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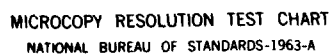
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This report summarizes experimental and theoretical studies, performed with the partial support of AFOSR grant 81-0027, regarding the molecular dynamics of exoergic chemical reactions that yield products in both ground and electronically excited states. The work stressed simple processes in which theory and experiment could be pursued interactively. Findings summarized here are reported in full in the referenced publications.

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→ The objective of this research was to improve understanding at a fundamental level of chemical processes leading to the formation of electronically excited products (~~nonadiabatic~~ processes). The work stressed simple systems for which theory and experiment could be pursued interactively.

→ The quasi-classical trajectory (QCT) method was used in order to map out various types of nonadiabatic dynamics, and to correlate these types of behaviour with the interaction potentials that give rise to them. Three dimensional trajectory surface hopping (TSH)^{1,2} was applied to pairs of potential energy surfaces that interacted along a seam in the exit valley (i.e. as products separated), (a) with an early (E) or late (L) seam, (b) with a small or a large energy-gap, ϵ , at the intersection. The relative yield of electronically-excited product, ρ^* , was determined as a function of E, L, ϵ , type of reagent excitation (translational or vibrational), and also for contrasting reagent mass combinations. The quantity ρ^* could be understood in terms of the local dynamics at the seam (cf. 'transition state spectroscopy', below). The same model potentials were employed in a subsequent study², also performed under this grant, of the effect of nonadiabatic reaction on the product vibrational energy distribution. It was shown how the seam acted as a "filter" favouring reaction into selected vibrational energy states (high vibration or low vibration) in the electronically excited reaction product.

As an experimental 'case study' we examined³⁻⁸ in some detail factors governing the relative yields of electronically-excited atomic products in the reactions $F + Na_2 \rightarrow NaF + Na^*$, Na^{**} , where

Na^* , Na^{**} , ... represents 9 electronically excited states of atomic sodium. Three different experimental apparatuses were used in this work: (a) in the first apparatus atomic F at room temperature collided with Na_2 of fixed internal energy to yield Na^* , Na^{**} ...; (b) in the second apparatus a heated seeded supersonic jet of atomic F collided at enhanced collision energy with Na_2 of fixed internal energy to yield Na^* , Na^{**} , ... and (c) in the third apparatus F is at room temperature and the Na_2 internal energy is varied (this work is continuing). The findings from (a) and (b) are that, though the yields of $\text{Na}^*/\text{Na}^{**}/...$ vary substantially with reagent excitation (the variation being over several orders-of-magnitude for the high-lying electronically excited product states) the variation can be accounted for adequately in terms of statistical models. We have, in addition, developed a simple deterministic model of the choice of reaction pathway, to improve our understanding of this statistical (or near-statistical) outcome.

As exemplified above, nonadiabatic reactive processes transfer from one potential-energy surface to another en route from reagents to products; i.e., in the "transition state". Transfers of this sort can be induced by laser radiation of the appropriate wavelength. Determination of the probability of such a radiation-induced transfer as a function of wavelength is termed "transition state spectroscopy". In the course of this work we have computed, for the first time, transition state spectra (collinearly, and also in 3D) for the fundamental exchange reaction $\text{H} + \text{H}_2 \rightarrow (\text{H}_3^\ddagger) \rightarrow \text{H}_2 + \text{H}$ ⁹⁻¹¹.

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MATTHEW J. KEEFER
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Transition state spectroscopy is also relevant to the case in which electronically excited products are formed photolytically³. We computed the transition state spectrum for such a case, viz. $\text{NaI} \xrightarrow{h\nu} \text{NaI}^{\ddagger*} \rightarrow \text{Na}^* + \text{I}$, and found that for a realisable dressing-laser intensity the transition state, $\text{NaI}^{\ddagger*}$, could be trapped, i.e., could have its lifetime increased by many orders-of-magnitude. In parallel with these calculations we conducted experiments designed to detect emission from the transition state $\text{KI}^{\ddagger*}$ in the course of the ultraviolet photolysis of KI in a molecular beam. The results are extensive, and are in the process of being analyzed.

In the final year of this grant we extended our studies of nonadiabatic processes from gases to the gas-surface interface. An excimer laser (222 nm) was used to photodissociate CH_3Br in the adsorbed state within an ultrahigh vacuum (UHV) chamber. In the gas phase this photolytic process yields approximately equal amounts of ground state photoproduct, $\text{Br}(^2\text{P}_{3/2})$, and electronically excited product, $\text{Br}^*(^2\text{P}_{1/2})$, as inferred from the translational energy of $\text{CH}_3\cdot$. When CH_3Br is adsorbed on the relatively inert substrate, crystalline $\text{LiF}(001)$, we find that the product energy distribution, (determined from the translational energy of $\text{CH}_3\cdot$ as in the gas-phase studies) is markedly altered. The $\text{CH}_3\cdot$ coming from $\text{CH}_3\text{Br}(\text{ad})$ at the surface moves more slowly, and fails to show the energy-bimodality regarded as being characteristic of the formation of $\text{Br}^* + \text{Br}$. Further work is underway to ascertain the details of this change in dynamics, and its causes.

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