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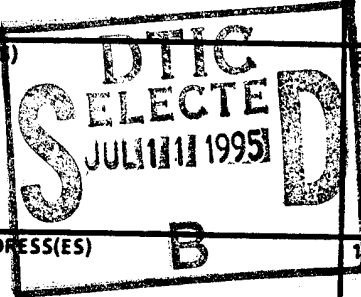
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A collaborative experimental and theoretical study of a number of elementary collisional processes involving small molecular free radicals of importance in combustion and in the decomposition of propellants has been carried out. These have involved chemical reactions and photodissociation, as well as nonreactive collision-induced rotational and electronic transitions. Information on non-bonding interactions involving free radicals was also obtained from analysis of the electronic spectrum of van der Waals complexes of these species.

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**COLLISIONAL AND DISSOCIATIVE PROCESSES
INVOLVING MOLECULAR FREE RADICALS**

FINAL REPORT

Paul J. Dagdigian and Millard H. Alexander

April 13, 1995

U. S. Army Research Office

Grant Number DAAL03-91-G-0129

**The Johns Hopkins University
and The University of Maryland**

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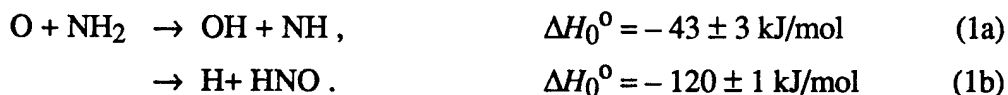
I. STATEMENT OF WORK AND DESCRIPTION OF WORK ACCOMPLISHED

In this project, we have carried out a collaborative experimental and theoretical study of a number of elementary collisional processes involving small molecular free radicals of importance in combustion and in the decomposition of propellants. These have involved chemical reactions and photodissociation, as well as nonreactive collision-induced rotational and electronic transitions. In addition, we have obtained information on the non-bonding interactions between a free radical and a rare gas partner through analysis of the electronic spectrum of the van der Waals complex of these species. The close interaction of our experimental and theoretical groups has allowed much greater insights to be obtained on the dynamics of these collisional processes than would have been obtained by the effort of these groups working independently.

This report summarizes the specific systems studied during the past 3-year period and the insights we have obtained from our collaborative investigation. The principal scientific accomplishments are briefly described in the sections below.

A. Dynamics of Several Reactions of NH, NH₂, and CN

We have carried out both crossed beam and photolysis-probe experiments to elucidate the dynamics of several reactions of the NH and NH₂ radicals. We have investigated both the major channels of the reaction of NH₂ with oxygen atoms through determination of the internal state distribution of the molecular reaction products:



The branching ratio for these two channels have previously been determined¹ to be (13 ± 5)% and (87 ± 5)% for pathways (1a) and (1b), respectively.

In our experiments, the NH₂ free radical was prepared as a pulsed supersonic beam by 193 nm excimer laser photolysis of an ammonia/nitrogen mixture at the tip of the nozzle, and oxygen atoms were produced in a microwave discharge source. For our study² of the hydroxyl product in pathway (1a), deuterated ND₂ reagent was employed and OD product was detected because of interference with the small amount of OH impurity in the O atom source. The internal state distribution of the OD product was found to be very cold, both rotationally and vibrationally, with only ~8% of the available energy appearing as OD internal excitation. Pathway (1a) can be accessed from the reactants through D₂NO and DNOD intermediates, or by direct abstraction along

a quartet potential energy surface (PES).³ In the former mechanism, pathway (1a) is thought to proceed by initial formation without an activation barrier of D₂NO and then hydrogen migration to yield DNOD, which would subsequently decay to yield OD + ND. Our measured OD distribution is much colder than that predicted by statistical theories of the decay of a DNOD intermediate. Our results are consistent with a direct abstraction mechanism on the quartet potential energy surface through a linear transition state, as in the O(³P) + hydrocarbon reactions.^{4, 5}

We have also detected the HNO product from pathway (1b).⁶ This product can be formed from the decay of either the H₂NO or HNOH intermediate.^{3, 7} The HNO product was detected by laser fluorescence excitation in its $\tilde{A}^1A'' - \tilde{X}^1A'$ band system in the $K_a = 0$ and 1 stacks of the ground (000) vibrational level. While pathway (1b) is thought to be the main channel of the O + NH₂ reaction,¹ the HNO fluorescence signals were quite small, because of the small oscillator strength of the $\tilde{A} - \tilde{X}$ band system. The rotational state distribution was nevertheless found to be very cold. This is consistent with the presence of a barrier^{3, 7} (in excess of the dissociation energy) for the decay of the intermediates.

We have also carried out a crossed beam study⁸ of the reaction of imidogen radicals with nitric oxide, for which there are two possible exothermic pathways:



This reaction is important in the combustion of ammonia, etc., and in various schemes for the control of NO_x emissions from fuel nitrogen.⁹ We have determined the internal state distribution of the OH product from pathway (2a). The NH reagent was prepared by 2-photon photolysis of ammonia in a pulsed beam.

Despite the large exothermicity for pathway (2a), very little of the available energy appeared as internal energy of the OH product. This reaction is thought¹⁰⁻¹² to proceed through formation of a HNNO intermediate, which isomerizes with a barrier to yield the products. Our OH internal state distribution is similar to that observed by Flynn, Wittig, and their coworkers^{13, 14} for the reaction of hot H atoms with N₂O. This reaction, which involves the products of both pathways (2a) and (2b), also proceeds through the HNNO intermediate. Very recently, Schatz and co-workers have carried out a quasiclassical trajectory study of the dynamics of the NH + NO reaction.¹⁵ Their calculations agree with our findings that very little energy appears as OH product rotational and vibrational excitation in pathway (2a). They find that the bulk of the exoergicity appears as relative translation; this indicates that the reaction exoergicity is released as the products

are separating, and not while the reagents are approaching.

Another particularly important reaction of the imidogen radical is that with oxygen atoms:



We have characterized the lower v portion of the internal state distribution of the NO product from pathway (3a).¹⁶ This experiment was carried out in a cell at a total pressure of 60 mTorr. The O atoms and NH radicals were prepared by a microwave discharge in oxygen and by 193 nm 2-photon dissociation of ammonia, respectively. Only a small fraction of the available energy was found as vibrational excitation of the NO product in pathway (3a), and the NO vibrational state distribution was found to be monotonically decreasing with increasing v . There is considerable information on the low-lying HNO potential energy surfaces, on which reaction (3) occurs. Pathway (3a) can occur¹⁷ on $1A'$, $1A''$, and $3A''$ PES's without a significant barrier through the formation of a HNO complex, which can decompose to yield H + NO products. For the NO($v = 1$) product, we were able to reduce the pump-probe delay so as to probe the rotational state distribution. Extrapolating back to zero delay, we estimate that the nascent distribution can be characterized as a 1130 ± 50 K Boltzmann distribution.

Other reactions on HNO PES's have been investigated by other research groups. OH($v = 0$) product has been observed in the reaction of hot H atoms with NO.³⁶ Recently, Smith and coworkers¹⁸ have reported the NO vibrational state distribution from the N + OH reaction. In contrast to our results on pathway (3a), their vibrational state distribution was hotter and consistent with phase space theory. This reaction probably proceeds on a $3A''$ surface, on which there is a deep NOH minimum.

Recently, Schatz and co-workers¹⁹ have carried out trajectory calculations on newly derived HNO PES's.²⁰ Their calculated NO vibrational state distribution agrees reasonably well with our measured distribution for reaction (3a) for low v . However, a second peak in the distribution is also predicted for $v \approx 9$, beyond the range of levels sensitively probed in our experiment.

Several years ago, we carried out a study²¹ of the dynamics of the CN + O₂ reaction:

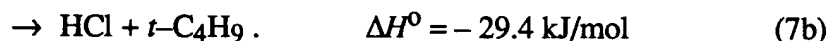
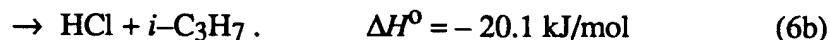


The CN reagent was prepared by 193 nm photolysis of (CN)₂ in a cell, and the NCO product was detected by laser fluorescence excitation. We found considerable NCO product vibrational (primarily bending) excitation. By contrast, a crossed beam study of this reaction by Liu and co-

workers²² with rotationally cold (10 K) CN found little NCO product vibrational excitation. These contrasting observations can be rationalized if reaction (4) has a very strong dependence of the dynamics on the CN rotational excitation, as might be expected from theoretical calculations on the energetics and geometry of the transient NCOO intermediate.^{23, 24}

In order to explore the possibility of a strong dependence of the collision dynamics on the CN reagent rotational excitation, we have carried out a study of reaction (4) in which the CN precursor was prepared by 193 nm photolysis of BrCN, for which the nascent CN rotational excitation is considerable (*ca.* 1 eV).²⁵ We find extensive vibrational excitation of the NCO product. We have also followed the collisional rotational relaxation of the CN reagent as a function of the photolysis-probe delay and have found that the NCO product bending excitation decreases as the CN relaxes (on a time scale faster than the known NCO bending collisional relaxation rate²⁶) We believe that this provides evidence for the role of CN rotational excitation in the dynamics of reaction (4). We are in the process of preparing a manuscript describing this study.

In a slight departure from our studies of reactions of molecular free radicals, we have studied the reactions of Cl atoms with the simple hydrocarbons methane, propane, and isobutane:²⁷



These reactions are of importance as a temporary sink for chlorine atoms in the atmosphere.

The HCl product from reactions (6) – (7) were detected state specifically through resonance enhanced multiphoton ionization (REMPI) in a time-of-flight mass spectrometer. The reactions were initiated in a crossed, pulsed flow of the reagents by 355 nm photolysis of Cl₂ to produce the Cl atom reagents. In order to see the signal due to the HCl reaction product over HCl background signals, it was necessary to purify the Cl₂ reagent by fractional distillation and to segregate the reagents and inject them separately into the photolysis-ionization zone. The rotational state distributions in the observed HCl(*v* = 0 and 1) vibrational levels were found to be quite cold. Because of the known speed and angular distribution of the photolytically prepared Cl reagents, it was possible to gain information on the product c.m. angular distribution from measurement of the product laboratory velocity distribution.²⁸ This velocity distribution could be

derived from the observed mass 36 time-of-arrival profile. The HCl($v = 0$) product from the Cl + isobutane reaction was found to be mainly backward scattered with respect to the incoming Cl atom. These observations of the product internal state and angular distributions are consistent with a mechanism involving abstraction of hydrogen atoms from the hydrocarbon reagent through a collinear Cl-H-R geometry. Quantum chemical calculations do obtain a linear geometry for the transition state of reaction (5).²⁹

B. State-Resolved Rotationally Inelastic Collisions of Free Radicals

In recent years there have been a considerable number of studies of inelastic collisions of open-shell molecules. These have included both formal and computational theoretical, as well as state-resolved experimental, investigations; the latter have principally employed molecular beam or laser double resonance techniques. Supported by the present grant, one of the Co-Principal Investigators has written a comprehensive review of state-resolved experiments on inelastic collisions of small molecular free radicals.³⁰ The overwhelming bulk of these studies have dealt with molecules in $2\Sigma^+$, 1Π , and 2Π electronic states. From this body of work, considerable insight into the dynamics of such inelastic collisions, for example, the origin of spin state and Λ doublet propensities, has been obtained.

By contrast, considerably less attention has been paid to collisions of molecules in electronic states of triplet spin multiplicity. We have carried out fully-quantum calculations of inelastic cross sections for collisions of NH($A^3\Pi$) with helium,³¹ based on the *ab initio* potential of Jonas and Staemmler.³² Rate constants derived from these calculated cross sections were found to agree reasonably well with experimental rate constants measured by Stuhl and coworkers.³³ These calculations showed that a simple analysis is capable of understanding the relative ordering of most state-to-state cross sections for inelastic scattering of a molecule in a 3Π state. In particular, for transitions between low J levels, where NH(A) is closest to Hund's case (a) coupling, we observed a strong tendency toward conservation of the *ef* label, as predicted initially by Pouilly and Alexander.³⁴

In a study of the collisional relaxation of highly rotationally excited CH($X^2\Pi$) by Ar, Hancock and co-workers³⁵ (U. of Oxford, U. K.) found that a substantial imbalance of Λ doublet populations builds up. As discussed below in Sec. I.E, we have collaborated with the group of Ross Sausa at ARL and have carried out calculations of the interaction of CH radicals with Ar in order to provide additional insights into the spectroscopic observations of the ArCH van der Waals

complex. In this way, we have derived interaction potentials which have been validated through their ability to reproduce the experimental spectra. We have employed these surfaces to calculate Ar-CH state-to-state cross sections in order to explain the origin of the collision-induced Λ doublet preferences.³⁶ In a full kinetic simulation of the collisional rotational relaxation, we have been able to reproduce the experimental observations. Moreover, analysis of the calculations have allowed us to deduce the mechanism inducing the preferential Λ doublet populations. This involves the large difference in the interaction energy and its anisotropy when the Ar and CH species approach on the A'' vs. A' PES's (π electron perpendicular or in the triatomic plane).

We have also collaborated with F. Stuhl and co-workers (U. of Bochum, Germany) who have measured state-to-state rotationally inelastic cross sections for collisions of $\text{NH}(c^1\Pi)$ with Ar.³⁷ We have computed the relevant Ar-NH PES's and have used these to compute the inelastic cross sections. Good agreement with the experimental results was obtained. In contrast to the Ar-CH(X) system, only small Λ doublet effects are expected in Ar-NH(c) collisions. This can also be rationalized from the topology of the PES's.

C. State-Resolved Electronically Inelastic Collisions of Free Radicals

Despite considerable work on the collisional electronic quenching of electronically excited molecules, there have been relatively few examples in which the rotational/fine-structure state distribution has been determined for the product of a bimolecular electronic quenching process involving a selected initial state. In our laboratory, supported by an earlier ARO grant, we carried out a series of optical-optical double resonance (OODR) experiments probing the $\text{CN}(X^2\Sigma^+)$ products from collisions of specified states of $\text{CN}(A^2\Pi)$ with argon.^{38, 39} This experimental worked provided the impetus for theoretical work at the University of Maryland on the general formalism⁴⁰ for the treatment of inelastic scattering between $^2\Pi$ and $^2\Sigma^+$ diatomic electronic states and subsequent fully-quantum studies of $\text{CN}(A \rightarrow X)$ transfer in collisions with helium.^{41, 42}

In order to address some of the problems raised by our previous comparison of experimental and theoretical cross sections, we have recently performed a series of new OODR experiments to probe $v_A = 7 \rightarrow v_X = 11$ transitions of several initial rotational/fine-structure levels in collisions with *helium*,⁴³ instead of argon. We find that there is reasonable agreement between the experimental and calculated final state distributions. To compare more closely with theory we carried out a kinetic simulation using calculated CN-He cross sections in order to investigate the relaxation of the nascent X state distribution in our flow system. We find that this

relaxation results in some reduction of the previously noted^{38, 39} even-odd alternation in the final rotational state distribution and a slight broadening of the width of the distribution. Because of the rapid collisional equilibration, we did not carry out a more extensive experimental study of CN-He collisions with our current flow apparatus.

The concurrent scattering calculations were extended beyond those reported previously⁴² by the explicit inclusion of the small non-Born-Oppenheimer mixing between the $A^2\Pi$ and $X^2\Sigma^+$ states of the isolated CN molecule.⁴⁴ It is this mixing which was historically thought to be the origin of electronic quenching.^{45, 46} The effect of the $A \sim X$ mixing was found to depend very strongly on the value of J for initial A state levels in the F_1 manifold. A substantial enhancement in the $A \rightarrow X$ cross sections was observed for transitions out of the most perturbed A state level ($J = 13.5 F_1f$) when the perturbation was included. Overall, though, explicit inclusion of the perturbation was found to cause only a minor change in the total cross section for inelastic energy transfer.

We have also carried out a crossed beam experiment to determine the internal state distribution of $NH(X^3\Sigma^-)$ products formed by the collisional electronic quenching of $NH(a^1\Delta)$ by Xe and CO.⁴⁷ The process is enabled by collision-induced spin-orbit coupling. A monotonically decreasing vibrational population was found for $v = 0 - 4$. Despite the large energy gap, the rotational distributions were quite cold. A nearly statistical spin state distribution was observed, in sharp contrast to that observed in the spin-forbidden decomposition of HN_3 , for which no significant population was observed in the F_2 ($J = N$) level.⁴⁸

D. Predissociation and Photodissociation of Free Radicals

In a collaborative project with F. Stuhl and D. R. Yarkony, we have investigated both experimentally and theoretically the predissociation of the $NH(c^1\Pi)$ electronic state.⁴⁹ We find that this process is mediated by dipolar spin-spin coupling to the $^5\Sigma^-$ curve which correlates with the ground state atomic asymptote $N(^4S) + H(^2S)$. Because of their differing reduced masses, the $NH(c^1\Pi, v=0)$ level undergoes predissociation with a ~ 10% branching ratio, while $ND(c^1\Pi, v=0)$ decays almost exclusively radiatively.

The NCO free radical has been proposed as an important intermediate in the combustion of nitrogen rich fuels,⁵⁰ as well as nitramines⁵¹ and energetic materials in general⁵². Recently, we²¹ and others⁵³⁻⁵⁵ have studied direct formation of NCO under single collision conditions as a product of the $CN + O_2$ reaction. The decomposition of NCO in its lowest excited electronic states

($\bar{A}^2\Sigma^+$ and $\bar{B}^2\Pi$) has been investigated experimentally by Crosley, Neumark, and their co-workers.^{56, 57}

By means of extensive CASSCF and MR-CI calculations, we have investigated two internal conversion crossing regions in the NCO molecule: the crossing between the $\bar{A}^2\Sigma^+$ and $\bar{B}^2\Pi_A$ states, and the crossing between the $\bar{A}^2\Sigma^+$ state and the $^4A''$ state which correlates asymptotically with the lowest energy dissociation channel [$N(^4S) + CO(X^1\Sigma^+)$].

Serendipitously, the minimum on these two crossing seams to occur at virtually the same energy, roughly 600 cm^{-1} above the minimum of the $\bar{B}^2\Pi$ state. The $\bar{A} - \bar{B}$ crossing seam approaches so closely the minimum of the $\bar{B}^2\Pi$ state that even the lowest vibrational level of this state will be perturbed by the neighboring $\bar{A}^2\Sigma^+$ state, as conjectured by Dixon and co-workers.⁵⁸ An experimental manifestation of the $\bar{A} - \bar{B}$ crossing will be loss of excited state population into high vibrational levels of the $\bar{A}^2\Sigma^+$ state, which explains the rapid decrease in radiative lifetime of the $\bar{B}^2\Pi$ state with increasing vibrational excitation, observed by Crosley and co-workers.⁵⁶ This is also the origin of the products seen in the recent experiment of Cyr and co-workers⁵⁷ at energies below the threshold for spin-allowed dissociation of the $\bar{B}^2\Pi$ state.

E. The Structure of Weakly Bound Complexes of Free Radicals

There has been considerable recent experimental interest in weakly bound complexes involving diatomic molecular radicals.⁵⁹ For these systems the electronic spectrum of the complex, which occurs near electronic transitions in the free diatomic, can be interpreted to obtain information on the binding energy and structure of the complex. Theory can provide invaluable assistance in such investigations. *Ab initio* calculations of the PES's provides templates for the subsequent development of more refined, phenomenological PES's.⁶⁰⁻⁶² Similarly, theoretical studies based on simplified, model descriptions of the interaction,⁶³⁻⁶⁶ can lead to increased understanding of how the stretch-bend levels of the complex are reflective of the underlying PES's.

Supported by the present grant, we have been carried out a theoretical investigation of complexes of Ar with the CH radical.⁶⁷ New multi-reference, configuration-interaction calculations of the PES's for the interaction of Ar with CH in both its ground ($X^2\Pi$) and second electronically excited ($B^2\Sigma^-$) state, along with the subsequent determination of the bend-stretch levels of the $\text{ArCH}(X, B)$ complexes, were used to provide a more refined interpretation and analysis of the $\text{ArCH } \bar{B} \leftarrow \bar{X}$ spectrum, recorded last year by Sausa and co-workers^{68, 69} at

ARL. As discussed in detail in Sec. I.B, our ArCH(X) PES's, which have been validated by our success in modelling the electronic spectrum of the complex, have been used to calculate state-to-state CH($X^2\Pi$)–Ar rotationally inelastic cross sections in order to provide further insight into the collisional relaxation of highly rotationally excited CH radicals.

These potential energy surfaces were also used in a novel *adiabatic bender* analysis of the rovibronic levels of the ArCH complex in its ground and first excited electronic states.⁶⁷ Here one first diagonalizes the full Hamiltonian as a function of the atom-molecule separation, and then subsequently obtains the vibrational eigenvalues of the resulting one dimensional adiabatic bender potentials. These adiabatic bender approximations to the stretch-bend levels of ArCH were immensely helpful in providing a framework with which to interpret the experimental results.

Collisions of Ar atoms with NO in its electronic ground state have long-served as the paradigm, both in experimental and well as theoretical studies, of inelastic collisions involving molecules in Π electronic states. Molecular beam studies have been reported of total differential cross sections,^{70, 71} integral inelastic,⁷² and, just recently, differential inelastic cross sections.^{73, 74} Earlier, Howard and co-workers^{75, 76} reported molecular-beam, electric-resonance spectroscopic investigations of the ArNO($X^2\Pi$) van der Waals complex. Despite this interest, the only information on the ArNO($X^2\Pi$) potential energy surfaces were from phenomenological fits^{70, 71} to the experimental total differential cross section data and from an application⁷⁷ of the electron-gas model of Gordon and Kim.⁷⁸

Motivated by the recent differential scattering experiments,^{73, 74} and supported by another grant we determined⁷⁹ the first *ab initio* ArNO($X^2\Pi$) potential energy surface using the Correlated Electron Pair (CEPA) method.^{80, 81} In collaboration with the group of Pavel Rosmus at the University of Frankfurt (Germany), we then used these *ab initio* PES's to determine the energies and wavefunctions of the lower rovibronic states of the ArNO($X^2\Pi$) complex.⁸² On the whole, we found the CEPA PES's provided a good description of the measured^{75, 76} values of both the parity and rotational splitting in the lowest bend-stretch level of the complex. The CEPA PES's should provide a reliable template for a more refined characterization of the electronic ground state of ArNO, particularly when more experimental information becomes available on the excited rovibronic states of this complex.

We have also employed the ArNH PES's which we calculated in order to interpret state-to-state rotationally inelastic cross sections for NH($c^1\Pi$)–Ar collisions, as discussed in Sec. I.B, to interpret fluorescence excitation spectra of the ArNH complex recently obtained by Lester and co-

workers (U. of Pennsylvania).⁸³ The experimental spectra were found to be very complicated because of the small anisotropy of the Ar-NH(*a*) interaction, which leads to considerable overlapping and interaction of the bender curves. The assignment of the experimental spectra, including the identification of new bands, was only possible with our theoretical input.⁸⁴

F. Redistribution of Flux in Molecular Collision Processes and Photodissociation

In a major theoretical advance, we described⁸⁵ a new method for the study of the mechanism of inelastic atomic and molecular collisions. This involves the determination of the current density associated with, separately, the incoming and outgoing scattering wavefunctions in either an asymptotic (diabatic) or locally adiabatic basis. This yields a picture of how the incoming flux, initially associated with a given internal state, redistributes itself as a function of the interparticle separation both as the particles approach, and, subsequently, as the particles recede. Analysis in a fully adiabatic basis, which corresponds to the local eigenvectors of the collision system, provides the most meaningful physical insight. This flux method provides mechanistic information which is complementary to that given by application of time-dependent wavepacket methods. Conceptually, our approach is equivalent to placing a series of detectors along the reaction path, which can measure the distribution of the system among the internal states which are locally energetically accessible, either as the collision partners approach or as they recede.

A first application⁸⁶ was to the study of collision induced transitions among excited electronic states of atomic Ca, a system of considerable recent experimental⁸⁷ and theoretical^{88, 89} interest. This application of our quantum flux method to collisions of Ca atoms, initially excited to the $4s5p\ ^1P$ state, allowed us to investigate, in a fully quantum manner, the dynamics of the transfer of flux to the nearby $4s5p\ ^3P$ state, and, subsequently, the redistribution of flux among the multiplet levels of the 3P state. We were able to see, in detail, how the singlet \rightarrow triplet transfer occurred exclusively by means of the crossing between the CaHe $^1\Pi$ and $^3\Sigma_1$ curves and, further, to understand why this transfer is sensitive to the initial polarization of the $4s5p\ ^1P$ state. All of the above mechanistic implications were consistent with the predictions of models based on semiclassical treatments of the collision dynamics. The advantage of the fully quantum flux analysis is the freedom from any inaccuracies or ambiguities which might arise from the separation of classical and quantum degrees of freedom.

Our flux method has now been extended to photodissociation (in work done in collaboration with David Manolopoulos of the University of Nottingham, U. K. and supported by

another grant).^{90, 91} Here, by obtaining the current density associated with the photofragment wavefunction, we can investigate the dependence of the photodissociation process on the interfragment separation: flux rises in the various channels of the unbound excited state as the initially bound fragments move through the region where the photon is absorbed, and then is redistributed because of interactions in the excited state. The time-independent analysis of the redistribution of photofragment flux complements the well established time-dependent wavepacket approach to photodissociation.^{92, 93}

Using this quantum flux method we investigated⁹⁴ the photodissociation of HCl into $H(^2S) + Cl(^2P_{1/2,3/2})$, as a prototype for understanding the factors which control the distribution of products among the accessible spin-orbit states of open-shell fragments. We calculated new *ab initio* curves for the relevant potential energy curves (for the attractive $X^1\Sigma^+$ and the repulsive $A^1\Pi$, $a^3\Pi$, and $1^3\Sigma^+$ states) which enter into the exact quantum description of the process, and subsequently carried out the calculation of photodissociation cross sections and branching ratios. The branching ratios are in considerable disagreement both with earlier calculations and with the recently revised experimental values.^{95, 96} Application of our flux method reveals clearly that the branching among the Cl fine-structure states is controlled by transfer of flux from the initially populated $A^1\Pi$ state into the $\Omega = 1$ component of the $1^3\Sigma^+$ state at relatively large internuclear separations, far outside the Franck-Condon region. This work was done in collaboration with Brigitte Pouilly of the Université de Lille; initiated during a visit by MHA to the Université of Lille supported by a two month visiting professorship at that institution.

A second application⁹⁷ was to the photodissociation of the ClNO molecule in the lowest (T_1) triplet excited state, studied in a series of experiments by Reisler and coworkers⁹⁸ The clearest picture emerges from the analysis of the photofragmentation flux in a mixed representation, in which the photofragment flux associated with each NO *vibrational* state was also expressed as a function of the ClNO *angle*. We found that the dissociation of ClNO(T_1) was not completely adiabatic in the NO vibrational motion. For excitation of the low-frequency features of the absorption profile, approximately 11 % of the total photofragmentation flux is associated with the $v > 1$ states of NO in the Franck-Condon region. As the Cl – NO separation increases, however, this component of the photofragmentation flux subsides into the flux associated with the $v = 0$ states, so that the final product state distribution *appears* to be vibrationally adiabatic. This is an unequivocal example of vibrational relaxation during a half-collision.

In these calculations of the flux redistribution, only the component of the flux along the

dissociation coordinate was calculated. We have been able to extend our analysis of the quantum mechanical flux to allow the calculation of *all* components of the current density field.⁹⁹ This provides even more mechanistic information on a photodissociation process. This methodology has been applied to two model photodissociation problems: CH₃I, where the dissociation dynamics is dominated by a crossing of two excited state PES's, and CH₃ONO, where a local minimum in the excited state PES, which is located near the Franck-Condon region, gives rise to a series of strong vibrational resonances in the absorption spectrum.

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**III. LIST OF PUBLICATIONS PREPARED UNDER ARO GRANT NO.
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