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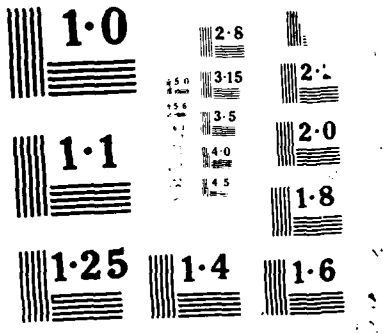
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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Collisional energy transfer, free radicals, optical-optical double resonance, collision-induced electronic transitions, chemical reactions, spin-orbit effects.

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

Rotationally and electronically inelastic collisions in small molecules and free radicals have been studied with both initial and final state resolution in a joint theoretical-experimental project. Particular emphasis has been placed on ditaomic free radicals of importance in combustion (continued on reverse side)

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20. Abstract (continued)

environments. State-to-state cross sections for transitions within the $A^2\Pi$ and to the $X^2\Sigma^+$ state of the CN radical in collisions with argon have been measured in a discharge-flow technique. These experiments have been interptreted by means of our recently developed quantum theory for collision-induced transitions between $^2\Pi$ and $^2\Sigma$ states. Theoretical computational studies of rotationally inelastic collisions in open-shell molecules, including NO($X^2\Pi$), CaF($A^2\Pi$), and CaCl($X^2\Sigma^+$), as well as ^1P to ^3P transitions in highly excited alkaline earth atoms, have been completed. Experimental investigation on the mechanism for the dependence of chemical reactivity on the fine-structure level of a reactant atomic multiplet has also been carried out.

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ENERGY TRANSFER PROCESSES IN FREE RADICALS:
A Collaborative Experimental and Theoretical Investigation

FINAL REPORT

Millard H. Alexander and Paul J. Dagdigian

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I. STATEMENT OF WORK AND DESCRIPTION OF WORK ACCOMPLISHED

New experimental and theoretical advances permit the study of energy transfer processes in free radicals with a far greater degree of both initial and final state resolution than has been hitherto possible. The present grant has involved the collaborative investigation of these processes, with particular emphasis on collisions of diatomic free radicals of importance in combustion systems. State-to-state cross sections for transitions within the $A^2\Pi$ and to the $X^2\Sigma^+$ state of the CN radical by collisions with argon have been measured in a discharge-flow apparatus by means of an optical-optical double resonance technique. These experiments have been interpreted by means of the recently developed quantum theory for collision-induced transitions between $^2\Pi$ and $^2\Sigma$ states. Theoretical computational studies of rotationally inelastic collisions in open-shell molecules, as well as ^1P to ^3P transitions in highly excited alkaline earth atoms, have been completed. Experimental investigation on the mechanism for the dependence of chemical reactivity on the fine-structure level of a reactant atomic multiplet has also been carried out.

One of the most exciting areas of chemical physics is the investigation of the dependence of kinetic processes on the internal electronic degrees of freedom of the species involved. New experimental advances, in particular the advent of powerful tunable dye lasers, permit a far greater degree of both initial and final state resolution than has been hitherto possible. On the theoretical side, sophisticated angular momentum algebra, as well as fast scattering codes, have made accessible accurate quantum studies of inelastic collisions involving open-shell atoms and molecules. The study of these processes provides a direct probe of how the anisotropies of intermolecular potentials can affect changes in the electronic states of the collision partners. From a more practical viewpoint, a detailed understanding of the rates of collisional relaxation of open-shell radicals underlies our ability to model the temporal and spatial profiles of these species in combustion environments. The present grant has involved a collaborative study of inelastic and reactive processes of open-shell atoms and molecules. The principal scientific accomplishments are as follows:

A. Measurement of Quantum-State-Resolved Cross Sections for Collision-Induced Transitions in the CN Radical. Inelastic cross sections for collisional transfer within the CN $A^2\Pi$ electronic state and to high-lying vibrational levels of the $X^2\Sigma^+$ state have been determined with initial and final rotational state resolution by a two-laser optical-optical double resonance (OODR) technique.[1-4] This experiment, along with the contemporaneous experiments of Katayama on the isoelectronic N_2^+ molecule,[5] represent the first observations of electronic collisional quenching processes with both initial and final rotational state resolution.

The CN radical is prepared in a flow system at several Torr through collisional dissociation of cyanogen by metastable argon atoms. Individual rovibrational levels in the A state are initially excited by pulsed Nd:YAG pumped dye laser excitation on isolated rotational lines in the A - X band system. After a delay (<32 nsec) short compared to the average time between collisions, a probe dye laser monitors the collisionally populated levels in both electronic states by $B^2\Sigma^+ - X^2\Sigma^+$ and $B^2\Sigma^+ - A^2\Pi$ fluorescence excitation. In this way, the relative efficiency of collisional interelectronic vs. intraelectronic transfer can be determined.

Collision-induced electronic transitions have been investigated between the nearly isoenergetic v_A and $v_X=v_A+4$ vibrational manifolds for $v_A=3$,[3] 7,[1,2] and 8.[4] In all cases, this process is facile, with rates comparable to pure rotationally inelastic rates, even for $v_A=3$ to $v_X=7$ transitions for which the energy gap is approximately 3kT. The efficiency with which spectroscopically perturbed[6] vs. relatively unperturbed A state levels undergo collision-induced transitions was found to be the essentially the same. The final X state rotational distributions are quite similar in general shape for comparable incident rotational levels in all three v_A manifolds, despite wide variation in the $v_A - v_X$ energy gap. This suggests that it is the anisotropy of the CN-Ar interaction potentials, rather than energy resonance effects, that governs the change in rotational angular momentum. The most interesting result from these experiments is the observation of an even / odd oscillation in the final X state rotational populations. This has been interpreted, with the help of the quantum scattering theory worked out by Alexander and Corey[7] (described in the next section) for $^2\Pi$ to $^2\Sigma$ collisional transitions, as being due to the near homonuclear nature of the CN-Ar interaction.

We have also carried out a one-laser study[8] of collision-induced transitions between the $A^2\Pi$ and $B^2\Sigma^+$ states of CN by monitoring B - X emission upon laser excitation of the $v_A=10$ manifold, which is nearly isoenergetic with and perturbed[9] by the $v_B=0$ manifold. For unperturbed levels the rate of collision-induced transitions appears to be approximately constant and independent of initial level.

B. Development of the Quantum Theory of $^2\Pi$ to $^2\Sigma$ Collision-Induced Transitions. Motivated by current experimental studies of E-E energy transfer in CN in our laboratory[1-4] and N_2^+ at AFGL,[5] we developed[7] the exact, fully quantum treatment of collision-induced transitions between a $^2\Pi$ and $^2\Sigma$ electronic state. This exact theory goes considerably beyond the simple models developed earlier,[10,11] which attributed E-E transfer between near-degenerate electronic states to the presence of non-Born-Oppenheimer perturbations[12] in the isolated diatomic. We now understand that electronically inelastic collisions result from a mixing between the Σ and Π electronic states of the isolated molecules which is provoked by the approach of the collision partner. The presence of a perturber atom lowers the symmetry of the system, so that one component of the asymptotically degenerate wavefunction for the combination of the molecule in a Π state and the target atom will mix with the wavefunction which corresponds asymptotically to the combination of the molecule in a Σ state and the target atom. As the collision partner recedes, molecules, initially in the $^2\Pi$ state, say, have a finite probability of ending up the $^2\Sigma$ state. In a complete description it is necessary to determine the dependence on geometry of the matrix elements of this electrostatic potential in a *diabatic* (isolated molecule) basis. These matrix elements can be obtained from knowledge of the electronically *adiabatic* energies and wavefunctions which would result from an *ab initio* quantum chemical calculation.[7] The formulation of the scattering problem in a diabatic basis then allowed the derivation of several general scaling relations and propensity rules, which provided a useful framework for the interpretation of Katayama's experiments[5] on N_2^+ and Dagdigian's experiments[1-4] on CN.

C. Theoretical and Experimental Investigation of Rotationally Inelastic Collisions of Molecules within $^2\Sigma$ and $^2\Pi$ Electronic States. In earlier work,[13] one of us showed from a consideration of the general quantum scattering equations that there should be a propensity for conservation of the *e/f* fine-structure label in rotationally inelastic collisions of $^2\Sigma$ molecules. This propensity rule has been observed in a number of collision studies of molecules in $^2\Sigma$ states, including our molecular beam state-to state studies on CaCl($X^2\Sigma^+$).[14] We have since been able to develop analytic expressions for the ratio of *e/f* changing to *e/f* conserving cross sections in collisions of molecules in $^2\Sigma$ electronic states.[15] This work was based on the use of semiclassical expressions for the important angular momentum coupling coefficients as well as on the physical interpretation of the relevant tensor opacities for collisions of open-shell molecules. The resulting high-J limit expressions should be useful in the modelling of the relaxation kinetics of hot free-radical species.

In a collision between an open-shell molecule and an open-shell target, the electrostatic intermolecular potential will, in general, vary with the total spin of the composite atom-molecule system. In the laboratory,we have determined state-to-state rotationally inelastic cross sections for collisions of CaCl($X^2\Sigma^+$) with the open-shell NO($X^2\Pi$) target.[16] These measurements were carried out in a molecular beam-target gas scattering configuration with incident state preparation by an electric quadrupole and final-state detection by single-mode cw dye laser fluorescence excitation. Motivated by these experiments, we were able to show how to describe collisions of molecules in multiplet-Σ electronic states with atoms in ^2S states. The cross section for a $JN \rightarrow J'N'$ transition can be expressed as the sum of a *spin-independent* and a *spin-correlated* cross section. For a $^2\Sigma$–^2S collision, the former depends on the sum of the resulting singlet and triplet interaction potentials, while the latter arises from the singlet-triplet difference. Hence, spin-correlated scattering will be important for collision systems where a chemical bond, and hence large spin-exchange interaction, is present. We have begun the extension of this formal treatment to describe collisions of molecules in $^2\Pi$ electronic states with ^2S atoms and, similarly, molecules in multiplet-Σ states with ^2P atoms.

Additionally, we have continued our study of energy transfer in collisions of open-shell radicals. We were able to carry out a new derivation of the useful and popular infinite-order sudden (IOS) approximation for rotationally inelastic collisions of a diatomic molecules in a Π electronic state.[17] This derivation clearly demonstrated the role of scattering on the two adiabatic surfaces of A' and A" symmetry which characterize the interaction of atoms with Π-state molecules. The A' and A" potential surfaces arise in this case because the interaction potential depends on whether the unfilled π orbital lies in or perpendicular to the scattering plane. Numerical studies on collisions of NO($X^2\Pi$) with various partners indicated that the IOS approximation can be expected to be valid only for the light, rapidly moving partners (e.g. H_2, He).[17] In related work we carried out calculations of inelastic cross sections for collisions of CaF($A^2\Pi$) with Ar and He,[18] to compare with the experimental values of Dufour *et al.*[19] in France and Norman and Field[20] at MIT. The magnitude of the cross sections was interpreted using a fully-adiabatic treatment of the dynamics. Because of the small rotational constant of CaF(A) ($B=0.349$ cm^{-1} [21]), rotationally inelastic transitions in CaF can be produced even at large distances.

D. Theoretical Study of Collision-Induced Transitions in Atoms. In collaboration with B. Pouilly at the Université de Lille, France, we have succeeded in the analysis of the dependence on orbital orientation of cross sections for spin-changing collisions of atomic calcium in the 4s5p Rydberg level with He. This theoretical work, both formal[22] as well as computational,[23,24] which goes considerably beyond earlier semi-classical models, provided real insight into the recent experiments of Leone and co-workers.[25] In particular, we were able to show how the observed polarization dependence is a sensitive function of the exact form of the $^{1,3}\Sigma$ and $^{1,3}\Pi$ CaHe potential curves which correlate with the Ca(4s5p $^{1,3}P$) + He asymptote. An adiabatic formulation of the collision dynamics was used to put into doubt the validity of the simple "orbital locking" models[26] previously used to interpret these experiments, and a new, simple model was developed[22] to predict the polarization dependence.

A similar adiabatic treatment was also used to analyze further the mechanism of fine-structure changing transitions in collisions involving atoms in ^2P electronic states.[27] This long-range mechanism is responsible for the pronounced peaking in the energy dependence of the $Na(^2P_{1/2}) \rightarrow Na(^2P_{3/2})$ cross sections.

In concert with an experimental project involving Andrzej Miziolek and William Anderson at the Ballistic Research Laboratory (BRL), Aberdeen Proving Ground, MD, we initiated the study of collision induced transitions between triplet and quintet states of the O atom, in the $...2s^2 2p3p$ Rydberg state. We have developed a general description of the $^3P \rightarrow {}^5P$ collision-induced transitions, specifically involving collisions with H atoms and a covalent-ionic crossing involving the H^-O^+ ion-pair state. These ideas were useful in the interpretation of the preliminary experimental results.[28] This theoretical work is now continuing under the support of a Scientific Services Agreement monitored by BRL.

F. Determination of the Dependence on Initial Spin-Orbit State of Reactions of Ca($^3P^o$) with Alkyl Halides. In our laboratory, we have utilized an optical pumping state selection technique[29] to determine the reactivity of individual spin-orbit states of the Ca(4s4p $^3P^o$) multiplet. Spin-orbit effects in the chemiluminescence channels of a number of reactions of Ca($^3P^o$) with alkyl bromides[30] and iodides[31] have been investigated. With the exception of the Ca($^3P^o$) + SF_6 reaction, for which no spin-orbit dependence was observed,[31] the chemiluminescence cross sections were found to vary significantly with incident atomic spin-orbit level. In all cases, the highest-energy J=2 level possessed the largest cross section, with successively smaller values for the J=1 and 0 levels and a factor of 5 to 10 difference between J=2 and 0. In other experiments,[32] supported by NSF, an opposite ordering of reactivity was found for production of ground-state alkaline earth reaction products. Such spin-orbit effects in chemical reactivity have been interpreted with the aid of a pseudo-quenching model calculation by Alexander[33] (supported under a previous ARO grant) and can be explained as arising from difference in the evolution of the asymptotic spin-orbit levels onto the various electrostatic potential energy surfaces. In a recent article, we have reviewed the literature on spin-orbit effects in simple gas-phase chemical reactions.[34]

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