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Collaborative theoretical and experimental studies of a variety of elementary chemical reactions and collisional energy transfer processes involving small molecular free radicals, with particular emphasis on the NH and CN molecules, have been carried out.

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# STUDY OF ELEMENTARY REACTIONS AND ENERGY TRANSFER PROCESSES INVOLVING THE NH AND CN FREE RADICALS

FINAL REPORT

Paul J. Dagdigian and Millard H. Alexander

June 14, 1991

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# I. STATEMENT OF WORK AND DESCRIPTION OF WORK ACCOMPLISHED

The present grant has involved a collaborative theoretical and experimental study of elementary reactions and energy transfer processes involving small molecular free radicals, with particular emphasis on the important NH and CN molecules. Over the past decade there has been growing interest in reactions proceeding via several potential energy surfaces, as exemplified particularly by reactions of atoms with free radicals.[1] Multiple surfaces and nonadiabatic transitions between them are also important factors in determining the branching of products of both reaction and photodecomposition among energetically accessible electronic and/or fine-structure levels. The full understanding of electronic branching in both entrance and exit channels depends on our ability to describe the electrostatic interaction between two open-shell species in both a *diabatic* (asymptotic) and *adiabatic* basis, and our ability to describe the transfer of reaction flux between electronic states which coalesce asymptotically.

Molecular beam and laser techniques have been extensively employed to study, under single-collision conditions, a large number of reactions of atoms with closed-shell stable species. Because of the difficulty in preparing beams of *unstable* molecular free radicals, atom-radical reactions are a relatively unexplored field of reaction dynamics, which we have now begun to investigate. Our particular interest in these experiments is the measurement of branching ratios between different electronic states and different product channels, as well as the product fine-structure state distributions. These observations can provide important keys in deducing which potential energy surfaces are strongly influencing the dynamics. In many systems, one might expect the reactive flux to proceed primarily over the lowest potential energy surface. However, nonadiabatic couplings in the entrance and exit channels will undoubtedly have a significant effect on the product state distributions.

This report summarizes the progress of our progress in the elucidation of the dynamics of various collisional processes of small molecular free radicals involving multiple potential energy surfaces. The principal scientific accomplishments are described in the sections below.

## A. Crossed Beam Study of Inelastic Collisions of the NH and $NH_2$ Radicals.

A new crossed molecular beam scattering apparatus has been set up in order to investigate collisions, both inelastic and reactive, of small molecular free radicals. For this purpose, we have set up a pulsed photolysis supersonic source of free radicals, in which a beam of a free radical is prepared by photolysis of a suitable precursor in a buffer gas at the beam orifice. This technique has been extensively utilized in other laboratories for the generation of cold beams of free radicals for spectroscopic studies. In our laboratory, we have prepared rotationally cold beams of $NH_2(\tilde{X}\,^2B_1)$,[2] $NH(X^3\Sigma^-)$,[3] and $NH(a^1\Delta)$[4] and have measured state-to-state rotational excitation cross sections in collisions with a number of targets. For the first two radicals, ammonia was employed as the precursor, while hydrazoic acid was employed as the precursor for $NH(a^1\Delta)$. In these experiments, the target was also produced as a pulsed supersonic beam, and the collisionally populated rotational states of the free radical interrogated by laser fluorescence excitation.

With this apparatus, rotational excitation of $NH_2$ in its lowest ortho rotational level ($0_{0,0}$) in collisions with helium was investigated.[2] The populations of the final rotational levels in the $K_a$ = 0 and 1 manifolds were determined by laser fluorescence excitation in the $\tilde{A}\,^2A_1 - \tilde{X}\,^2B_1$ band system. Because of the rotational selection rules for this transition, it was not possible to put the cross sections for the two $K_a$ manifolds on the same scale. Within a given $K_a$ manifold, a marked preference for collisional transitions with the smallest $\Delta J$ was displayed; this preference is significantly more pronounced than that seen in calculated[5] $H_2O$–He cross sections. This implies that the anisotropy of the $NH_2$–He and $H_2O$–He interaction potentials differ significantly.

Collisional excitation out of the lowest rotational levels of the NH ground $X^3\Sigma^-$ and metastable $a^1\Delta$ electronic states was also investigated. For the former, relative state-to-state cross sections out of the $N=0$, $J=1$ $F_1$ level in collisions with argon were determined.[3] The spin-state distributions within a given N' rotational manifold were found to be well described by the general formulas[6] for inelastic collisions of a case (b) $^3\Sigma^-$ molecule. Cross sections for excitation of the lowest level ($J=2$) of $NH(a^1\Delta)$ in collisions with a number of targets were also measured.[4] This study represents the first state-resolved investigation of rotationally inelastic scattering of a molecule in a $^1\Delta$ electronic state, and the general theory for inelastic scattering of $^1\Delta$ states was outlined.

In a related theoretical project we have become involved in the past year in the study of inelastic collisions of NH in the $A^3\Pi$ electronic state with noble gases. Experiments on this system are being carried out in Bochum[7] and Santa Cruz. Our work is the first computational study of inelastic collisions of a molecule in a $^3\Pi$ electronic state, and builds upon our earlier[8-10] formal work on $^3\Pi$ systems, partially supported by previous ARO grants. The quantum scattering calculations are based on the CEPA potential energy surface of Jonas and Staemmler[11] for $NH(A^3\Pi)+He$, for which we have constructed a global fit. The calculated cross sections exhibit an interesting propensity toward population of those final state Λ-doublet levels which are *antisymmetric* with respect to reflection in the plane of rotation of the molecule.[9,12] This is a manifestation of quantum interference between the *two* potential energy surfaces (of A' and A" symmetry),[8] similar to that which we have already analyzed in collisions of the $^2\Pi$ hydrides CH and OH with He.[13] In recent work we have used a new *ab initio* potential energy surface[14] to determine the energy dependence of inelastic cross sections for the collision of $CH(X^2\Pi)$ with He. In the region of the energetic threshold the calculated cross sections differ significantly from experimental values. This discrepancy can not be attributed to a variation in the CH spin-orbit coupling constant as the He collision partner approaches.

### B. Determination of the Product State Distributions in the $H + NO_2$, $CN + O_2$, and $O + NH_2$ Reactions.

As a prelude to carrying out reactive scattering studies with such photolytically prepared free radical beams, the internal state distribution of the NO product from the reaction,

$$H + NO_2 \rightarrow OH(X^2\Pi) + NO(X^2\Pi), \qquad \Delta H_0^{o} = -123.5\pm2.0 \text{ kJ/mol.} \qquad (1)$$

was investigated in our crossed beam apparatus.[15] This is nominally an example of an atom-radical reaction; however, it is relatively simple to study since $NO_2$ is a stable free radical. There have been a number of previous studies of the energy disposal into the translational and OH internal degrees of freedom for this reaction.[16] However, prior to this study, the only direct information on the NO product was a determination of the ratio of the v=1 to v=2 vibrational populations in an infrared chemiluminescence experiment.[16(b)]

From the energy previously found in translation and OH internal excitation, *ca.* 28% of the available product energy $E_{tot}$ is predicted to reside in NO internal excitation. Nitric oxide product in the v=0-2 vibrational levels was observed by laser fluorescence excitation in its $A^2\Sigma^+ - X^2\Pi$

band system, with 9.5±2% of $E_{tot}$ found in NO internal excitation. It is troubling that the energy seen in the NO product in this experiment is so much less than that predicted from the previous information on the translational energy[17] and OH internal energy disposal.[16] In experiments carried out at essentially the same time as ours, Smith and coworkers have very recently remeasured the OH product state distribution up to v=3[18(a)] and the NO distribution up to v=3[18(b)] by laser fluorescence detection of the products in a crossed flow of the reagents. The OH vibrational energy disposal determined by Irvine *et al.*[18(a)] agreed with the earlier experiments. Their results on NO are consistent with ours. Based on these measurements of the OH and NO state distributions, Smith *et al.*[18] suggest that the energy released as product translational energy disposal should be revised upward from 20%[17] to 30% of $E_{tot}$ to explain the energy disposal in reaction (1).

In contrast to the nearly equal spin-orbit populations observed in the OH product,[16,18(a)] the lower ($\Omega=1/2$) spin-orbit level in NO is preferred by a ratio of 1 : 0.52±0.11 over $\Omega=3/2$.[14,17(b)] A preferential spin-orbit population cannot arise by reaction on the HONO($^1A'$) surface. A possible mechanism for production of unequal spin-orbit population is mixing in the exit channel with a triplet surface correlating with the OH + NO products. This will allow a preferential electron spin along a molecular axis because of symmetry restrictions in the spin-orbit mixing, as least for planar geometries. An unequal spin-orbit population will result in the products only if this preferential spin direction can be transferred to the molecular axis of the free diatom. In contrast to the case (a) NO product, we would not expect this preferential spin to be retained in the free OH product since the electron spin is weakly coupled to the axis [Hund's case (b)] in OH.[15]

We have used photolysis in a cell experiment as a means to prepare the cyanide radical to determine the vibrational state distribution of the NCO product from the reaction of CN with oxygen molecules:

$$CN + O_2 \rightarrow NCO(\tilde{X}\,^2\Pi) + O, \qquad \Delta H_0^0 = -29\pm 6 \text{ kJ/mol.} \qquad (2)$$

This reaction is known to have a large rate constant which decreases with increasing temperature.[19] We have detected NCO by laser fluorescence excitation in its $^2\Sigma^+ - {}^2\Pi$ band system over the region 520-420 nm in a cell experiment at total pressures of 140 mTorr in which CN is prepared by 193 nm photolysis of $C_2N_2$ and NCO is detected after a variable delay. We have observed a large number of previously unobserved vibrational levels of NCO, with bending excitation as high as

$v_2$=6.[20] In a previous, early study of the NCO product from reaction (2), only the (000) and (010) levels were observed;[21] however, the delay between CN production and product detection was long.

The NCO radical is one of the class of 15-valence electron molecules, whose ground $\tilde{X}\,^2\Pi$ states have an equilibrium linear geometry and possess both nonzero $\Lambda$ and S. As such, the vibronic and rotational energy level patterns exhibit the complicated interaction between the Renner-Teller effect and the spin-orbit interaction.[22,23] From our wavenumber measurements of the these newly observed band heads, we have been able to extend considerably our knowledge about the vibronic levels in NCO($\tilde{X}\,^2\Pi$) up to energies as high as 4300 cm$^{-1}$. These vibronic energies have been fit[20] to a hamiltonian[23] including the Renner-Teller effect, the spin-orbit interaction, anharmonic corrections, as well as the Fermi resonance between the $v_1$ and $v_2$ modes. These parameters are important in the calculation of NCO $\tilde{A}\,^2\Sigma^+ - \tilde{X}\,^2\Pi$ vibronic band strengths.

We have used the information gained from our spectroscopic study[20] to extract nascent vibronic populations of the NCO product from reaction (2).[24] We have detected by laser fluorescence excitation both the CN fragment from the initial photolysis of $C_2N_2$ and the NCO product as a function of the photolysis-probe delay. A finite induction time (4.5 μs at a total pressure of 140 mTorr) was observed for the formation of the NCO product in all detected vibronic levels, indicative of the necessity to moderate the translational and rotational of the CN reagent before appreciable reaction can occur. A vibronic state distribution among the various ($v_1$,$v_2$) Renner-Teller components was estimated from the relative intensities of the various bands, using calculated vibronic band strength factors. It was not possible to determine distributions in the $v_3$ levels because the ground and excited state bond lengths are not sufficiently accurately known from the experimentally measured rotational constants of isotopically substituted molecules.[25] By extrapolating back to short photolysis-probe delays, it was possible to estimate the nascent NCO vibronic state distribution. It clear that NCO is formed from reaction (2) with considerable internal excitation, especially in the $v_2$ bending mode. This is consistent with previous kinetic studies[19] which suggest that the reaction occurs on an attractive potential energy surface, with no activation barrier.

In related theoretical work we have initiated the study of the potential energy hypersurfaces of the degenerate pair of states which become the $^2\Pi$ ground state of NCO, as well as the three excited surfaces which correlate with the $^2\Sigma^+$ and $2^2\Pi$ excited states of NCO. This work is an extension to this heteronuclear system of our extensive investigation of the isoelectronic azido radical, $N_3$.[26] Our initial work used complete-active-space self-consistent-field (CASSCF) calculations with a triple-zeta plus polarization orbital basis to investigate the potential energy surfaces of both NCO and its isomers CNO and NOC. Contrary to earlier predictions using a single-reference calculations,[27] the NOC radical was not found to be stable with respect to dissociation into N($^2$D) + CO. A linear minimum was found for the CNO isomer with bond lengths $R_{CN} = 2.27$ bohr and $R_{NO}= 2.32$ bohr, which should be compared with the NCO bond lengths of $R_{CN} = 2.30$ bohr and $R_{CO} = 2.23$ bohr. At the CASSCF+CI level the CNO minimum is predicted to lie 23,200 $cm^{-1}$ above the NCO minimum.

Our most recent study of the dynamics of a free radical reaction has involved the study, in a crossed beam experiment utilizing our photolytically produced free radical beam source,[2,3] of the reaction of oxygen atoms with amidogen:[28]

$$O + NH_2 \rightarrow OH(X^2\Pi) + NH(X^3\Sigma^-), \qquad \Delta H_0^\circ = -43\pm3 \text{ kJ/mol.} \tag{3a}$$

$$\rightarrow H + HNO(\tilde{X}\,^1A'), \qquad \Delta H_0^\circ = -120\pm1 \text{ kJ/mol.} \tag{3b}$$

This reaction plays an important role in the oxidation of ammonia and other nitrogen-containing fuels, as well as in the reduction of nitrogen oxides. The 300K thermal rate for this reaction is large [ $(8.8\pm2.5) \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (Ref. 29)]; moreover, the branching ratio for pathways (3a) and (3b) have been found[29] to equal (13±5)% and (87±5)%, respectively. There are several other possible exothermic pathways, but these appear to be insignificant.

There are two intermediates which are important in the dynamics of this reactions, namely $H_2NO$ and HNOH. With quantum chemistry calculations utilizing fourth-order Møller-Plesset perturbation theory with bond additivity corrections, Melius and Binkley[30] concluded that this reaction proceeds by formation of the $H_2NO$ intermediate without an activation barrier; HNOH can be formed from the initial intermediate by a 1,2-hydrogen shift. The products of pathway (3b) can be formed by dissociation of either intermediate, while the OH + NH products can be reached by dissociation of HNOH or by direct abstraction on a quartet potential energy surface, whose barrier was estimated to be *ca*. 20 kJ/mol.

We have determined the internal state distribution of the OD product from O($^3$P) + $ND_2$.[28] [The deuterated analog of pathway (3a) was studied to avoid interference from OH impurity emanating from the O atom source.] Since both the OD and ND products are open-shell species, we might expect that dissociation of the DNOD intermediate would proceed without a significant barrier, implying a loose transition state for this process. Experimentally, we find that the OD product has only a small degree of internal excitation, comprising only 8% of the total available energy. The experimental rotational distribution is very much colder than that predicted by several statistical theories. This disagreement between our experimental measurement and statistical predictions is very surprising. The low degree of OD product internal excitation can be reconciled by assuming that this pathway proceeds instead by direct abstraction through a linear transition state, as in the reaction of $O(^3P)$ with hydrocarbons.[31] This would imply that the barrier on the quartet surface estimated by Melius and Binkley[30] is too high.

## C. Initiation of the Study of Reaction and Decomposition on the HNCO Potential Energy Surface.

As further example of an atom-radical reaction, we have also studied the reaction of hydrogen atoms with the cyanate radical:[32]

$$H + NCO \rightarrow NH(X^3\Sigma^-, a^1\Delta) + CO, \qquad \Delta H_0^o = -128\pm3 \text{ kJ/mol.} \qquad (4)$$

This reaction system is isoelectronic with the H + $N_3$ reaction, which we have studied with AFOSR support.[33] Reaction (4) is substantially less exothermic than H + $N_3$. We have observed both $NH(X^3\Sigma^-)$ and $NH(a^1\Delta)$ products from H + NCO and have obtained a value for the $a^1\Delta$ to $X^3\Sigma^-$ state branching ratio of 0.0023±0.0009 : 1.[32] The formation of $NH(a^1\Delta)$ is significantly endothermic, and the small branching ratio reflects this. We also compared the total reaction cross sections for the H + NCO, $N_3$ reactions and found them to be approximately equal. Very recently, NCO product has been detected in the quenching of $NH(a^1\Delta)$ by CO,[34] namely the reverse of reaction (4). The fraction of quenching collisions which lead to $NH(X^3\Sigma^-)$ ground state products was found to be only 12%.[34]

In related theoretical work we have extended our *ab initio* study[35] of spin-allowed and spin-forbidden decomposition of $HN_3$ to examine the similar process,

$$HNCO \rightarrow NH(X^3\Sigma^-, a^1\Delta) + CO. \qquad (5)$$

The spin-forbidden channel takes place by means of a crossing between the lowest singlet surface, which correlates with the ground state of HNCO, and the lowest triplet surface. The height of this crossing above the asymptote will determine the activation energy and also critically influence the branching ratio into triplet products for reaction (4). In addition, the topology of the potential surfaces in the region of the singlet-triplet crossing will effect the product internal energy distributions in both reactions (4) and (5). By multireference CI calculations with a large orbital basis we have determined that the lowest singlet-triplet crossing occurs ~4,500 $cm^{-1}$ above the $NH(X^3\Sigma^-)$ + CO asymptote. Further calculations have been performed to look at the height of the exit channel barrier in the singlet [$NH(a^1\Delta)$ + CO] channel, which will influence the overall rate of quenching of NH by CO, through both electronically inelastic and reactive channels.

## D. Predissociation in NH/ND($A^3\Pi$, $c^1\Pi$) and Spectroscopy of ND.

Despite the excellent spectroscopic data available on the NH $A^3\Pi - X^3\Sigma^-$ band system,[36] only the $\Delta v=0$ sequence[37] has been reported for the isotopic ND molecule. In the course of preparing for the study of reactions of the NH radical, we were motivated to search for ND bands in order to check our fluorescence detection sensitivity because of the small natural isotopic abundance of deuterium (0.015%). As a result of this experiment, we observed the ND $A^3\Pi - X^3\Sigma^-$ (1,0), (2,1), and (3,2) bands.[38] These data, in conjunction with the older data,[37] allowed accurate calculation of ND vibrational intervals in both the A and X electronic states.

We also determined lifetimes for ND $A^3\Pi$ v'=1-3 and NH v'=2 in specified low J' rotation/fine-structure levels, by laser excitation of molecules in a pulsed supersonic beam.[39] As has been previously observed for high N' levels of v'=0 and 1,[40] the observed lifetimes for NH v'=2 were found to be significantly shorter than that expected for purely radiative decay, indicative of additional removal by predissociation. The NH v'=2 decay rates were found to display a strong dependence on the fine-structure label, with the largest predissociation rates for the $F_1$ ($\Omega=2$) levels. This fine-structure dependence is consistent with a mechanism of predissociation involving spin-orbit coupling to the repulsive $^5\Sigma^-$ state correlating with the ground state $N(^4S) + H(^2S)$ asymptote. By contrast, no significant predissociation was found for the decay of ND v'=1-3 in any of the low J' levels excited. These experimental observations were complemented with *ab initio* electronic structure studies, involving calculation of the potential energy curves of the spin-orbit matrix element between the $A^3\Pi$ and $^5\Sigma^-$ states, and coupled semiclassical electronic state dynamics calculations. The calculated total decay rates were in excellent agreement with the available experimental observations, confirming the mechanism of predissociation.

The radiative and predissociative decay rates of the NH and ND $c^1\Pi$ excited state have also been calculated.[41] In this case, the mechanism of predissociation involves dipolar spin-spin coupling to the repulsive $^5\Sigma^-$ state. We found that the radiative lifetime of the ND v'=0 level is predicted to be significantly longer than that for NH v'=0, a result very recently confirmed by Stuhl and coworkers.[42] While it has been known for some time that NH v'=1 is predissociated,[40] we see that v'=0 also predissociates with a rate close to that for purely radiative decay, indicating that the zero-pressure quantum yield for fluorescence is not unity, as has been supposed.

## E. Search for Amidogen Radicals, $R_1R_2CN$.

In a collaborative effort with William Anderson, Ross Sausa, and Andrzej Miziolek of the U. S. Army Ballistic Research Laboratory (BRL) at Aberdeen Proving Ground, MD, we have studied the photolysis of formaldoxime ($H_2CNOH$) and its methylated homologues in order to search for laser-induced fluorescence from the $R_1R_2CN$ radical (where $R_1$ and $R_2$ = H or $CH_3$).[43] Electronic transitions of these species had previously been observed near 280 nm in flash photolysis experiments.[44] Our main objective here was to see if fluorescence could be detected upon excitation of these bands. The $H_2CN$ molecule is an important intermediate in the decomposition of nitramines,[45] and a sensitive laser diagnostic would be very useful. We chose to use the oximes as photolytic precursors rather than the azines [e.g. formaldazine, $(H_2CN)_2$ ] in order to use the other photoproduct, OH, as an internal concentration calibrant. We observed the OH product in the 193 nm photolysis of $H_2CNOH$, $CH_3CHNOH$, and $(CH_3)_2CNOH$; in all cases, only a small fraction of the available energy appeared as OH internal excitation. No fluorescence due to $R_1R_2CN$ could be detected. Based on a comparison of the OH signals, we estimate an upper limit for the fluorescence quantum yield of 0.01 for $CH_3CHN$ and $(CH_3)_2CN$ and 0.1 for $H_2CN$. Thus, fluorescence excitation of the bands near 280 nm does not appear to be suitable as diagnostics for these molecules.

## F. Spin-changing Collisions of Rydberg States in the Oxygen Atom.

In a further collaborative project with workers at BRL, this time with Brad Forch and Andrzej Miziolek, we have also investigated collisional quenching and excitation transfer between the oxygen atom 3p $^3P$ and $^5P$ Rydberg states in a discharge-flow reactor with $O_2$ and $N_2$ collision partners.[46] A knowledge of such collisional rates are important in converting measured O atom 2-photon fluorescence intensities to populations in finite-pressure combustion environments. The $^3P$ state was prepared by two-photon excitation at 225.6 nm from the $2p^4\ {}^3P_2$ ground state, and temporal profiles of the $^3P \rightarrow {}^3S$ and $^5P \rightarrow {}^5S$ emission at 844.7 and 777.5 nm, respectively, to the lower 3s manifold were recorded. From analysis of the emission profiles, quenching rate constants for the $^3P$ and $^5P$ states were derived. Comparison of the integrated fluorescence intensities in the two lines allowed estimation of $k_{35}$, the $^3P \rightarrow {}^5P$ excitation transfer rate constant. We find that $k_{35}$ is only a small fraction of the total $^3P$ quenching rate (8% and 3%, for $O_2$ and $N_2$, respectively, with a factor of 2 uncertainty). It seems reasonable to conclude that $k_{35}$ is small, in part, because of the large energy gap between the states (1998 $cm^{-1}$) and the large number of possible acceptor electronic states near the $^3P$ energy (88631 $cm^{-1}$) in the collision partners. Moreover, there is sufficient energy available for reactive quenching to occur in $O^* + N_2$ collisions.

## H. Theoretical Study of Electronically Nonadiabatic Processes in Collisions involving Open-Shell Atoms and Molecules.

In work related to the above study of spin-changing collisions of O atoms, and in collaboration with B. Pouilly at the Université de Lille, France, we have carried out an detailed investigation of the dependence on orbital orientation of cross sections for spin-changing collisions of atomic calcium in the 4s5p Rydberg level with various noble gas (Ng) atoms. This theoretical work[47-50] provided an understanding of the recent experiments of Leone and co-workers.[51] 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 $^{1,3}\Pi$ CaNg potential curves which correlate with the Ca(4s5p $^{1,3}P$) + M asymptote. A new method was developed[47,49] to examine the distribution of flux among the coupled electronic potential surfaces as a function of the approach of the two atoms, by inward propagation of the full wavefunction of the system followed by projection of the incoming flux onto the adiabatic states appropriate to the description of the molecular region. For the spin-changing collisions of Ca atoms, analysis of the flux redistribution and of the partial cross sections for the inelastic process allowed a fully quantum verification of simpler dynamical models.

Recently, we have incorporated this procedure for the study of flux redistribution into our Hibridon inelastic scattering code.[52]

Another technique we have used[53] to study flux redistribution in collision processes involving several electronic potential surfaces utilizes the time-honored classical trajectory method modified to allow trajectories to "hop" from one electronic surface to another.[54,55] In contrast to earlier application of this surface-hopping method, we allow hopping to occur even in situations where the surfaces do not actually cross. In an application to collisions of CN molecules in the $A^2\Pi$ electronic state,[53(b)] we found that although detailed kinetic information at the fine-structure level is lost, comparison with our prior quantum scattering calculations[56] indicated that the trajectory surface hopping method could yield excellent agreement, after averaging over the fine-structure levels of the initial and final states.

## H. Theoretical Study of Electronically Nonadiabatic Effects in the Collisions of NO with Surfaces.

In a continuation of our long-standing interest in collisions of molecules in $^2\Pi$ states, and relevant to the intense experimental interest in collisions of NO with and desorption of NO from surfaces, we have become involved with Andrew DePristo, at Iowa State University, in the determination of a semi-empirical potential for the interaction of NO($A^2\Pi$) with the (111) face of a silver surface. These calculations, based on the Corrected Effective Medium method of Kress and DePristo,[57] take into account the non-zero electronic angular momentum of the NO molecule as well as the corrugation of the surface, and are, to our knowledge, the first non-phenomenological potential energy surfaces for a molecule-surface system. The more than 600 calculated points were fit to a global functional form which correctly describes both the open-shell character of the NO molecule as well as dependence with respect to the position of the surface atoms.[58] The resulting potential is totally different from the purely phenomenological model potentials which have been used to describe the NO-Ag(111) system.[59] Quantum close-coupling scattering studies using this fitted potential energy surface[60] showed a tendency for equal population of both spin-orbit manifolds as the final state rotational quantum number increased, as well as a strong propensity for population of the antisymmetric[12] ($\Pi_{A''}$) Λ-doublet levels. As we have seen in gas-phase collisions,[13] this propensity is a manifestation of quantum interference between the *two* NO–

Ag(111) potential energy surfaces. Recent work involves the extension of this scattering study to look at direct vibrational excitation of the NO molecule during energetic collisions with the metal surface.

## J. Prediction of $\Lambda$ Doublet Propensities in the Decomposition of Vibrationally Excited $HN_3$

Often in photodissociation or a chemical reaction, one or more of the diatomic products are formed in open-shell electronic states. The distribution of the products among the various possible fine-structure levels can, in principle, provide considerable insight into the photolysis or reaction mechanism. Particular attention has been focused on fragments in $^2\Pi$ electronic states, for which the $\Lambda$ doublet levels have opposite symmetry with respect to reflection through the plane of rotation, for sufficiently high angular momentum J.[12,61] The preferential production of a given $\Lambda$ doublet level can be interpreted by analysis of the evolution of the molecular orbitals of the precursor species which correlate with the unfilled $\pi$ molecular orbital in the diatomic fragment.

In more sophisticated models for dissociation leading to fragments in $\Pi$ electronic states,[62,63] the relative populations of the $\Pi(A')$ and $\Pi(A'')$ $\Lambda$ doublets can be predicted by projection of a transition state of constrained geometry onto the asymptotic fragments. We have extended[64] this type of argument to processes leading to fragments in $\Delta$ electronic states, in particular the spin-allowed decomposition of vibrationally excited hydrazoic acid:

$$HN_3^{\dagger} \rightarrow NH(a^1\Delta) + N_2(X^3\Sigma_g^+). \qquad (6)$$

The infrared multiphoton[65] and vibrational overtone[66] decomposition of $HN_3$ has been studied in pioneering experiments by King, Stephenson, Foy and Casassa. In recent work,[66(b)] they have characterized the $NH(a^1\Delta)$ v=0 product from decomposition of $HN_3$ excited to the $7\nu_{NH}$ overtone level and found a preference for $\Delta(A')$ levels which increased with larger J.

We have constructed a model[64] to explain quantitatively these observed $\Lambda$ doublet propensities. Our Franck-Condon type model involves the projection of the electronic-rotational wavefunction of the HN···NN system at the transition state onto the electronic-rotational wavefunction of the free NH rotor. *Ab initio* calculations were used to estimate the angular extent of the torsional degrees of freedom which subsequently become converted to rotations of the NH fragment. This model, which dealt explicitly with the 2-electron character of the $^1\Delta$ state, well predicts the experimentally observed ratios of Δ(A') to Δ(A") populations as a function of J. This model represents an advance over those previously developed to explain Λ doublet propensities in that it is based on the properties of the specific system under consideration.

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