Intramolecular Dynamics and Unimolecular Reactions

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In this article we describe recent research of our group on the rate constants and the distribution of quantum states of the reaction products of unimolecular dissociations and on methods to treat intramolecular dynamics. Connections among various transition state type theories are also discussed.

1. Introduction

In the present paper some recent work of our group is described on specific rate constants k_{EJ} of unimolecular dissociations for reactions with flexible transition states (Sec. 2) and on the distribution of the quantum states of the reaction products (Sec. 3). The systems considered are those for which there is no potential energy barrier for the reverse reaction of recombination. The relationship between several transition state (TS) theories for the rate constants is discussed in Sec. 4. In a concluding section (Sec. 5) several approaches to the topic of intramolecular dynamics are summarized. The methods in Sec. 5 are based on a generalized moment expansion, a partitioning, and an artificial intelligence method.

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2. Unimolecular Reaction Rate Constants k_{EJ}

The rate constant for a unimolecular dissociation or isomerization of a molecule at a given energy E and total angular momentum quantum number J is given in RRKM theory by [1]

$$k_{EJ} = \frac{N_{EJ}^{\neq}}{h\varrho_{EJ}}, \tag{1}$$

where $N_{EJ}^{\neq}$ is the number of quantum states of the transition state at the given E and J, and ϱ_{EJ} is the density of states of the parent molecule, determined by state counting, taking vibrational anharmonicity into account when practical. $N_{EJ}^{\neq}$ can be determined variationally, from the minimum in a plot of $N_{EJ}(R)$ versus some reaction coordinate R [2]. The

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main task, given any potential energy surface for the dissociating molecule, is to calculate this $N_{EJ}(R)$.

Simple analytic models can be used when the transition state (TS) is "tight" or "loose". In the intermediate case the state counting for N_{EJ} is more difficult, because of the highly coupled nature of the hindered rotational-overall rotational motion in the TS. In principle, at each R one could solve the relevant Schrodinger equation for the nuclear motion to obtain the energy levels, and so obtain $N_{EJ}(R)$. We have adopted instead the following procedure [3,4].

The degrees of freedom are classified into two groups: (i) the "conserved" modes, for which the motion in the TS is similar to that in the parent molecule, as for example, certain vibrations which only undergo some change of vibration frequency during the reaction; (ii) the "transitional modes", which undergo a considerable change in the nature of their motion. For example, the rocking vibrations of the separating fragments of a dissociation become hindered and subsequently free rotations of the products. Also included in the transitional modes are the overall rotations, since they are strongly coupled to the other rotations. $N_{EJ}(R)$ at any R is then given by a convolution of the number of states $N_v(E-\varepsilon)$ of the conserved modes and the density of states $\varrho_J(\varepsilon)$ of the transitional ones at that R:

$$N_{EJ} = \int_0^E N_v(E-\varepsilon)\varrho_J(\varepsilon)\mathrm{d}\varepsilon. \tag{2}$$

A quantum count was used for the $N_v(E-\varepsilon)$, while $\varrho_J(\varepsilon)$ was expressed in terms of the corresponding classical phase space integral. Initially, to facilitate the imposition of a constant total angular momentum quantum number J in a microcanonical ensemble, action-angle variables were used to treat the transitional modes [3], modes which were, for the case of two polyatomic fragments, typically six in number [3,4]. Later, a constant J was achieved using conventional coordinates [4]. A simple Monte Carlo importance sampling was also introduced, particularly effective for transition states which were close to being loose [4]. The calculation of each k_{EJ} for a given E and J was easily programmed and required little computer time, about 10 to 15 minutes on a VAX 11/780 [4].

Quantum corrections for the transitional modes, for thermally averaged k_{EJ}'s, were calculated using a Feynman path integral method and found to be negligible for the system studied: $2CH_3 \rightarrow C_2H_6$ recombination at 300° K to 2000° K [5]. Application of a Wigner-Kirkwood perturbation formula gave similar results [5].

3. Distribution of Quantum States of Products

Two of the treatments of the products' distribution of states have been phase space theory (PST) [6] and the adiabatic channel model (ACM) [7]. The former assumes a loose transition state (free rotations) and has been useful in predicting the distribution of states of the products of unimolecular processes which have no barrier for the reverse reaction of recombination. However, many examples exist where PST yields too high a rate for the reverse reaction and hence too high a unimolecular dissociation rate constant k_{EJ} [8]. The experimentally observed slower rate can be understood in terms of the $N_{EJ}(R)$ in the TS being less than would be predicted by PST: The rotational motion of the fragments in the TS is frequently somewhat hindered, rather than being free as postulated in PST, and so has more widely spaced energy levels and hence a smaller number of states $N_{EJ}(R^{\neq})$. ($R^{\neq}$ denotes the position of the TS.) Two methods which incorporate hindered rotations in the TS are the adiabatic channel model (ACM), which is a microcanonical version of vibrationally-adiabatic TS theory [9], and RRKM theory [1].

RRKM theory was designed to calculate rates. To use it to calculate the products' distribution of states it is necessary to introduce some dynamical approximation for the motion in the exit channel after passing through the TS. We restrict our attention to the case where the reverse reaction of recombination of the fragments has no potential energy barrier.

It will be recalled that when the TS is "loose", as in PST, there is only a radial interaction between the two fragments in the vicinity of the transition state. The TS of PST occurs at a value R_l of the reaction coordinate where the radial interaction force just balances the centrifugal force. The latter, in turn, depends on the orbital angular momentum quantum number l. In PST the internal state distribution of the reaction products ($R = \infty$) is given by the statistical distribution in the loose TS ($R = R_l$).

On the other hand when the rotations of the fragments in the TS are hindered, they are coupled to l, which is no longer a good constant of the motion in the vicinity of the transition state. J, its projection, and E remain good constants. In RRKM theory the TS involves an $R^{\neq}$ which depends on J and E and so involves an ensemble of l's, rather than there being (as in PST) a separate TS for each l.

Elsewhere, we have described a dynamical approximation for predicting the quantum state distribution in the fragments, incorporating RRKM theory in the process [10]: the conserved modes were treated as vibrationally-adiabatic (VA) between $R^{\neq}$ and $R = \infty$. Since in a VA approximation, no state is reflected during its flow from $R^{\neq}$ to ∞, the distribution of quantum states for the conserved modes in the products at $R = \infty$ is the same as that in the TS at $R^{\neq}$. The latter distribution was calculated statistically. Given this distribution, that of the transitional modes was then calculated assuming them to be determined statistically at R_l. It was assumed, thereby, that they are nonadiabatic between $R^{\neq}$ and R_l. The transitional modes are typically expected to be low frequency modes at the R's involved and so to be susceptible to nonadiabatic effects, much as rotations are in collisions. The details of the formulation are given elsewhere [10].

The net result of the treatment is to yield a predicted rotational state distribution of the products which is the same as that of PST, when the energy of the products is insufficient to excite them vibrationally [10]. Differences from the state distribution of PST occur at higher energies [10].

Some similar results have been found experimentally: for energies insufficient to excite the products vibrationally [11]. Wittig and coworkers indeed found good agreement with PST for NCNO decomposition, as did Moore and coworkers at this meeting for CH_2CO dissociation [12]. The NCNO results for higher energies showed small deviations from PST, and these have been discussed [10,11]. Qualitatively they are in a direction consistent with the present model and we are currently exploring them quantitatively. Results for H_2O_2 dissociation using the fifth OH overtone excitation of H_2O_2 by Crim and coworkers showed reasonable agreement with PST and ACM [13]. (Results with the fourth overtone require additional thermal excitation for the dissociation, thus introducing some additional complexity in the interpretation.) Comparisions with ACM and PST were described [13].

4. Various TS's and the Dynamical TST

Since there exist various types of TS theory (TST, such as PST, VA theory, ACM, RRKM theory, an adiabatic-statistically adiabatic theory) it is useful to note here the relationship of some of them to Wigner's classically-derived transition state theory [14], and thereby to each other. It will be recalled that Wigner showed that given an equilibrium statistical ensemble in phase space for the reactant(s), a classical mechanical transition state theory could be derived dynamically, rather than merely postulated *ad hoc*. In particular, he showed that if a hypersurface, positioned between reactants' and products' portions of phase space, could be found such that no trajectories emanating from the reactants recrossed that surface, that none emanating from the products recrossed it, and finally that none emanated from the hypersurface itself without reaching reactants or products, i.e., if all of this hypersurface were effectively used for reactive trajectories, a classical mechanical transition state theory would follow rigorously from the classical dynamics, given an equilibrium ensemble for the reactant(s).

One particular approximation in some TS-type theories is to assume that the above critical hypersurface in phase space is for the given J and E one with a specified value of a coordinate, which we will designate by R = constant; the "constant" depends on J and E. This hypersurface corresponds to the R for which $N_{EJ}(R)$ is a minimum [2,15,16]: the flux for motion from the reactant(s) to the products along some reaction coordinate R is proportional to $N_{EJ}(R)$ [17]. Suppose that this $N_{EJ}(R)$ has a minimum at some $R = R^{\neq}$. For R's on the parent molecule's side of $R^{\neq}$, the situation that $N_{EJ}(R)$ exceeds $N_{EJ}(R^{\neq})$ corresponds classically to trajectories starting from that molecule's side of $R^{\neq}$ and recrossing each R (for $R < R^{\neq}$) more than they recross $R^{\neq}$. Similarly, the $N_{EJ}(R)$ being greater than $N_{EJ}(R^{\neq})$ for $R > R^{\neq}$ corresponds to trajectories starting from the separated fragments and recrossing that R more than they recross $R^{\neq}$. Thus, for $R = R^{\neq}$, there is the least recrossing of the hypersurface R = constant, and so one obtains the closest approximation to Wigner's choice of the hypersurface, for the case (for the given E and J) of a coordinate hypersurface. This approach is also frequently referred to now as variational TS theory and has been used both microcanonically and canonically (given temperature T). In the canonical case, $R^{\neq}$ depends only on T.

To consider further the relation between Wigner's classically-derived TS theory and some of the others it is useful, first, to recall the connection between quantum and classical variables. Semiclassically, it will be recalled, in one dimension a quantum state corresponds to a particular value of a classical momentum – the action variable – and to a uniform range (2π or 1, depending on the definition) of the canonically conjugate coordinate, the angle variable [18]. For N dimensions each quantum state has a specified value for each of the N action variables. In phase space theory, where l is a good quantum number and the $R^{\neq}$ depends on l as indicated earlier (denoted by R_l), the critical hypersurface is the one which gives this functional relationship between R and an action variable l and is independent of all other coordinates and momenta. In RRKM theory it describes, instead, a functional relationship $R^{\neq}(J)$ between R and J for the given E.

We consider next the vibrationally-adiabatic (VA) TS theory [9], and denote the totality of quantum numbers for each state by n (which includes J). The transition state value of $R, R^{\neq}(n)$, corresponds to the maximum energy $E_n(R)$ in a plot of the energy of this quantum state n vs. R. Thus, the critical hypersurface here is the one giving this functional relationship between R and n, and is independent of the remaining variables (the angle variables and the momentum conjugate to R). At first glance such a hypersurface might appear to be more general than one which merely yielded an $R(J)$. However, because of nonadiabaticity there can be extensive transitions between the VA states during the motion along R (e.g., at vibrational-rotational "avoided crossings") and the apparent generality of VA theory then disappears. Adiabaticity in the vicinity of $R^{\neq}$ would be expected to be more valid for the conserved modes, especially the high frequency ones or the less interactive ones, than for the transitional modes.

5. Intramolecular Dynamics

When an isolated molecule is excited in some manner, for example, vibrationally via a high OH or CH overtone, or vibronically, by some laser pulse, the ensuing time-evolution of the vibrational-rotational motion is of particular interest. In principle, it can be described in terms of eigenvalues and eigenvectors of the relevant Schrodinger equation for this nuclear motion. For the higher energies, such a description is not practical. Its level of detail is also considerably more than that provided by the relatively few time constants experimentally measurable from the evolution. In this section several recent approaches in our group to this problem of intramolecular dynamics are described, each intended to simplify the treatment of the time-evolution [19–22].

In one method [19] some appropriate basis set is introduced for the nuclear motion for the case that only a relatively small number of basis set states desribe the dominant initial or final states, with the remainder never building up a significant concentration during the time-evolution [19]. A steady-state treatment of the latter then yielded a result which we subsequently obtained also with a partitioning argument [19]. This method is complementary to two others we have explored, summarized below, and indeed can be combined with them.

In one of these the low-frequency behavior is obtained from moments of reciprocal powers of an energy-shifted

Hamiltonian, in the case of vibrational quantum beats or, in the case of dissipative behavior, by introducing also an experimental "decay" time, and varying the latter to obtain an extremum in the calculated relaxation time [20]. High frequency properties were obtained from an expansion in positive powers of the Hamiltonian. Details of the method and various results obtained with it are described elsewhere [20, 21].

A third method which we have formulated for this problem involves the use of an "artificial intelligence" (AI) approach [22]. An AI method had been used by several authors to treat a state-to-state multiphoton absorption [22], and we have found that we could use a related method for treating this intramolecular energy redistribution problem. We have applied it to both an oscillatory case, where there were quantum beats, and to a dissipative one [22]. Particularly in the latter, there are many acceptable final states, rather than just one, which distinguished the treatment from a particular multiphoton application [23]. The present calculations reduced enormously the number of states needed to describe the phenomenon of intramolecular dynamics for the various cases treated. We are further exploring their application to actual systems.

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