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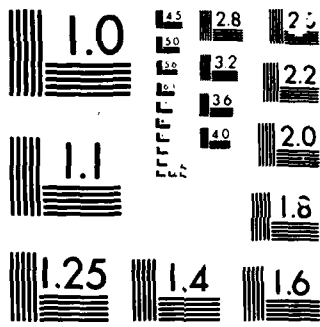
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Most of the molecules were dissociated either via IRMPD (CF_3CN , $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$) or by electronic excitation followed by radiationless transitions (NCNO , $(\text{CH}_3)_3\text{CNO}$). They exhibited statistical behavior, and the results were compared with the predictions of statistical theories. The most detailed experiments involved the photodissociation of NCNO , which provided complete mapping of product internal states with E^* in the range $0-5000 \text{ cm}^{-1}$. The CN and NO E,V,R distributions are textbook examples of statistical product state distributions deriving from a unimolecular reaction with well specified E^* and J_0 . The distributions can be predicted over the entire range of excess energies by using the separate statistical ensembles (SSE) method which we developed, and which is a modification of the phase space theory.

In our studies of the direct photodissociation of ICN , we obtained sub-Doppler LIF spectra of nascent $\text{CN}(X^2\Sigma^+)$, following the 266 nm photolysis of 300 K molecules. These studies provided a detailed picture of the fragment recoil spatial anisotropies as well as CN E,V,R,T and I/I* excitations. The CN rotational distributions were dissected into two separate distributions for the channels producing I and I*. The results could be accounted for with a model in which excitation to a single potential surface is followed by a nonadiabatic transition to a second surface.

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FINAL REPORT

AFOSR GRANT 83-0022

PERIOD COVERED: 1 OCTOBER 1982 - 30 SEPTEMBER 1985

**LASER KINETIC SPECTROSCOPY OF UNIMOLECULAR
AND BIMOLECULAR PROCESSES IN THE GAS PHASE**

Prepared for

THE AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFOSR)

Submitted by

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**Approved for public release,
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Trifluoromethylamine

Nitrosomethane

ABSTRACT

Benzylamine

Our research in the past 3 years was concerned with the study of unimolecular processes in the gas phase. We concentrated on simple bond fission reactions, and determined both the collision free unimolecular rates ($C_6H_5CH_2NH_2$), $(CH_3)_3CNO$, and the energy disposal in the products ($NCNO$, CF_3CN , ICN).

Nitrosyl Cyanide

Most of the molecules were dissociated either via IRMPD (CF_3CN , $C_6H_5CH_2NH_2$) or by electronic excitation followed by radiationless transitions ($NCNO$, $(CH_3)_3CNO$). They exhibited statistical behavior, and the results were compared with the predictions of statistical theories. The most detailed experiments involved the photodissociation of $NCNO$, which provided complete mapping of product internal states with E^* in the range 0-5000 cm^{-1} . The CN and NO E,V,R distributions are textbook examples of statistical product state distributions deriving from a unimolecular reaction, with well specified E^* and J_0 . The distributions can be predicted over the entire range of excess energies by using the separate statistical ensembles (SSE) method which we developed, and which is a modification of the phase space theory.

(X) + Stat

In our studies of the direct photodissociation of ICN , we obtained sub-Doppler LIF spectra of nascent $CN(X^2\Sigma^+)$, following the 266 nm photolysis of 300 K molecules. These studies provided a detailed picture of the fragment recoil spatial anisotropies as well as CN E,V,R,T and I/I* excitations. The CN rotational distributions were dissected into two separate distributions for the channels producing I and I*. The results could be accounted for with a model in which excitation to a single potential surface is followed by a nonadiabatic transition to a second surface.

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I. INTRODUCTION

This final report outlines our research results obtained on AFOSR Grant 83-0022 during the period 1 October 1982 through 30 September 1985.

Our research in the past three years was concerned mainly with the detailed study of unimolecular reactions in the gaseous phase. Our objective was to study in microscopic detail the events that transpire following laser excitation of isolated polyatomic molecules. To this end, we employed several excitation schemes and diagnostic techniques that allowed us to follow in detail the energy disposal in the fragments and the temporal evolution of the unimolecular reactions. By using expansion cooled molecules, we achieved excitation to discrete vibronic levels without interference from hot bands.

In our studies, we concentrated mainly on simple bond fission reactions which can be treated using statistical theories. As a result of our work on NCNO, we developed a general statistical theory, called the Separate Statistical Ensemble (SSE) method, which gave excellent agreement with E,V,R,T distributions in both CN and NO fragments. We believe that this theory has general validity, and will be widely used in the study of simple bond fission reactions.

Our results have been very rewarding, and were summarized in numerous publications which are listed in Section IV. These publications are enclosed with this report as an Appendix, and thus only a summary of the most significant accomplishments is given below, with relevant publications indicated in the text.

II. INFRARED MULTIPLE PHOTON DISSOCIATION (IRMPD)^{2,4}

During the first year, we completed our studies on the IRMPD of polyatomic molecules. We pursued a theoretical study in which we compared the experimental energy distributions in CN following IRMPD of CF_3CN with the predictions of statistical theories of unimolecular decay.⁴ More specifically, we compared phase space theory and the adiabatic channel theory, and found that the latter gives a better description of the experimental results. The data were also qualitatively consistent with a simple model which assumed that fragment rotational and translational excitations derive from parent R,T motions in combination with the kinetic energies of those parent vibrations which are converted to product R,T excitations. This model later evolved into the SSE method.¹⁴

The IRMPD of benzylamine molecules was studied in real time, and both NH_2 and the benzyl radicals were identified as primary dissociation products.² The unimolecular reaction rate of benzylamine was determined as a function of fluence by monitoring, in real time, the appearance of NH_2 , and the average energy above dissociation threshold was derived from the appearance times using RRKM calculations.

III. PREDISSOCIATION FOLLOWING ELECTRONIC EXCITATION AND RADIATIONLESS TRANSITIONS^{1,3,6-11,13,14,16}

Many molecules undergo predissociations following electronic excitation in their S_1 state with energies in excess of the dissociation energy. In many cases, dissociation is relatively

slow, allowing time for energy randomization, and involves simple bond cleavage. In such cases, energy disposal into product excitations may be statistical, but the validity of statistical theories has not been extensively confirmed in the laboratory. We have shown that nitrosyl cyanide, NCNO, is an excellent test case for careful and detailed examination of simple bond fission reactions. Although somewhat chemically unstable, NCNO can be expanded in a helium jet, and excited to its S_1 electronic state over a wide tunable range (450-585 nm). Both CN and NO nascent state distributions were quantitatively measured using LIF, and it was possible to examine the partitioning of available energy into E,V,R,T (and spin) degrees of freedom of both fragments, i.e., both the nuclear and electronic motions of the fragments could be compared to theory. The result has been a long and involved study spanning several publications, and the important points learned from this work are summarized below:

- (i) NCNO predissociates upon electronic excitation ($\tilde{A}^1A'' \leftarrow \tilde{X}^1A'$), providing $h\nu$ exceeds D_0 ($17,085 \text{ cm}^{-1}$).⁸
- (ii) Perturbations indicate that vibrational predissociation occurs from the \tilde{X} state following internal conversion.⁹ This is supported by independent calculations showing a large barrier ($> 5000 \text{ cm}^{-1}$) to direct \tilde{A} state dissociation.
- (iii) At dissociation threshold, no product translational or rotational energy could be detected. This is consistent with dissociation in the absence of a barrier.⁸

- (iv) At dissociation threshold, there is a small centrifugal barrier ($< 3 \text{ cm}^{-1}$) and a measurable reaction time (20-40 ns), which is consistent with tunneling to products.⁸
- (v) Above the threshold region, the product appearance time is less than our time resolution (10 ns).⁸
- (vi) Predissociation takes place via a 'loose transition state,' as evidenced by (iv) and by indirect estimates of the transition state effective rotational constant.¹¹
- (vii) At room temperature, 1-photon photodissociation at wavelengths $> 592 \text{ nm}$ occurs predominantly from hot bands, whereas molecules near the ground state dissociate following the stepwise absorption of 2-photons.^{3,7} The upper dissociative electronic state involved in the 2-photon process can easily be reached using the A^1A'' state as a gateway. This state may be repulsive in nature, and may be the same as the state involved in the UV absorption system peaking at 270 nm .^{6,7}
- (viii) The rotational distributions of both CN and NO are statistical and can be predicted by PST when product vibrational excitation is inaccessible (i.e., excess energy $< 1876 \text{ cm}^{-1}$ when monitoring CN).^{8,12-14}
- (ix) Above this energy, experiment and PST differ, but both CN and NO rotational and vibrational distributions can be predicted using the SSE method, which is a

modification of PST and which is expected to have general applicability.¹³

- (x) The CN spin-rotation states are equally populated, indicating no preferential spin alignment.¹¹
- (xi) The relative populations of the NO spin-orbit states may also be statistically determined, but with a weighting factor which probably arises from angular momentum coupling during the dissociation processes. However, the lambda doublet states are equally populated, as expected.¹⁴

In the NCNO work, the fast dissociation rates could not be measured with our temporal resolution, and no direct information concerning the unimolecular reaction rates and the surfaces involved in the dissociation could be derived. To achieve this, we chose $(\text{CH}_3)_3\text{CNO}$ (t-BuNO), a nitroso compound with greatly increased number of vibrational degrees of freedom and density of states. Our initial work, carried out at room temperature, was dominated by hot band absorptions, and therefore state-specific rates could not be obtained.⁴ In our very recent work,¹⁶ we used expansion cooled t-BuNO and succeeded in separating in time the radiationless transition and the unimolecular reaction rates. We showed that at low excess energies, the NO appearance times are $> 1 \mu\text{s}$, indicating that dissociation proceeds on a low lying surface, most probably S_0 . At energies $> 600 \text{ cm}^{-1}$ above the S_1 origin, the NO appearance times decrease abruptly, indicating the opening of a second, higher energy dissociation channel, possibly involving T_1 .¹⁶

IV. PHOTODISSOCIATION DYNAMICS^{5,12}

Here, we concentrated mainly on the photodissociation of XCN (X=I,Br,Cl) molecules. The dissociation of these molecules in their continuum is direct, and dynamic effects are manifest in the energy disposal in the fragments, and in recoil anisotropies. In our first experiments we compared the V,R energy distributions in the CN fragments obtained via photolysis of XCN at 300 K and following jet expansion.⁵

We then detected nascent CN(X) following the 266 nm photodissociation of 300 K ICN, using sub-Doppler resolution LIF and polarized photolysis and probe lasers.¹² When monitoring a particular CN internal state, the translational energies of the I + CN and I* + CN channels differ by the iodine spin orbit splitting, 7603 cm⁻¹. This was used to determine the separate contributions from each channel. For I + CN, high N" are selectively produced, with little population below N"=20, whereas the I* + CN channel is associated with a distribution peaked sharply at low N". The low and high N" channels derive from linear and bent exit channel geometries respectively. The spatial anisotropy is high, and initial excitation is via a parallel transition(s), probably to a state which begins correlating with I* + CN in the linear configuration. Nascent spin-rotation states are also resolved for each channel, and their populations were quite different. We concluded that subsequent to initial excitation, both adiabatic and/or nonadiabatic processes can ensure access to potential surfaces not excited directly, and a model was discussed which rationalized the experimental results.

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