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MICROSCOPIC THEORY OF ELECTRONIC TRANSITIONS IN MOLECULAR RATE --ETC(U)
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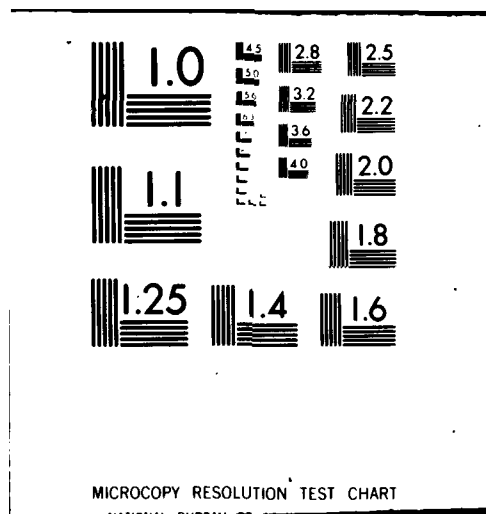
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Grantee: The University of Rochester

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Gas-phase molecular rate processes involving electronic transitions have been studied theoretically, both in the absence (field-free) and in the presence of a laser field. Field-free studies have been carried out for the reaction $F + H_2 \rightarrow HF + H$ involving the dynamic coupling between two potential energy surfaces. This reaction has also been considered in the presence of a near-infrared laser. Other laser-stimulated gas-phase processes include energy transfer in the $Na + Xe$ collision system, collisional ionization in the $He^*(1s2s) + Ar$ system and the spectroscopy of field-dressed quasibound states in the $Xe + F$ system. Laser-												

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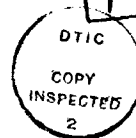
stimulated processes at a gas-surface interface have been studied, including desorption, migration, predissociation and atom-surface scattering

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COMPLETED PROJECT SUMMARY

1. TITLE: Microscopic Theory of Electronic Transitions in Molecular Rate Processes

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9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objectives were to help establish a theoretical foundation for the description of gas-phase molecular rate processes involving electronic transitions, both in the absence (field-free) and in the presence of an external laser field. Such processes can be viewed in terms of the dynamic interaction between two or more potential energy surfaces. For field-free processes (Part I below) this interaction is associated with the coupling between electronic and nuclear degrees of freedom, and for processes in a laser field (Part II) this coupling occurs in conjunction with radiative coupling. During the course of the research, an interest developed in laser-stimulated molecular rate processes occurring at a gas-surface interface (not necessarily involving electronic transitions), and this is mentioned in Part III. The following is a summary of the main papers, where the bracketed numbers refer to the list of publications in #8 above.

I. Field-Free Processes

A fully quantum mechanical (coupled-channel) calculation was carried out for the reaction $\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$ restricted to collinear collisions [23]. The calculation included the coupling of two potential energy surfaces, where the ground-state surface correlates from $\text{F}(2\text{P}_{3/2}) + \text{H}_2$ to $\text{HF}(1\Sigma^+) + \text{H}$ and the excited-state surface from $\text{F}^*(2\text{P}_{1/2}) + \text{H}_2$ to a set of excited electronic states of HF which are not energetically accessible for collision energies of chemical interest. A conclusion drawn from the results is that the dynamics associated with transitions between surfaces, occurring in the reactant region, is essentially decoupled from the dynamics associated with chemical rearrangement in the reaction barrier region. Removing the restriction to collinear collisions but then restricting the study to nonreactive collisions, a fully quantum mechanical calculation was carried out for the quenching process $\text{F}^*(2\text{P}_{1/2}) + \text{H}_2 \rightarrow \text{F}(2\text{P}_{3/2}) + \text{H}_2$ for three-dimensional collisions, with H_2 considered as a rigid rotor [16]. There is a near-resonant electronic-to-rotational energy transfer process when H_2 makes a transition from its ground to its second-excited rotational state, and plots of partial cross sections of different parity (even and odd) vs. total angular momentum are seen to interweave with each other. In addition to the above quantum mechanical studies, semiclassical methods, where the nuclear degrees of freedom are treated classically, were refined for describing resonant vibrational-to-electronic energy transfer in model atom-diatom collision systems [33].

II. Laser-Stimulated Gas-Phase Processes

With sufficient power density (typically greater than a MW/cm^2 , although as low as a kW/cm^2 for special cases - see Part II.B.4), a laser can actually interact directly with the dynamics of a molecular collision process. The focus has been on situations where a laser photon comes into resonance between two potential energy surfaces during the course of a collision [12,27].

It is important to realize that the resonance need not occur between asymptotic levels of individual reactants or products.

A. Theory

The theory has been refined to include specific characteristics of the laser field. One characteristic is the photon angular momentum, which couples different total molecular angular momentum states [1]. Since the spaced-fixed projections of the molecular angular momentum are no longer conserved, an exact solution of the problem is intractable due to the huge number of coupled-channel equations. An approximation has been developed, which averages over the angular dependence of various matrix elements, in order to substantially reduce the number of coupled equations without a significant loss in accuracy [6,18]. Other laser characteristics considered were the linewidth [5], pulse shape [13], multiple modes and the effect of time variation in the intensity [8]. Provided the average laser intensity is less than 10 GW/cm^2 , the single-mode approximation is seen to be very accurate.

B. Applications

1. Energy Transfer. Quantum coupled-channel calculations were carried out for $\text{Na} + \text{Xe}$ collisions in the presence of two lasers: the rhodamine-110 dye laser ($0.55 \mu\text{m}$) and the Nd:glass laser ($1.32 \mu\text{m}$) [28,34]. The two lasers are not resonant with the asymptotic atomic states but do come into resonance with the molecular electronic states for finite internuclear separations. For intensities of each laser at 10 MW/cm^2 , the cross sections for the single-photon excitation of $\text{Na}(3s)$ to $\text{Na}^*(3p)$ and the two-photon excitation to $\text{Na}^*(4s)$ are as high as 0.3 and $0.0008 \text{ \AA}^2$, respectively. Calculations were carried out for $\text{Na} + \text{Ar}$ in the presence of the two lasers, with results similar to those for $\text{Na} + \text{Xe}$ [47]. Calculations were also carried out for three-dimensional nonreactive $\text{F}^*(2p_{1/2}) + \text{H}_2$ (rigid rotor) collisions, where the presence of a laser field is seen to enhance the quenching cross section [19].

2. Chemical Reaction. A semiclassical calculation was performed for the collinear $\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$ reaction in the presence of a Nd:glass laser ($1.06 \mu\text{m}$) [9]. While the laser comes into resonance between two potential energy surfaces, the reactive process involves no net photon absorption (i.e., the photon acts as a "catalyst"). No appreciable effect of the laser is observed until the intensity is raised higher than a TW/cm^2 , where the branching ratio $\text{HF}(v=3)/\text{HF}(v=2)$ changes from less than unity to greater than unity. The reason for the high laser intensity threshold is twofold: (1) the photon catalytic process is second-order, and (2) the shapes of the two potential energy surfaces are significantly different from each other in the region of resonance with the laser.

3. Collisional Ionization. Fully quantum mechanical calculations have been carried out for the laser-modified Penning ionization process where Ar undergoes ionization by collision with $\text{He}^*(3^1P)$ [3,17]. The excited-state potential curve correlating to $\text{He} + \text{Ar}$ is embedded in the electronic continuum, and the laser couples discrete and continuum electronic states. There is a

field-free peak in the emitted-electron energy spectrum which exists in the presence of the laser, and the laser produces two additional peaks on either side of the field-free peak, which are separated by $2\hbar\omega$. The lower-energy peak corresponds to stimulated photon emission while the higher-energy peak corresponds to photon absorption. Two separate calculations were carried out using the 10.6- μm line of a CO_2 laser and the 1.315- μm line of the iodine atom laser. Experimentally measurable results are predicted for laser intensities less than 200 MW/cm^2 .

4. Transition State Spectroscopy. A quantum mechanical theory has been developed to describe the spectroscopy of quasibound molecules in a laser field [42]. One laser is used to link two electronic states of the collision system, giving rise to a set of field-dressed quasibound states which can be spectroscopically probed by a second laser. Calculations were carried out for $\text{Xe} + \text{F}$ collisions, where the first laser was in the ultraviolet region (305-nm line of the XeCl laser) and the second was in the infrared region. Provided that the collision energy is properly chosen, reasonably high total cross sections (up to $1 \text{ \AA}^2$) can be achieved at fairly low intensities for both lasers (down to $1 \text{ kW}/\text{cm}^2$).

III. Laser-Stimulated Gas-Surface Processes

As a first step toward understanding how laser radiation might affect or induce rate processes at a gas-surface interface, quantum mechanical models have been developed to study infrared photon energy absorption by an adspecies with subsequent desorption and/or migration [2,10,26,29,36-38,45]. Desorption is possible with laser intensities as low as $10 \text{ W}/\text{cm}^2$, and both multiphoton and multiphonon effects have been considered. A kinetic model suggests that the measurement of the partial pressure of selectively excited adspecies as a function of laser intensity can yield information on properties such as coverage of the adsorbate and the structure of the adsorbent surfaces [20]. A classical model based on a linear chain has also been developed for the laser excitation of the O-Si and H-Pb adspecies-surface systems [40]; the laser intensity required to achieve desorption is weakly sensitive to the surface chain length (for four or more atoms).

The cooperative role of a surface and high-power visible and ultraviolet laser radiation in the predissociation of diatomic molecules has been studied semiclassically for H_2 , NO and O_2 adsorbed on metal surfaces [35,43,44]. The theoretical approach includes the effect of the surface magnetic field, which leads to Zeeman splitting of the multiplet molecular terms. There is an enhancement of the predissociation rate due to the adsorbent, as compared with pure gas-phase laser-induced predissociation. While the enhancement persists for H_2 and NO as the laser intensity increases, there is a diminution for O_2 as compared with the gas-phase situation.

A classical perturbation treatment of atom-surface scattering in the presence of a laser field has been performed [15], where the laser frequency is chosen to directly excite a surface vibration. The energy transfer to the surface can be expressed as the sum of the energy transfer by the gas atom, the energy transfer by the laser and an interference term. Under certain limiting conditions, such as a high velocity of the gas atom or a short-range gas-surface interaction, the interference is constructive (i.e., positive)

if the laser frequency is greater than the surface vibrational frequency and destructive (i.e., negative) if the laser frequency is less than the surface vibrational frequency.

AFOSR Program Manager: William G. Thorpe, Capt., USAF

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