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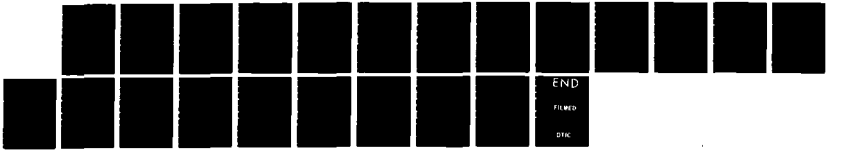

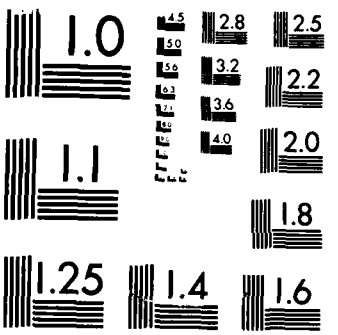

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6c. ADDRESS (City, State and ZIP Code)
Department of Chemistry
River Campus
Rochester, New York 14627

7b. ADDRESS (City, State and ZIP Code)
Bldg. 410
Bolling AFB, D. C. 20332-6448

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Theoretical studies of molecular rate processes were carried out, with an emphasis on how such processes can be induced or affected by external laser radiation. The processes were classified into two types: I. Gas-Phase Processes and II. Surface Processes. Within the first type a variety of laser-assisted collisional processes were investigated, including chemical reactions in a laser field, laser-induced resonance scattering with applications to transition-state spectroscopy and line broadening in general, laser-induced curve switching, isotope separation by selective radiative scattering and laser-induced associative ionization. Several related problems not necessarily involving a laser field were investigated, such as fine-structure transitions in alkali-noble-gas collisions and nonlocal potentials in bound-continuum problems. In regard to the second type of processes, the following dynamical processes were considered: electron transfer in positive-ion-surface collisions, where one-electron transfer leads to ion neutralization and two-electron transfer leads to negative-ion formation (the latter necessitates the inclusion of the Anderson correlation energy); surface-state excitation and laser-enhanced ion-semiconductor electron transfer;

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22a. NAME OF RESPONSIBLE INDIVIDUAL
Major Larry P. Davis

22b. TELEPHONE NUMBER (Include Area Code)
(202) 767-4963

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NC

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(19. continued) laser-induced electron-phonon processes on metal surfaces; formation of electron-hole pairs in a semiconductor by vibrationally-excited molecules; vibrational (both energy and phase) relaxation of a laser-excited adspecies; and laser-induced migration. Spectroscopic processes included resonance fluorescence of atoms near a metal surface and Stark quantum beats from beam-foil excited hydrogen atoms. Other topics of investigation were laser-induced surface excitations on a grating and static electric field effects at the surface of a metallic cluster.

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Department of Chemistry
The University of Rochester
Rochester, New York 14627

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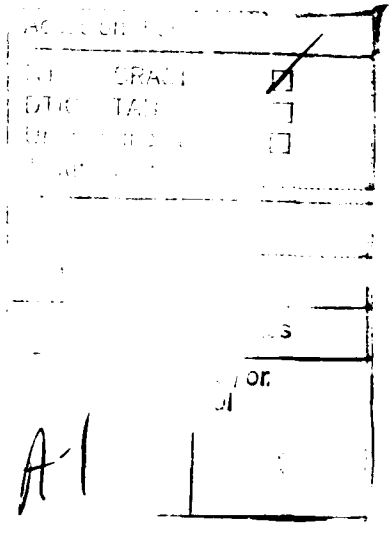

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Department of Chemistry
The University of Rochester
Rochester, New York 14627

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6. SENIOR RESEARCH PERSONNEL:

Dr. D. Agassi	Dr. H. W. Lee
Dr. A. C. Beri	Dr. K. T. Lee
Dr. X. Y. Huang	Dr. J. T. Lin
Dr. M. Hutchinson	Dr. K. C. Liu
Dr. K. S. Lam	Mr. W. C. Murphy
Dr. I. Last	

7. JUNIOR RESEARCH PERSONNEL: Mr. F. Battaglia

8. PUBLICATIONS:

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9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objectives were to help establish a theoretical foundation for the description of laser-induced molecular rate processes, including spectroscopy as well as dynamics. Two general types of processes were considered -- I. Gas-Phase Processes and II. Surface Processes -- and selected accomplishments with respect to these two general types are summarized below.

A. Gas-Phase Processes: Molecular Collisions in a Laser Field

Chemical Reactions. Quantum mechanical and semiclassical calculations were carried out for the collinear reaction $F^*(^2P_{1/2}) + H_2(v=0) - h\nu \rightarrow HF(v') + H$, where $h\nu = 0.469$ eV is the field quantum of the HF laser. It is resonant with the $v' = 1$ to $v' = 2$ vibrational transition of HF, but this resonance is not a factor in the collision and was thus ignored. Within the collision region the photon comes into resonance with two potential energy surfaces, one correlating to $F(^2P_{3/2}) + H_2$ and the other to $F^*(^2P_{1/2}) + H_2(v)$. Transmission to $HF(v') + H$ or inelastic reflection to $F(^2P_{3/2}) + H_2(v)$ takes place by stimulated emission of a photon (corresponding to the minus sign in front of $h\nu$ in the above reaction). The nominal threshold for the reactive transition to $v' = 2$ occurs at an initial translational energy of 0.004 eV. This long delay is due to the introduction of a potential barrier which is absent in the field-free case.

Curve Switching and Transition-State Spectroscopy. Laser-induced

curve switching has been studied for the process $F(^2P_{3/2}) + Xe \rightarrow F^*(^2P_{1/2}) + Xe$ in the presence of two lasers, L1 (XeCl laser) and L2 (CO_2 laser). While there is no net photon absorption from L1, the final collision energy of the Xe + F system is increased (relative to the initial energy) by the energy of the photon(s) absorbed from L2. A single L2 photon is near resonant with the v = 12 and v = 16 levels of XeF, and due to the $\Delta v = 4$ transition the intensity of L2 is on the order of a MW/cm^2, whereas L1 is only on the order of a kW/cm^2. The initial kinetic energy was chosen low enough such that transition between the spin-orbit states of fluorine could not occur due to the collision or the "collision + L1" alone; the energy required for the spin-orbit transition was supplied by L2. An exact dynamical theory, based on a Feshbach projection operator formalism, has been derived for this process. The theory is capable of describing transition-state spectroscopy, where either L1 or L2 can be viewed as a spectroscopic probe depending on the laser frequencies and powers. Introducing suitable approximations, such as replacing certain angular momentum coupling coefficients by average values, we have carried out calculations for the kinetic-energy-averaged scattering cross section of the spin-orbit transition as a function of the frequency of L2, tuned over a range of 0.1 cm^{-1} (centered at 1076.35 cm^{-1}). For a specific rotational transition $\Delta j = 1$ of the XeF complex, the cross section forms a symmetric peak with values as high as 65 $\mathring{A}^2$. We have also considered the situation with L2 turned off, where now the initial kinetic energy is greater than the fluorine

spin-orbit splitting. Plotting the cross section as a function of the frequency of L1 over a range of 0.1 cm^{-1}, we observe an asymmetric peak, where the asymmetry is due to the interference between the laser-induced resonance scattering and nonradiative potential scattering.

Isotype Separation. Related to the above work, an experimental procedure for isotope separation by selective radiative scattering has been suggested. Two colliding partners are prepared in a single beam which is formed by supersonic expansion. At some point downstream of the source, the kinetic energy of relative motion reaches a certain low value. Here two plane-polarized lasers intersect the molecular beam at right angles. Certain molecular pairs, which have the correct vibrational-rotational spacing to undergo a bound-to-bound transition $(v,\ell \rightarrow v',\ell)$, can pick up extra translational energy equal to the photon energy $h\nu_2$ of the second laser. While there is photon absorption from this laser, there is no net absorption from the first laser:

$$A + B(E_i) \xrightarrow{+h\nu_1} AB(v,\ell) \xrightarrow{+h\nu_2} AB(v',\ell') \xrightarrow{-h\nu_1} A + B(E_f).$$

The minus sign in front of $h\nu_1$ indicates stimulated emission. Since the extra translational energy of $h\nu_2$ is much greater than the initial kinetic energy, and comparable with the forward translational energy of the beam, such molecular pairs will tend to be scattered out of the beam and can then be skimmed off. The dynamics of this process is the same as for the work described in the previous paragraph. We

have tested this hypothesis for isotope separation by using the distorted-wave Born approximation to calculate cross sections for Xe + F collisions in the presence of a UV laser ($h\nu_1$) and IR laser ($h\nu_2$). Let us define a separation efficiency p by $p = \sigma_{130} / (\sigma_{129} + \sigma_{130})$, where σ_{129} and σ_{130} are kinetic-averaged cross sections for ^{129}Xe and ^{130}Xe collisions, respectively. For laser intensities on the order of a kW/cm^2, p is seen to be as high as 0.996. While certain aspects not taken into account in our calculations might reduce the efficiency, such as finite laser bandwidths and possible elastic collisions experienced by the deflected molecules before leaving the beam, it is clear that these velocity-changing radiative collisions should provide an efficient means of isotope separation.

B. Surface Processes

Electron Transfer in Ion-Surface Collisions. Based on the time-dependent Fano-Anderson potential, a diagrammatic expansion has been made for the reduced density matrix elements of the neutralized atom formed by one-electron transfer to an impinging positive ion. Neutralization probabilities have been computed for protons colliding with various alkali-halide surfaces, and the results are seen to be interpreted simply in terms of the collision energy and the properties of the systems, namely, the valence bandwidth of the solid and its position relative to the discrete atomic level. The theory of negative-ion formation has also been considered, where the treatment

of this two-electron transfer process now includes the effects of the Anderson correlation energy arising from the Coulombic repulsion between the two electrons of opposite spin in the same valence level of the ion. For the case of zero surface temperature, T = 0 K, the theory is in good agreement with molecular beam experiments on the conversion of $H^+(D^+)$ to $H^-(D^-)$ by scattering from a cesiated W(110) surface. At finite temperatures, the electrons in the solid lying within the range of k_BT below the Fermi level can be activated, where k_B is Boltzmann's constant. Calculational results show that the thermal energy may then be used to overcome the extra energy barrier U for the second electron, provided $k_BT \geq U$, and thus enhance negative-ion formation.

Surface-State Excitation. Quantum mechanical calculations have been carried out for laser-induced excitation of electrons from the valence band to surface electronic states in a one-dimensional semiconductor (silicon). These states are localized near the surface, and excitation cross sections as high as 20 $\mathring{A}^2$ are obtained for low laser intensities (less than 10 W/cm^2). The calculations have been extended to include a charged adspecies. The adspecies-surface potential has been determined as a function of both the adspecies-surface separation and the laser frequency, and the surface-state excitation is seen to enhance the repulsive (attractive) part of the potential for a negative (positive) adspecies, especially as the photon energy approaches half the band-gap energy.

This idea of using a laser to "charge" the surface region has formed the basis of a semiclassical theory of charge transfer, where a positively-charged particle picks up an electron from a semiconductor surface. The charge-transfer rate is larger by a factor of $2\kappa L$ for a surface electron than for a bulk electron, where κ is the imaginary portion of the crystal momentum for the surface state and L is the length of the solid. The theory has been used to determine the probabilities of electron transfer to Li^{3+}, He^{2+} and He^{+} undergoing thermal collisions with a Si(111) surface. The results show an enhancement of the production of excited states of Li^{2+}, He^{+} and He, respectively, receding from the surface, as compared to charge transfer in the absence of surface-state excitation. For example, for the process $He^{2+} + Si(111) + h\nu \rightarrow He^{+}(n=3) + Si^{+}$ under thermal conditions, we obtain a cross section as high as 4.19 $\mathring{A}^2$, where the power density of the laser pumping the surface states is only 1 W/cm^2 (the laser photon energy $h\nu$ is chosen to be 2/5 of the band-gap energy).

Formation of Electron-Hole Pairs in a Semiconductor by Vibrationally-Excited Molecules. A three-dimensional model of a vibrationally-excited molecule with a semiconductor has been developed, where the transfer of vibrational energy leads to the formation of electron-hole pairs.[29,30] Results for the HCl + InSb and HCl + PbSe systems under thermal conditions indicate transition probabilities in the range 0.1 to 10%, which can be readily observed by experimental measurements of the semiconductor electrical conductivity. The semiconductors considered here have similar lattice

parameters. However, the transition probabilities are higher for HCl + InSb, than for HCl + InSb, which is attributable to differences in the dielectric constant (18 for InSb and 280 for PbSe) and the energy gap (0.165 eV for InSb and 0.26 eV for PbSe -- the latter is closer to the vibrational energy level spacing of 0.358 eV in HCl).

Vibrational Energy Relaxation of a Laser-Excited Adspecies. Vibrational energy transfer between an infrared laser, a solid surface and an adatom has been studied by a generalized master equation which includes memory effects. Numerical results using the isomnesic (constant-memory) approximation for time scales ranging from 2 picoseconds to 2 microseconds for $H(H_2O)/KCl(001)$ show that bond-selective excitation is possible with a low-power laser in spite of fast phonon relaxation, and that the time evolution of the system is highly non-Markovian even for fairly long times. An overall residence time of the adspecies, up to the point of desorption, has been defined. This time is on the order of 10 nanoseconds for a laser whose power is 10 W/cm^2 and whose frequency is resonant with $v = 3$ and $v = 6$ of the adbond, where $v = 6$ is the highest vibrational level and the Debye frequency of the substrate is resonant with $v = 0$ and $v = 3$.

Laser-induced Migration. When a laser excites a plasmon on a metal surface, a wave of alternating charge is propagated along the surface. This charge has a varying electric field associated with it, and we have shown that this field can be coupled to a charged adspecies. In particular, it has been shown that if aluminum is exposed to CO_2 laser radiation of low intensity (1 W/cm^2), such a

plasmon will be excited. If an atomic oxygen ion of charge -1 were adsorbed on the surface, it would be coupled to the electric field and thus carried along with the plasmon. The velocity associated with this stimulated migration is 61.3 microns/s, which is five orders of magnitude greater than the usual thermal velocities observed at room temperature. Furthermore, the negatively-charged adspecies will only move in the direction of the plasmon; this, in turn, can be controlled by the exciting radiation. Thus a laser not only increases the speed of migration but can also select the direction.

Resonance Fluorescence at a Metal Surface. Surface-dressed optical Bloch equations, involving a treatment of surface-reflected photons and a surface plasmon, have been derived for a collision-damped two-level atom near or adsorbed on a metal surface. Effects of the laser bandwidth are included by means of a phase diffusion model for the driving field. In the weak-field or large-detuning limit, the power spectrum of scattered light has two peaks: one corresponding to Rayleigh scattering at the laser frequency ν_{21}. For a sufficiently strong driving laser field, the spectrum exhibits three peaks: a central one at $\nu_0 = \nu_L$ (Rayleigh component), a left one at $\nu_- = 2\nu_L - \nu_{21} - \delta$ (three-photon component) and a right one at $\nu_+ = \nu_{21} + \delta$ (fluorescence component), where δ is the ac Stark shift. The key feature of numerical results, which is a unique behavior due to the surface, is that for certain atom-surface distances the height H_- of the left peak is larger than H_+ of the right peak, whereas in the pure gas-phase resonance fluorescence spectrum H_- is always

less than H_+ (due to molecular collisions for the case of positive detuning).

Static Electric Field Effects at the Surface of a Metallic Cluster. A jellium/free-electron model has been used to estimate the static electric field at the surface of a spherical metallic cluster. By means of a WKB formula derived from the model, an accurate prediction can be made of the "magic numbers" (2, 10, 18, 20, 34, 40, 58, 90, 92, etc.) which refer to the enhanced abundances of certain clusters observed experimentally. Therefore, these numbers are likely to be determined by the symmetry of the problem and not by the detailed nature of the one-electron potential. The electric field near a cluster with a radius of 10-20 $\mathring{A}^2$ is found to deviate from the field at the same distance from an infinite metallic plane. Such a deviation might manifest itself by influencing physisorption.

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