion from the transition state ($R=R^{\ddagger}$) to $R=\infty$. For energies below that needed for vibrational excitation of the latter, the predicted distribution of states of the products proves to be the same as that of phase space theory, even though the predicted k_{EJ}'s can be very different. For energies sufficient to excite the products vibrationally, differences from the PST product state distribution occur. The relationship to a treatment of rates and product distributions of unimolecular ion dissociations [10] is discussed later.

The present theory aims at providing a benchmark model for comparison with experimental data on the products' state distribution. Only systems are considered for which there is no potential energy drop in the exit channel for the dissociation, i.e. for which there is no potential energy barrier for the reverse reaction of recombination. The theory is best tested with experiments in which the k_{EJ}'s, or k_{EJ}'s averaged over some range of J values and the products' distribution of states are measured for the same molecule and for the same energy range. Such experiments have been performed for NCNO. Microcanonical rate constants have been reported by Zewail and co-workers [11] and the products' rovibrational state distribution has been described by Wittig and co-workers [12].

2. RRKM theory and k_{EJ}

We first summarize briefly the recent formulation for implementing RRKM theory for unimolecular dissociations having highly flexible transition states [6,7]. In the transition state the rotations of the fragments can be free or hindered, depending on the potential energy surface and on E and J, and there can be extensive coupling between these rotations and the orbital motion of the two fragments at $R=R^{\ddagger}$. Since RRKM theory does not in itself yield predictions of energy distributions of the products, some additional approximation is needed for the details of the motion after leaving $R^{\ddagger}$, and is introduced in section 3.

The RRKM expression for the rate constant k_{EJ} is given by [13]

$$k_{EJ}=N^{\ddagger}_{EJ}/h\rho_{EJ}\ , \tag{1}$$

where $N^{\ddagger}_{EJ}$ is the value of $N_{EJ}(R)$ at the transition state $R=R^{\ddagger}$. $R^{\ddagger}$ and $N_{EJ}(R^{\ddagger})$ are obtained variationally, namely by minimizing the function $N_{EJ}(R)$ versus R; ρ_{EJ} is the density of states of the reactants at the given E and J.

In the calculation of $N_{EJ}(R)$ the degrees of freedom were classified into two types, the "conserved" and the "transitional" modes [6]. In the former, usually vibrational, the motion in the transition state is similar to that in the parent molecule but the vibration frequencies may differ. For the transitional modes, on the other hand, the motion may change considerably. In particular, the mutual bending vibrations of the two fragments in the parent molecule become hindered rotations at $R^{\ddagger}$ and ultimately free rotations at $R=\infty$. The orbital modes are coupled to these rotations and are included in the transitional modes. For the case in which the two polyatomic fragments are each non-linear there are, typically, six transitional modes [6,7]: When due account is taken of the role of total angular momentum conservation in reducing the number of relevant coordinates from eight to six, there are, for example, the six Euler angles describing the orientation of the fragments [7].

The number of states $N_{EJ}(R)$ was expressed as a convolution

$$N_{EJ}(R)=\int_0^E N_v(E-\epsilon)\,\rho_J(\epsilon)\,\mathrm{d}\epsilon\ , \tag{2}$$

where $N_v(E-\epsilon)$ is the number of quantum states for the conserved modes when their energy is equal to or less than $E-\epsilon$; $\rho_J(\epsilon)$ is for the given J the density of states of the transitional modes when their energy (including that of the R motion) is ϵ. At any R some of the energy E is "fixed" as potential energy of the R motion, and so is not available for distribution. This fact is taken into account in the counting. N_v was obtained by a direct quantum count and the ρ_J via a Monte Carlo count of the phase space for the transitional modes. In the process the integral in eq. (2) was first reduced in dimensionality, since the integrand (ρ_J itself involves a phase space integral) is independent of a number of the coordinates and momenta. Initially, action–angle variables were used for the transitional modes [6], and later it was found that ordinary variables could be used instead [7]. The initial impetus for using action–angle variables was, in part, to be able to fulfill immediately the conservation of total angular momentum.

This calculation of k_{EJ} proved to be a very simple one computationally (10 to 15 min on a VAX 11/780) [7]. Quantum corrections for the classically treated transitional modes were obtained for thermally averaged k_{EJ}'s. In the particular example treated the corrections were found to be negligible [8].

3. Distribution of states of the reaction products

The dynamical approximation made in this paper is twofold: The motion of the conserved modes is assumed to be vibrationally adiabatic (VA) between $R^\ddagger$ and $R=\infty$. In this VA approximation each state is presumed not to undergo any reflection in its flow from $R^\ddagger$ to ∞. The distribution of states for those modes at ∞ is then the same as at $R^\ddagger$. Given this distribution at $R^\ddagger$, calculated statistically, it is then assumed that there is a ready energy interchange among the transitional modes during the motion along R from $R^\ddagger$ to some value R_ℓ, the loose transition state value of R. These modes are usually of low frequency between $R^\ddagger$ and R_ℓ and, like rotations in collisions, are typically expected to undergo easy energy interchange. It is assumed that the distribution of states of the transitional modes is determined statistically (phase space theory) at R_ℓ. Specifically, R_ℓ is the value of R where the centrifugal force acting on the fragments, determined by an orbital angular momentum quantum number l, just balances the long range radial attractive force.

Since $R^\ddagger$ depends only on J and E, while R_ℓ depends on l, it could happen for some l's that $R^\ddagger \geqslant R_\ell$. For those l's we shall still, as a first approximation, use the same procedure: determine statistically the state distribution of the conserved modes at $R^\ddagger$ and, given that distribution, then determine that of the transitional modes at R_ℓ.

For all modes the quantum numbers (or action variables) between R_ℓ and ∞ are constants of the motion, when for $R \geqslant R_\ell$ there are no further interactions between the fragments, apart from a radial one. It is also possible that the interaction among the transitional modes and the R motion ceases before R_ℓ is reached. The present approximation for the distributions is perhaps the simplest (non-adiabatic) one for comparing with the data. Its assumption that the motion of the transitional modes is non-adiabatic between $R^\ddagger$ and R_ℓ distinguishes it from the vibrational adiabaticity postulated for all modes in ACM [3,4] and from the statistical adiabaticity postulated elsewhere [5].

We have referred above to a single $R^\ddagger$, the solution of

$$\partial N_{EJ}(R^\ddagger)/\partial R^\ddagger = 0\,, \tag{3}$$

in the interests of describing the basic idea in the simplest way. However, strictly speaking, in a VA approximation for the conserved modes each state i of these modes behaves adiabatically, and one should obtain an $R^\ddagger$ for each such state (i denotes the totality of quantum numbers of the conserved modes). We follow this procedure, in fact, in eq. (5) below, and denote that $R^\ddagger$ by $R_i^\ddagger$. Instead of calculating $N_{EJ}(R)$ via (2) we obtain $N_{iEJ}(R)$, the number of quantum states of the transition state having the specified value of i at the given E and J,

$$N_{iEJ}(R) = \int\limits_0^{E-E_i(R)} \rho_J(\epsilon)\,\mathrm{d}\epsilon\,. \tag{4}$$

Here, $E_i(R)$ is the energy of the ith state of the conserved modes. In the adiabatic approximation $E_i(R)$ can vary with R at fixed i.

By minimizing $N_{iEJ}(R)$ with respect to R the transition state $R=R_i^\ddagger$ is found for each i,

$$\partial N_{iEJ}(R)/\partial R = 0 \quad \text{at } R = R_i^\ddagger\,. \tag{5}$$

We denote $N_{iEJ}(R_i^\ddagger)$ by $N_{iEJ}^\ddagger$. Eq. (5) recalls an earlier instance where the position of the transition state varied from state to state [14].

The probability p_{iEJ} that the conserved modes of the products are in a quantum state i at $R=\infty$ is the same as it is at $R_i^\ddagger$, and so is given by

$$p_{iEJ} = N_{iEJ}^\ddagger / \sum_i N_{iEJ}^\ddagger\,. \tag{6}$$

With this formalism in which the set of $R_i^\ddagger$'s replaces a single $R^\ddagger$ eq. (1) is replaced by

$$k_{EJ} = \sum_i N_{iEJ}(R_i^\ddagger)/h\rho_{EJ}\,. \tag{7}$$

The quantum number i is, in the VA approximation for the conserved modes, a constant of the motion in the entire region from $R_i^\ddagger$ to ∞. On the other hand, l and t, the totality of quantum numbers for the remaining transitional modes, are constants of the motion only in the region R_ℓ to ∞, in our present approximation. For a given i, the conditional probability $p_{tEJ,i}$ that the products at $R=\infty$ are in a state t for the transitional modes thus equals the probability that they are in that state t at $R=R_\ell$ and so is obtained using phase space theory for these modes.

Specifically, for the given i, $p_{tEJ,i}$ is given by its phase space theory value $p^{\mathrm{PST}}_{tEJ,i}$ for the given available energy,

$$p_{tEJ,i}=p^{\mathrm{PST}}_{tEJ,i}=N_{tEJ,i}/\sum_t N_{tEJ,i}\ , \tag{8}$$

where the number of states $N_{tEJ,i}$ in the numerator is the usual phase space theory sum (but for fixed i) in which the energy of the transitional modes in state t, the energy of the conserved modes in state i, the centrifugal energy and the R-potential energy, all at $R=R_\ell$, do not in their sum exceed E, and in which the various triangle inequalities are satisfied [1]. Typically, the energies of the i and t modes at R_ℓ may be set equal to their values at $R=\infty$. The t in eq. (8) is intended to represent only the rotational quantum numbers that are determined experimentally for the fragments.

The joint probability p_{itEJ} that the reaction products are formed in the rotational–vibrational quantum state (it), for the given E and J, is the product

$$p_{itEJ}=p_{iEJ}p_{tEJ,i}\ , \tag{9}$$

where p_{iEJ} and $p_{tEJ,i}$ are given by eqs. (6) and (8). For molecules prepared with an energy E there will be a distribution function p^0_J for J, the function depending on the mode of preparation. The observed probability function p_{itE} for forming product molecules in a state (it) at the given E is then given by

$$p_{itE}=\sum_J p^0_J p_{itEJ}\ . \tag{10}$$

There is one approximation which will sometimes be made, particularly if there are many states i energetically accessible at $R=\infty$, at the given E. This added approximation saves some computation. Namely, instead of determining an $R^{\ddagger}_i$ for each state i of the conserved modes, a single $R^{\ddagger}$ is determined, as the solution of eq. (3). The distribution of i states at this $R^{\ddagger}$ is also the distribution at $R=\infty$. E.g., if the contribution of state i to $N_{EJ}(R)$ is denoted by $N_{iEJ}(R)$ the latter is given by eq. (4), and then eq. (6) still applies for p_{iEJ}, but now $N^{\ddagger}_{iEJ}$ denotes $N_{iEJ}(R^{\ddagger})$ instead of $N_{iEJ}(R^{\ddagger}_i)$. There is one caveat, however. Even when the total energ E is insufficient to excite a particular state i for the conserved modes at $R=\infty$, and so when the "channel" of excitation i is "closed" at $R=\infty$ at that E, this state of excitation i may exist at $R^{\ddagger}$[#1], because of the energy made available at $R^{\ddagger}$ due to the attractive potential. Because of the adiabaticity assumed for the conserved modes, systems in this state i at $R^{\ddagger}$ would, however, be reflected before reaching $R=\infty$, when the channel is "closed", and so not contribute to p_{iEJ}. Thus, for such i's the$N^{\ddagger}_{iEJ}$ in eq. (6) should be replaced by zero wherever it appears, both in the numerator and in the denominator. This problem does not arise in the formulation (eq. (5)) in which a different $R^{\ddagger}_i$ is determined for each i.

Eqs. (3–10) are the desired final equations for the products' state distribution using the present dynamical assumptions for the motion in the exit channel.

4. Discussion

One alternative dynamical approximation, simple at first glance, woud have been to assume that the distribution of states of the reaction products is the same as the distribution at $R^{\ddagger}$. However, to implement such a possibility would require either that the motions at $R^{\ddagger}$ be the same as those at ∞ (i.e. separable) or that there be an appropriate method of connecting the states at $R^{\ddagger}$ with those at ∞ even though at $R^{\ddagger}$ the coupling (fragment rotational-orbital, for example) of the transitional modes may be very strong. One such way of making the connection for those modes is the statistical adiabaticity described in ref. [5] or the adiabaticity in ACM. Instead, we have made in this paper a connection which incorporates what we believe may be a somewhat more realistic picture of a non-adiabaticity for the transitional modes during their motion between $R^{\ddagger}$ and R_ℓ. The experiments should resolve this question.

We first compare the above results with those of phase space theory (PST), which has frequently been used in comparisons with the experimental distribution of states of the reaction products, e.g., refs. [10,12,15,16]. The RRKM k_{EJ} values themselves will usually be equal to or less than the PST values, when there is steric hindrance (or its equivalence, hindered rotations of the fragments) in the transition state.

[#1] I am indebted to Mr. Stephen Klippenstein of this laboratory for calling my attention to this point.

For energies below those needed to excite a conserved vibrational mode in the products, the p_{iEJ} appearing in eqs. (6) and (9) is unity for unexcited i modes and zero for all i excitations. The distribution of the states of the products is then determined only by the distribution at $R=R_\ell$, and so eq. (10) for p_{itE} reduces to the PST value. For higher energies, the result for p_{itE} will differ from that of PST, since in the present theory the distribution of the i states, p_{iEJ} in eq. (6), is determined by the behavior at $R_i^\ddagger$ (or $R^\ddagger$) instead of at the PST value, R_ℓ. It is readily seen that the conserved modes will now usually be more vibrationally excited than they would be in PST, when their vibration frequencies at R_ℓ are approximately the same as that at $R^\ddagger$: at $R=R^\ddagger$ the t modes are somewhat hindered, and so their energy levels are more widely spaced than they are at R_ℓ. As a result, the t modes have a smaller share of the excess energy and so the excitation of the i modes becomes correspondingly greater than that in PST. (There is also, usually, more energy available for excitation of the i modes at $R^\ddagger$ than at R_ℓ.)

An extra predicted excitation of the products' vibrations (the present i modes) was also achieved by Wittig et al. in a different way, in their modification (labeled SSE) of PST [12]. In effect, to calculate a *vibrational* distribution, they assumed $l=$constant in the exit channel and, via their eqs. (7)–(10), neglected the centrifugal and radial potential. Given the resulting vibrational distribution they then used the standard PST theory to calculate the rotational state distribution of the products for each vibrational state of the latter. They had obtained excellent agreement between their experimental data for the rotational distribution of the products and PST where the products were in their ground states vibrationally, but found some deviations from PST for the products' rovibrational state distribution at energies sufficient to excite the products vibrationally. The present model offers a different interpretation of the latter, with trends in the same direction as that of SSE.

We have seen that two aspects of unimolecular studies are the rate constants k_{EJ} and the products' state distributions. (A third aspect is, of course, the question of intramolecular dynamics before reaching the critical configurations for dissociation.) We have also seen that the present model will differ from PST in the rate constants k_{EJ} when there are steric effects, but will agree with it for the products' rotational state distribution when the energy is insufficient to excite the products' "conserved" vibrational modes. The k_{EJ}'s calculated from ACM can be expected to be closer to the present k_{EJ}'s, at least if the former are calculated from the actual vibrationally adiabatic curves, obtained from a potential energy surface. The products' distribution of states will, however, differ from that of the ACM, because of the non-adiabaticity assumed in the present model for the transitional modes during motion from $R^\ddagger$ to R_ℓ. It will also differ from that of a statistically adiabatic model [5] for the same reason.

In recent experiments on the unimolecular dissociation of CH_2CO molecules having a particular energy, Moore and co-workers found that the distribution of states of the products agreed with PST but differed from the ACM predictions or, more precisely, from a form of ACM which assumes a universal interpolation formula having the usually employed parameter range for the ACM interpolation [16]. The experiments were with energies E sufficient to excite the rotation of the products, but not to excite the conserved modes (the products' vibrations). Since the present treatment of products' distribution of states agrees with that of PST, it agrees with the results of Moore and co-workers. Comparison of the present formulation with future results at higher energies, as well as measurement of k_{EJ}'s, or of k_{EJ}'s averaged over some ensemble of J's, should prove to be especially interesting.

A related situation, but for the unimolecular dissociation of ions, has been reported by Chesnavitch et al. [10]: The rates agreed with RRKM theory (in a form using a tight transition state), but the energy distribution of the products, in this case the translational energy distribution, agreed with an "orbiting transition state theory", i.e. with PST. While the details of the treatment differ (we use a variationally calculated flexible transition state, classify the modes as conserved or transitional, and treat their motion differently as regards the energy distribution) the experimental and theoretical situation for the ionic system is seen to be similar to that for the neutrals.

As with other models for the distribution of quantum states of the reaction products the present one is aimed, by comparison with the experimental data, at providing further information on the sources of energy redistribution along the exit channel, as well as on the question of whether or not there is a statistical energy distribution in the transition state.

As was the case with the k_{EJ}'s classical trajectories could also be used, in conjunction with RRKM theory at $R^\ddagger$, to test the utility of the present dynamical approximation, for various assumed potential energy surfaces. Typically, in classical trajectory studies for unimolecular reactions a microcanonical ensemble of initial states for the parent molecule is used, e.g., as in ref. [17]. Such classical trajectory studies have permitted, among other things, a test of intramolecular vibrational energy distribution, which in turn can influence both the rates and the product energy distribution (e.g., ref. [18] and references therein). Instead, in the more restricted use of the trajectories just mentioned only a narrow subset of the microcanonical ensemble would be employed, namely those originating at $R=R^\ddagger$, with $\dot{R}>0$. The resulting product energy distribution (or the distribution of classical action variables of the products) could then be found from the trajectories and compared with that predicted from the present model.

In our current applications the systems and energies chosen have been such that a suitable reaction coordinate R has been the fragment–fragment separation distance [6–8]. The transition state has been very flexible. However, for higher energies the transition state determined variationally tends to move to shorter separation distances, and a different reaction coordinate might be needed there, for example, in some instances at least, the minimum potential energy path (the "reaction path"). The potential energy function also would have to be appropriate to that R region, as Klippenstein in our group has found in his calculations.

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