COO-2873-1

THEORY OF CHEMICAL KINETICS

Progress Report
for Period May 1, 1976 - April 30, 1977

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January 1977

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Prepared for

The U.S. Energy Research and Development Administration
under Contract No. E(11-1)-2873

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ABSTRACT

Progress has been made in the following areas of the theory of chemical reactions. Starting with formal expressions for rearrangement collisions we show how to reduce these to a form in which a Franck-Condon approximation for the transition probability can be usefully applied. The simple theory so obtained yields qualitative predictions of vibrational and rotational distributions of reaction products in reactions such as $F + H_2(D_2) = FH(FD) + H(D)$ and others. The theory further provides simple useful expressions with which to assess variations in mass ratios, exoergicities and various features of the potential energy surface governing the reaction. Chemical reaction systems with many degrees of freedom provide intense challenges and we have formulated a stochastic reduction theory in which a subset of degrees of freedom in the system can be treated approximately. The subset needs to be weakly correlated with the remainder, not necessarily weakly interacting. Weak correlations are available, for instance if separate time scales for the motions of the subsets exist. We apply the theory to vibration-translation transfer and show that low order moments of the distribution are given quantitatively correctly. We have made a suggestion concerning the interpretation of certain laser induced chemical reactions and chemical activation experiments. The suggestion stipulates the existence of non-statistical energy distributions in reacting molecules due to effective vibration-vibration and ineffective vibration-translation energy transfer. We have completed an article on the analysis of the basis of orbital symmetry rules for concerted and non-concerted reactions; the analysis is based on formal scattering theory and shows

that such symmetry rules can be viewed as selection rules of electronic transitions among quasi-adiabatic energy surfaces of reactants and products. For an array of catalytic sites on which potentially unstable reaction mechanisms may occur, we have shown the existence of cooperative instability phenomena.

Progress has been made on the theory of chemical reactions in a number of areas: (a) on the analysis of details of chemical dynamics by the use of Franck-Condon factors; (b) on stochastic reduction of collision dynamics; (c) on interpretation of some experiments in laser-induced chemistry; (d) on the study of a basis for orbital symmetry rules; and (e) on cooperative instability phenomena in arrays of catalytic sites on which potentially unstable reaction mechanisms may occur.

A. Franck-Condon factors in studies of dynamics of chemical reactions.

Consider a chemical reaction occurring on a single adiabatic potential energy surface. Formal scattering theory provides expressions for the reaction cross section leading from reactants to products. Quantum mechanical calculation of such cross sections is a lengthy, expensive task; the calculation of classical trajectories takes less time but it is still an extensive procedure. Many approximations to the quantal and classical theories have been proposed. In a series of papers we have attempted to develop systematically from formal scattering theory a qualitative theory of chemical dynamics to begin to fulfill the need for an approximate theory which can be derived by means of precisely stated approximations and which is cast in the form of easily interpretable equations solvable with a minimum of computational effort. In Ref. 1 we show how the general expression for the transition matrix for an electronically adiabatic reaction may

be rewritten in terms of a transition between two surfaces through the use of a quasi-adiabatic representation. This exact transition matrix is then reduced by neglect of virtual transitions to excited electronic states, by the application of the Born-Oppenheimer approximation, the neglect of terms involving gradients of the nuclear wave function, and finally by a Franck-Condon approximation. We then evaluate the remaining overlap integral by means of some simple physical arguments and show the importance of the coupling (in a simple tri-atomic reaction such as $F + H_2 = HF + H$) of the translational degree of freedom of reactants with the vibrational degree of freedom product and the vibrational degree of reactant with the relative translation of product. We test our theory for the cases $F + H_2(D_2)$ and $H(D) + Cl_2$. We find that the Franck-Condon overlap expression can qualitatively predict the vibrational product state distribution (see Fig. 7, ref. 1) including the dependence of that distribution on reagent translational energy, mass ratios, and various features of the potential energy surface.

In Ref. 2 we study vibration-rotation distributions in 2 and 3-dimensional atom-diatom chemical reactions. Here we first need to reduce the Franck-Condon overlap form for the transition amplitude from reactants to products in a partial wave series. We affect an approximate separation of angular coordinate factors and vibration-translation factors. For the study of the angular coordinate factor we examine limits of weak and strong potential and kinematic coupling.

and find possibility of relatively simple approximations in these four limits. We study the application of this theory to the reaction $\text{H} + \text{H}_2$ and are able to predict quite well rotational distributions of reaction products. Next we applied our results to the reactions $\text{F} + \text{H}_2(\text{D}_2)$ and $\text{H}(\text{D}) + \text{Cl}_2$ and again find it impossible to predict vibrational and rotational distributions of reaction products (see Fig. 8, Ref. 2). The predictions give all the trends correctly and are frequently quantitatively useful.

In Ref. 3 we study our expressions based on generalized Franck-Condon factors in relation to information theoretic analysis of vibration-rotation distributions and of isotopic branching ratios. For rotational distributions we find linear surprisal behavior for low rotational excitation in the limit of strong potential and weak kinematic coupling, but nonlinear surprisals for high rotational excitation in that limit. In addition, nonlinear rotational surprisals are generally obtained for any degree of rotational excitation in the limit of strong kinematic and weak potential coupling. For both rotational and vibrational surprisals we find that linearity occurs in the surprisal plots when the potential constrains the reaction to occur through a highly localized set of nuclear configurations, situations which occur in the limit of strong potential coupling and of highly localized overlap integrals. For the prediction of isotopic branching ratios, as for instance in the reaction $\text{F} + \text{HD} = \text{FH}(\text{FD}) + \text{D}(\text{H})$, we show that the purely dynamical Franck-Condon factors for the transition amplitude provides a correct qualitative description of the

branching ratio, particularly on its dependence on reagent rotational excitation. We also use information theory to predict the same ratio and find some points of similarity to the dynamical result such as the dependence on parameters of the product state distribution but also important points of difference such as the dependence on the degree of reagent rotational excitation.

In Ref. 4 we present a theoretical study of the relation of the description of a chemical reaction by means of adiabatic as well as quasiadiabatic representations. This study was necessary in order to distinguish between the application of a Franck-Condon approximation and a first-order perturbation approximation.

B. Stochastic reduction in molecular collision theory.

One of the problems in the development of theories of molecular scattering processes is the treatment of a large number of degrees of freedom which are coupled during the reaction. Although significant advances have been made in accurate quantum and classical dynamical methods, these are largely limited to systems with few degrees of freedom. In Reference 5 we develop an approach to the approximate treatment of the collisions of systems with many degrees of freedom by means of a stochastic reduction analogous to that used in nonequilibrium statistical mechanics, quantum optics, and theories of unimolecular decay. This approach leads to a partial uncoupling of degrees of freedom weakly correlated (although not necessarily weakly interacting with the remaining degrees of freedom.) Such weak correlations between sets of degrees of freedom can frequently be found, for

example in cases where there are substantial differences in the time scales associated with the motion of the separate sets of degrees of freedom. Furthermore, we find in some cases that equations of motions for averaged dynamical quantities such as low order moments of energy state distributions can be determined without having to solve for the distributions themselves. We begin by describing a projection-operator method for decomposing a complicated collision system into two or more sub-systems, each of which is weakly correlated with the others. Approximations to this correlation are then introduced and there result sets of coupled equations for the reduced density operators associated with each sub-system. For the particular case of vibration and translation energy transfer we use arguments of multiple time scales to uncouple the stochastically reduced equations of motion. This leads to a single diffusion equation for the time evolution of the action in the oscillator during the collision. Comparison with the corresponding exact results indicate excellent agreement of low order moments of the classical distributions of vibrational energy in the limit of small energy transfer.

C. Nonstatistical behavior in laser-induced chemistry and chemical activation.

The issue of the usefulness of laser-induced chemistry (and its preference to simple heating) is intimately related with the relative time scales of reactivity of an excited molecule, energy transfer from one mode to another within the molecule, vibration-vibration energy transfer between molecules and vibration-translation transfer in the system. In Ref. 6 we propose an interpretation of some recent

laser-induced chemical reactions and chemical activation experiments. Based on experimental results we find the intriguing possibility of the existence of highly non-statistical vibrational distributions in molecules exposed to laser radiation. These non-statistical distributions are set up under conditions where vibration-vibration transfer from one molecule to another by collision occurs on a relatively short time scale compared to both the reaction and vibration-translation transfer. The non-statistical distribution occurs due to a set of modes (oscillators) established at high vibrational temperatures due to effective vibration-vibration transfer but that set being coupled to a lower translational temperature due to slow vibration-translation energy transfer. We believe that this interpretation may have important consequences for the consideration of certain types of unimolecular reactions.

D. Symmetry in chemical reactions.

In Reference 7 we attempt to provide a basis for orbital symmetry rules for both concerted and non-concerted reactions. In an article which is partly review and partly presents new results we show how orbital symmetry rules can be obtained as selection rules for electronic transitions in a derivation based on formal scattering theory. We proceed to show that a hierarchy of symmetry rules are available in close analogy to a hierarchy of selection rules in spectroscopy based on the degree of approximation employed. We apply our results to some well known concerted and nonconcerted reactions and conclude with a brief discussion of the principle of maximum bonding.

E. Cooperative instability phenomena.

We investigate cooperative instability phenomena in arrays, regular or random, of localized catalytic sites immersed in a bulk system (Ref. 8). Nonlinear reaction mechanisms may occur on the catalytic sites; the reactions in the bulk are stable. We derive from the partial differential reaction-diffusion equations for the total system for homogeneous bulk conditions ordinary integral equations and obtain from these, by linearization, stability conditions as a function of catalytic site density. The theory is applied to one-dimensional lattices of catalytic sites with several model reaction mechanisms. For a product activated enzyme mechanism occurring on each catalytic site we show that there exist cooperative effects among sites due to reaction and diffusion. For given constraints, the number of stationary states available (one or three) depends on the density of catalytic sites, such that as the density increases, first three, then one, then three stationary states exist. For the Prigogine-Lefever mechanism the constraint concentration necessary to produce chemical oscillations is shown to depend on the catalytic site density; the functional dependence has a maximum due to cooperative interactions among the sites. We study next a linear array of two types of alternating catalytic sites on which occur reactions of mutual activation of two species. Multiple stationary states are found and again the number of such states available depends on the site density. We believe that the results may be of importance for the study of arrays of catalytic beds as well as the study of the interactions of immobilized enzymes.

References

1. Franck-Condon factors in studies of dynamics of chemical reactions I. General theory application to collinear atom-diatom reactions, " George C. Schatz and John Ross, accepted for publication in J. Chem. Phys.
2. "Franck-Condon factors in studies of dynamics of chemical reactions II. Vibration-rotation distributions in atom-diatom reactions, " George C. Schatz and John Ross, accepted for publication in J. Chem. Phys.
3. "Franck-Condon factors in studies of dynamics of chemical reactions III: Analysis of information theory for vibration-rotation distributions and isotopic branching ratios, " George C. Schatz and John Ross, accepted for publication in J. Chem. Phys.
4. "On stochastic reductions in molecular collision theory: projection operator formalism; application to classical and quantum forced oscillator model, " George C. Schatz, Frank J. McLafferty and John Ross, submitted to J. Chem. Phys.
5. "On the quasi-adiabatic description of the dynamics of electronically adiabatic chemical reactions, " Shaul Mukamel and John Ross, accepted for publication in J. Chem. Phys.
6. "Comment on non-statistical behavior in laser chemistry and chemical activation, " Shaul Mukamel and John Ross, submitted to J. Chem. Phys.
7. "A Basis for Orbital Symmetry Rules, " Horia Metiu, George M. Whitesides and John Ross, submitted to Angew. Chemie.
8. "Cooperative Chemical Instability Phenomena in Arrays of Catalytic Sites, " E.K. Bimbong-Bota, A. Nitzan, P. Ortoleva and John Ross, submitted to J. Chem. Phys.

Lectures

The principal investigator presented invited lectures at:

Max Planck Institute for Biophysical Chemistry

Plenary Lecture, Bunsengesellschaft Annual Meeting

Gordon Conference on Dynamical Instabilities

Gordon Conference on Chemical Dynamics

IBM Research Laboratory, Yorktown Heights

University of Massachusetts, Boston