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Reactions of $N_2(A^3\Sigma_U^+)$
and
Candidates for Short Wavelength Lasers

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I. INTRODUCTION

There are several potential schemes for efficiently generating high concentrations of the first electronically excited state of nitrogen, $N_2(A^3\Sigma_u^+)$, 6.2 eV) by either chemical or electrical pumping. The goal of this proposal is to study ways of utilizing the energy of the $N_2(A)$ molecules for developing efficient, short wavelength gas lasers. Such lasers are of potential interest for laser fusion. We will investigate both excitation-transfer and dissociative excitation-transfer reactions of $N_2(A)$ that yield electronically-excited diatomic molecules as products. We will not address the problem of the generation of $N_2(A)$ or the desirable/undesirable qualities associated with N_2 as a laser medium, except to note that N_2 has more desirable qualities than nearly any other gaseous medium, except the rare gases. Both excitation-transfer and dissociative-excitation reactions of $N_2(A)$ can be efficient; two examples^{1,2} from the literature document this claim.

Unfortunately, the $NO(A-X)$ transition is not a good laser candidate and there are even better ways to generate $HgBr(B)$, i.e., electron impact dissociative excitation.³ Other evidence that can be quoted as supporting the possibility for efficient excitation-transfer reactions with $N_2(A)$ are studies with metal atoms. Recently a careful study has been done with Cu vapor.⁴

This work, together with other studies, has shown that the Franck-Condon restriction in the $N_2(A) \rightarrow N_2(X)$ transition, is important for excitation-transfer reactions and that the most favored final states are $N_2(X^1\Sigma_g^+, v'' = 5 \text{ and } 6)$ and transfer of $\sim 80\%$ (or 4.5 eV) of the total available energy (6.2 eV) is the most favorable quenching pathway.

The reactions of $N_2(A)$ with the more conveniently available diatomic molecules have been studied. (In our laboratory we have just examined the reactions with halogens and interhalogens and, unfortunately, negligible yields of the halogen (D') state was found). Therefore, somewhat more exotic reagents must be investigated for laser applications. We believe that three excitation transfer reactions have potential promise as lasers. These are S_2 , SO and XeF ; all three molecules have electronic state transitions that can serve as lasers without bottlenecking. For dissociative-excitation transfer systems we will investigate $N_2(A)$ with the hydrazoic acid, halogen azides and XeF_2 . The azides have the potential for a chain reaction yielding electronically excited molecules in the presence of N atoms, e.g.,

The experimental details associated with investigating these particular molecular systems and some others of lower priority are given in the next section. During this work, we shall be searching for other potentially interesting energy transfer reactions for study. For example we suspect that phosphorus containing molecules, such as PF , P_2 , and PO could be quite interesting. We intend to systematically search for both excitation-transfer and dissociative excitation-transfer reactions with high branching fractions for electronically excited state products. After high branching fraction cases are found, more detailed study of those systems which seem suitable for high power lasers will

be proposed. However, the first goal is to find efficient pumping reactions using energy transfer reactions of $N_2(A)$.

The work in this proposal is based on the expected effort of one postdoctoral fellow for two years. The experimental technique will be based on the established metastable Ar atom/ N_2 flowing-afterglow method for generating $N_2(A)$ in the absence of appreciable concentrations of N atoms.^{1,5} The total quenching rate constants are measured from the decay rate of $N_2(A)$ for known concentrations of reagent molecules. The $N_2(A)$ concentration can be observed directly via the $N_2(A-X)$ transition; $\tau = 2$ sec. The product branching fractions are assigned by comparing the emission in question to that of $NO(A-X)$ from reaction (1). (These are standard techniques in our laboratory and a sample study is given in the reprint attached as an appendix.) The most difficult part of the work will be generating the rather unusual reagent species (SO , S_2 , etc.) and measuring their concentrations. This is the reason that a postdoctoral fellow is suggested, rather than a graduate student, for the work. In closing this section we note the long standing interest of our laboratory in the study of excited state chemistry of N_2 . Our latest effort dealing with the coupling of the $N_2(W)$ and $N_2(B)$ states has just been published.⁶

II. EXPERIMENTAL DESIGN

II-A. Excitation-Transfer Reactions

Excitation-transfer to diatomic molecules will be studied by measuring branching rate constants, product branching fractions and product state distributions. The expected reaction with S_2 , SO and XeF are given as examples

The excitation energies and other important properties of the reagents and product molecules are summarized in Table 1. As previously mentioned the $N_2(A)$ molecules will be generated in a flowing-afterglow system and the $S_2(X)$, $SO(X)$,

Summary of Relevant Molecular Properties

Molecule	Ground State		Upper State					
	$R_e''(\text{\AA})$	$\omega_e''(\text{cm}^{-1})$	$T_{0-0}(\text{eV})$	$R_e'(\text{\AA})$	$\omega_e'(\text{cm}^{-1})$			
S_2	$X^3\Sigma_g^-$	1.889	726	$A^3\Sigma_u^-$	3.93	2.170	434	35 nsec
SO	$X^3\Sigma_g^-$	1.4811	1149	$A^3\Sigma^-$	4.70	1.614	415.2	35 μsec ($v'=0$) 18 μsec ($v'=1$)
				$3\Sigma_1^-$	4.72	1.609	413.3	
				$3\Sigma_2^-$	4.74	1.602	412.7	
				$B^3\Sigma^-$	5.13	1.775	630	
XeF	$X^2\Sigma^+$		$B(1/2)$	3.54				13 nsec
			$C(3/2)$	3.49				100 nsec
NH	$X^3\Sigma^-$	1.0361	2398	$A^3\Pi$	3.69	1.007	2361	400 nsec

$\text{NO } X^2\Pi_{3/2}$ 1.15 1904 $A^2\Sigma^+$ 43,965.7 cm^{-1} 1.0637, 2371.3
 (44,078) obs / 5.45 eV

or XeF(X) molecules will be added to the flow reactor. By monitoring the decay rate of $[\text{N}_2(\text{A})]$ for various $[\text{S}_2]$, $[\text{SO}]$, and $[\text{XeF}]$ under pseudo first order conditions, the total quenching rate constant can be assigned. The rate constants for excitation can be measured by comparing the $\text{S}_2(\text{A-X})$, $\text{SO}(\text{A,B-X})$ and $\text{XeF}(\text{B,C-X,A})$ emission intensities to that of $\text{NO}(\text{A-X})$ from reaction (1). The only anticipated difficulty is knowing the $[\text{S}_2]$, $[\text{SO}]$ and $[\text{XeF}]$ concentrations. Each case presents its own problems and our preliminary plans for generating and measuring the $[\text{S}_2]$, $[\text{SO}]$ and $[\text{XeF}]$ concentrations are summarized in the following paragraph. Details of the experimental technique, as used in our recent work with mercury dihalides, is given in the appendix.

Sulfur vapor⁷ will be taken from a mildly heated ($\sim 150^\circ\text{C}$) solid sulfur sample. The mass flow of the sulfur vapor will be measured by condensing the sulfur from the flow stream and weighing the material for a certain period of time. Before the sulfur vapor is added to the reactor, the low temperature flow will be heated to $\sim 600^\circ\text{C}$ to achieve $\geq 95^\circ \text{S}_2$ composition.^{8,9} This flow of S_2 will be added to the $\text{N}_2(\text{A})$ flow reactor, which will be mildly heated, $\sim 200^\circ\text{C}$, to prevent the recombination of the S_2 molecules. The $[\text{S}_2]$ can be monitored in a relative sense by laser-induced fluorescence.

The XeF(X) molecule presents the opposite problem relative to S_2 . The XeF(X) molecule is bound¹⁰ by only 0.15 eV. Thus, at room temperature only a small fraction of a Xe/F gaseous system is bound. Therefore, we will study this reaction at reduced temperature, $\sim -100^\circ\text{C}$, adding an equilibrated mixture of Xe/F to the $\text{N}_2(\text{A})$ flow reactor. We estimated the equilibrium constant using standard

statistical mechanical equations. For a 5 torr Xe/F mixture with $10^{13} \text{ atom/cm}^3$ of F, the XeF concentration will be $\sim 1 \times 10^{11} \text{ molec/cm}^3$. This will be adequate to observe $\text{XeF}(\text{B,C})$ emission from (7) and confirm/deny the existence of the $\text{N}_2(\text{A}) + \text{XeF(X)}$ excitation-transfer reaction. The absolute concentration of XeF(X) will be uncertain and assignment of

k_Q and τ_{XeF^*} will be approximate. Since neither Xe or F quenches $N_2(A)$, any $XeF(B-X)$ or $XeF(C-A)$ emission will indicate the existence of (7) and lay the ground for further work.

The SO molecule must be produced by chemical reaction from a precursor. Since we will have prepared a source for S_2 molecules, we first will try the following set of reactions:

We can use an excess of S_2 in order to avoid the SO_2^* afterglow emission ($O + SO + M$) which would interfere with observation of reactions 6a and 6b. Reaction 8b has been studied¹¹ before ($k_{8b} = 2.1 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$). Although 8a apparently has not been studied, we expect k_{8a} to be $\geq k_{8b}$ based on the thermochemistry. Using reactions (8) in our system will have the advantage that the concentration of SO will be established via knowledge of the $[S_2]$. A second possible method to generate SO is to use reaction 9, which has been studied by Stedman and co-workers.¹²

An excess of S_2O can be used to avoid the SO_2^* afterglow problem. In their laser induced fluorescence studies of $SO(A)$, Clyne and coworkers¹³ used the $O + COS$ and $O + CS_2$ reactions to generate SO. The latter could be satisfactory for our purposes also; but, the $O + COS$ reaction is too slow. Finally we note the interesting possibility of using a microwave discharge on our S_2 flow (or the reaction of H with H_2S) to generate S atoms, which then could be reacted¹¹ with NO_2 . The equal molar mixture of SO and NO could be useful. Thus, there

are a variety of possible ways to generate SO, but all will require development and characterization for our purpose.

All of the upper states excited by reactions 5-7 have some potential as short wavelength lasers. The properties of XeF(B-X) and XeF(C-A) are, of course, well-documented and need no discussion. The $S_2(\text{A-X})$ transition has been demonstrated^{14,15} as a laser for optical pumping conditions. Clyne has discussed the possibilities of an SO(A-X) laser.¹³ The $S_2(\text{B-X})$ transition also has some possibilities; although quenching probably will be more serious for the higher energy state. The $S_2(\text{A})$ and SO(A) states are displaced to larger internuclear distances from the ground state, as is generally thought necessary for good laser candidates. The rather long lifetimes of SO(A) should ensure good energy storage properties. Further speculation about laser performance, without experimentation, is not warranted. Undoubtedly there will be problems; a quenching study of several v' levels of $S_2(\text{A})$ ¹⁶ implies that coupling exists to nearby electronic states. However, the quenching vs. vibrational relaxation of $S_2(\text{B},v)$ are not fully characterized, i.e., the coupling may not result in appreciable irreversible loss of population from $S_2(\text{A})$. Quenching studies of SO(A) are only preliminary¹³ and one can only speculate about quenching vs relaxation by buffer gases. Both $S_2(\text{A})$ and SO(A) could be expected to be reactive toward more chemically active quencher molecules. The more critical question is the rates of relaxation vs. quenching by buffer gases and N_2 .

The three chemical systems discussed above will provide enough work for the first year. However, we hope to extend our investigation to the iso-electronic molecules $\text{NX}(X=\text{H, F and Cl})$ and $\text{PX}(X = \text{H, F and Cl})$. The reactions analogous to that for SO looks very interesting,

By analogy to NH , Table 1, the R_0' values of the NX(A) states may not be shifted much relative to the X state; however, the SO analogy suggests that there may be an adequate

shift. We will reserve starting work on this series until after the dissociative excitation transfer reactions have been studied.

II-B. Dissociative Excitation-Transfer Reactions

The systems for which we have the most interest are the hydrogen and halogen azides, which were written in general form as reaction 3 and more particularly for FN-N₂ below.

Based upon previous qualitative work in our laboratory¹⁷ with HN-N₂ and NCN-N₂, we expect high branching fractions for electronic excitation in reactions with other azides. We plan to systematically investigate the quenching rate constants and branching fractions for HN-N₂, FN-N₂, ClN-N₂ and BrN-N₂. There is good reason, based upon work by ourselves¹⁸ and others,¹⁹⁻²⁰ to expect the reaction of N atoms with N-X molecules to generate electronically excited N₂ molecules (either N₂(A) or N₂(B)). Since all excited triplet states cascade to N₂(A), the identity of the N₂* state is not so critical. In the presence of N atoms the XN-N₂ molecules may be converted to NX(A³π) by a straight chain reaction; see reaction 3 and 4. Although the azide compounds are explosive, techniques for gas phase synthesis and handling have been recently developed,^{21,22} and these experiments should be straightforward.

The NX(A³π-X³L⁻) transition is analogous to the transition in the iso-electronic series S₂ and SO. Unfortunately these transitions are presently known only for NH--see Table 1. Therefore, our first objective is to find and analyze these transitions for NF, NCl and NBr. Based upon the similarity in R_eⁱ and R_e^o for NH, the NF, NCl and NBr(A-X) transitions may not be so favorable for high power lasers. However, R_eⁱ > R_e^o for S₂ and SO; thus, we have hope that the nitrogen halide molecules will fall toward the center of the two reference cases in terms of R_eⁱ(A) relative to R_e^o(X).

Identification of other dissociative excitation-transfer reactions with a high potential for formation of electronically excited state product molecules is difficult. The precursor molecule must have a bond energy less

than ~ 2 eV in order to have ~ 4 eV of energy remaining from the $N_2(A)$ energy transfer to provide excitation. One intriguing possibility is XeF_2 .

According to presently accepted thermochemistry, the reaction should be exoergic by 0.1 eV. Since two doublet state products are formed, there is no spin restriction. Dissociative excitation, rather than reactive quenching, was a major quenching pathway for $Xe(^3P_2)$ with XeF_2^{23} and, of course, photolysis of XeF_2 at ~ 193 nm gives $\sim$ unit quantum yield for $XeF(B)$. The critical factor is whether the available energy is high enough to populate the XeF_2^* state that dissociates to XeF^* .

Despite several weeks of thinking and searching, we failed to find other promising dissociative excitation precursor molecules.²⁴ This does not mean that suitable molecules do not exist. However, additional time and effort is required for their discovery. An interesting idea, which did not bear fruit, was the utilization of a precursor which would yield $CF_2(\tilde{A}^1B_1)$. The $CF_2(\tilde{A}-\tilde{X})$ transition has laser possibilities and the spectroscopy and quenching of $CF_2(\tilde{A})$ has received considerable attention²⁵ because of the use of the $CF_2(A-X)$ transition for laser induced fluorescence studies of $CF_2(X)$ following infrared multiphoton dissociation of various freon type molecules. We think CF_2 could be an interesting triatomic molecule for possible study, providing that a good excitation mechanism could be found. Unfortunately, $N_2(A)$ lacks sufficient energy to provide excitation from a likely precursor, CF_2N_2 . We give this example just to illustrate that new chemical systems are worthy of study. As our work progresses, we will search for other candidates.

II-C. Equipment and Apparatus

All experiments will be done using a conventional flowing-afterglow apparatus for generating $N_2(A)$ molecules and for handling the reagents. The apparatus that we utilized in the past for $N_2(A)$ work has been converted

into a system for study of $NF(b)$ chemistry. Thus, we need to construct a new $N_2(A)$ flow reactor capable of being heated for study of S_2 and of being cooled for study of $XeF(X)$. We have a reserve of hardware items such as large pumps and monochromators. However, it will be necessary to construct the $N_2(A)$ flow reactor and a gas handling system for storing and metering the reagents. Thus, the budget contains funds for such items as flowmeters, stopcocks (glass/teflon), metal valves, glass joints, and materials for construction in our glass and machine shops.

We also have requested funds to improve one of our monochromators by purchase of a higher resolution grating and a broad response photomultiplier tube and housing. This monochromator is computer interfaced so that spectra can be easily recorded, stored and corrected for the spectral response of the detection system.

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QUARTERLY REPORTS FROM KANSAS STATE UNIVERSITY
TO U.S. DEPT. OF ENERGY

Lawrence Livermore Labs.

Livermore, CA 94550

REACTIONS OF $N_2(A^3\Sigma_u^+)$ AND CANDIDATES FOR
SHORT WAVELENGTH LASERS.

Subcontract No: 4636105

Principal Investigator: D. W. Setser
Department of Chemistry
Kansas State University
Manhattan, KS 66506
(913)532-6692

Scientific Program Officer: Dr. Ken Kulander

Contract Duration: March 1, 1984 - Feb. 27, 1985

Monthly Progress Report (First Report)

Report Period: March 1 - May 31 (1984)

First Quarterly Report
(March 1 - May 3)

Mr. De-Zhao Cao arrived in early March to start work on the project. During the first quarter, a new flowing-afterglow apparatus was built and preliminary experiments have been done. The first chemical system selected for study was $N_2(A) + SO$. The $SO(X)$ molecules were successfully generated by microwave discharge in SO_2 . The $N_2(A)$ molecules were produced from the $Ar(^3P_{0,2}) + N_2$ reaction. Experiments in the first flow reactor showed that the desired excitation transfer reaction did occur.

The $SO(A-X)$ emission was relatively strong and we did not observe any $SO(B-X)$ emission. The preliminary experiments with S_2 were less successful because the microwave discharge in S_2Cl_2 did not appear to produce sufficient quantity of S_2 molecules. The first design of our flow-reactor had several flaws and we now are constructing a second generation reactor to specifically study the SO reaction. We will measure both the total $N_2(A)$ quenching reaction rate constant and the branching fraction for $SO(A)$ formation. The main question seems to be the branching fraction for $SO(A)$ formation vs. that for dissociation.

During the next quarter Mr. Cao should be able to quantitatively study the $N_2(A) + SO$ reaction and to begin preliminary work with S_2 . We currently plan to generate S_2 by thermal techniques from sulfur vapor. During the second quarter a technician at KSU also will be employed for one month. This technician will build an apparatus for synthesis of N_3H and ClN_3 so that the proposed N atom studies with these azide molecules can be started in the third quarter. Providing that our scheme for generating S_2 proves successful, substantial progress should be made on meeting the goals for the first year of effort.

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Contract Duration: March 1, 1984 - Feb. 27, 1985

Monthly Progress Report (Second Report)

Report Period: June 1 - August 31 (1984)

Second Quarterly Report
(June 1 - August 31)

Mr. De-Zhao Cao continued full time work on the project. A second generation design of a $N_2(A)$ generator was constructed for study of $N_2(A) + SO$. This design has proven satisfactory and good progress has been made with both the SO and S_2 reactions. The $SO(X)$ molecules were successfully generated by microwave discharge in SO_2 and $S_2(X)$ from microwave discharge in S_2Cl_2 . The $N_2(A)$ molecules were produced from the $Ar(^3P_{0,2}) + N_2$ reaction.

The new reactor design has proven to be adequate for studying $S_2(X)$ produced by a discharge in S_2Cl_2 and for our early concerns about this source for $S_2(X)$ have been resolved.

The attached SO emission spectrum shows that $> 95\%$ of the emission is from $SO(A)$. The vibrational distribution is $v_0:v_1:v_2:v_3:v_4:v_5:v_6 = 1.0:1.15:1.25:1.22:0.96:0.65:0.35$. This $SO(A,v)$ distribution is just about what one would expect from considering the Franck-Condon factors for excitation of SO and deactivation of $N_2(A)$. The $N_2(A) + SO$ system follows good pseudo first order kinetics and the total quenching rate constant of $N_2(A)$ by SO is $2.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This value depends upon our estimate of the SO concentration, which should be reliable to within a factor of 2. Based upon comparing the $SO(A-X)$ emission intensity to that for $NO(A-X)$, the $SO(A)$ excitation rate constant is $\sim 1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This measurement has yet to be done carefully (or, at least, the way that I wish). However, clearly the excitation transfer from $N_2(A)$ to SO has some promise. Mr. Cao will complete the measurements for the $SO(A)$ excitation rate constant and characterize the $N_2(A) + S_2$ system during the next quarter. We also plan to write a manuscript describing the SO and S_2 reactions for Chem. Phys. Letters

very soon.

The original budget had funds for one postdoctoral person. However, Mr. Cao, the visitor from China who works on the project, requested a salary somewhat less than the "normal" postdoctoral salary. Therefore, there is a little extra money and I have appointed a 2nd year student for the third and fourth quarters. Mr. Glen Lo will begin work trying to develop a pulsed source of $N_2(A)$ for kinetic studies. Work in the literature shows that $NO(D,E) + N_2$ gives $N_2(A)$ with high efficiency. Mr. Lo will investigate the possibilities of two-photon laser excitation for kinetic studies. Such a laser based technique will be complementary to the discharge-flow technique. Mr. Lo has no previous laboratory experience (although he is the best student in his class based upon classroom academic performance). Thus, I expect no significant experimental progress in the first 6 months, except apparatus construction and the training of a new student.

In the very near future I would like to discuss future work and administrative procedures in view of the new national program in short λ lasers. Mr. Cao wishes to stay at KSU for a second year, and I want him here also. We could study the $SO(A)$ state in some detail regarding vibrational relaxation, quenching, etc. The $SO(A)$ state kinetics are not so well characterized. Given the massive effort that the Weapons Lab is making in generation and utilization of $N_2(A)$, our one man effort will not be very competitive (after the SO/S_2 work is done). Therefore, one needs to exercise some care in deciding what to do in the next year. Of course, my preference is to continue with fundamental scientific work rather than the more specific applied work.

Handwritten notes and calculations, including the expression $E = \frac{1}{2} \mu \omega^2 r^2$ and other mathematical derivations.

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REACTIONS OF $N_2(A^3\Sigma_u^+)$ AND CANDIDATES FOR
SHORT WAVELENGTH LASERS

Subcontract No: 4636105

Principal Investigator: D. W. Setser
Department of Chemistry
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Manhattan, KS 66506

Scientific Program Officer: Dr. Ken Kulander

Contract Duration: March 1, 1984 - Feb. 27, 1985

~~Quarterly~~
Monthly Progress Report (Third Report)

Report Period: Sept. 1 - Nov. 31 (1984)

Third Quarterly Report (Sept. 1 - Nov. 30)

Mr. De-Zhao Cao continued full time work on the project. Good progress has been made with the $N_2(A)$ excitation-transfer reactions to SO and S_2 .

The SO(X) molecules were successfully generated by microwave discharge in SO_2 and $S_2(X)$ from microwave discharge in S_2Cl_2 . A description of our measurements of the total $N_2(A)$ quenching rate constants and the SO(A) and $S_2(B)$ product formation rate constants are provided by the attached preprint submitted to Chem. Phys. Lett. In addition to studying the S_2 and SO reactions, experiments were done to characterize the total quenching rate constants of the precursor molecules for SO and S_2 and the molecular halogens.

The original budget had funds for support of one postdoctoral person. However, Mr. Cao, the visitor from China who works on the project, requested a salary somewhat less than the "normal" postdoctoral salary. With the extra money a 2nd year student was appointed for the third and fourth quarters. Mr. Glenn Lo has been building an apparatus to develop a pulsed source of $N_2(A)$ for kinetic studies. Work in the literature shows that $NO(D,E) + N_2$ gives $N_2(A)$ with high efficiency. Mr. Lo will investigate the possibility of two-photon laser excitation of NO followed by transfer to N_2 as a N_2 system for kinetic studies. We also will investigate the two photon laser excitation of $Xe(6p, [1/2]_0)$ followed by collisional transfer to N_2 . The same apparatus can be used for both experiments. Such a laser based technique will be complementary to the discharge-flow technique. Mr. Lo has made moderately good progress and test experiments should be done during the final quarter.

EXCITATION TRANSFER REACTION OF $N_2(A^3E_u^+)$ WITH $SO(X^3E^-)$ AND $S_2(X^3E_g^-)$
AND QUENCHING RATE CONSTANTS OF SOME SULFUR AND HALOGEN
CONTAINING MOLECULES

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ABSTRACT

The reaction between $N_2(A^3E_u^+, v' = 0)$ and $SO(X^3E^-)$ has been studied at room temperature. The total quenching rate constant is $1.2 \pm 0.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and the $SO(A^3E)$ excitation rate constant is $0.5 \pm 0.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Although these rate constants have some absolute uncertainty because of the difficulty of measuring $[SO]$, the $SO + N_2(A)$ excitation transfer reaction appears to be an efficient system for utilizing the energy of the metastable $N_2(A)$ state. Less extensive results also are presented for excitation transfer between $N_2(A)$ and $S_2(X)$. The total quenching rate constant is $\sim 6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and the branching fraction for $S_2(B^3E_g^-)$ formation is ~ 0.3 . Total quenching rate constants are reported for SO_2 , $SOCl_2$, S_2Cl_2 , Cl_2 , Br_2 , and I_2 .

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INTRODUCTION

Although SO has been known for many years, only recently have its kinetics and spectroscopy begun to be studied in detail¹⁻¹². The recent interest in SO derive from its importance in stratospheric chemistry and for the development of short wavelength lasers. Since the $\text{SO}(\text{A}^3\Pi)$ state has a rather long radiation lifetime (10-35 μ s) and slow quenching rates for some gases⁴, and because its equilibrium nuclear distance is somewhat larger than that of ground state, the $\text{SO}(\text{A}^3\Pi \rightarrow \text{X}^3\Sigma^-)$ transition is potentially promising as a laser, if an effective pumping method can be devised. The $\text{SO}(\text{A})$ state is about 4.7 eV above the ground state and it can be excited by ordinary optical methods.^{3,4} We have investigated the excitation-transfer reaction between $\text{N}_2(\text{A})$ and $\text{SO}(\text{X})$.

The experiments were done in a flowing-afterglow reactor. The $\text{N}_2(\text{A})$ was generated by the $\text{Ar}(\text{P}_{2,0}) + \text{N}_2$ reaction^{13,14} and the $\text{SO}(\text{X})$ was produced by microwave discharge in Ar/SO_2 mixtures. The total quenching rate constant was observed by monitoring the decay of $\text{N}_2(\text{A})$ vs. $[\text{SO}]$ and the product formation rate constant was measured by comparing the $\text{SO}(\text{A-X})$ emission intensity with the $\text{NO}(\text{A-X})$ intensity from reaction 2.

Measurements also have been made for excitation transfer between $\text{N}_2(\text{A})$ and $\text{S}_2(\text{X}^3\Sigma_g^-)$ giving $\text{S}_2(\text{B}^3\Sigma_u^-)$.

We also report total quenching rate constants for SO_2 , SOCl_2 , Se_2 , S_2Cl_2 , Cl_2 , Br_2 and I_2 for comparison to SO and S_2 .

EXPERIMENTAL TECHNIQUES

Metastable $N_2(A)$ molecules were generated in a 3.0 cm diameter flowing-afterglow reactor operating with flow speed of 16 ms^{-1} at 3.5 torr. The $Ar(^3P_{2,0})$ atoms were generated by flowing Ar through a low power, hollow cathode discharge ($\sim 220 \text{ d.c.}$); N_2 is subsequently added and $N_2(A)$ is generated by the pre-reaction of $Ar(^3P_{2,0})$ with $N_2(X)$. The flow rates of Ar and N_2 were 95 and $20 \text{ mmole min}^{-1}$, respectively. The Ar and N_2 flows were purified by passing the gases through two dry ice cooled (high pressure) and a liquid nitrogen cooled (low pressure) molecular sieve filled traps. The maximum $[N_2(A)]$ is obtained for a N_2 flow rate equal to 1/4-1/5 of the Ar flow. In order to obtain good mixing of the reagent with the main flow, another Ar line was added to carry the reagents to the reactor. This Ar flow is 20 mmol/min . The tri-flat flow meters for Ar and N_2 were calibrated with a wet-test meter.

The N_2 and SO_2 (or other reagent) gases were added to the flow reactor via four small nozzles, which were radially distributed around the flow reactor. This inlet construction gave good mixing with only small disturbance to the gas flow, and it is a good design for the measurement of rate constants.

The SO was generated by microwave discharge of dilute ($\sim 0.1\%$) SO_2 in Ar. This method is experimentally convenient, but some $O(^3P)$ and $S(^3P)$ atoms are also produced. These atom concentrations were minimized by having a delay volume (50 cm length of 10 mm Pyrex tubing) between the microwave discharge and the entrance of the $SO(X)$ to the $N_2(A)$ flow line. We were unable to detect the ($^1S - ^1D$) emission¹⁶ from $N_2(A)$ excitation of either $O(^3P)$ or $S(^3P)$ or the $SO + O$ afterglow. All of these observations suggest that the $[O(^3P)]$ was very low in the flow reactor and that the stoichiometry

for the decomposition of SO_2 is $\text{SO} + 1/2 \text{O}_2$. The SO(X) concentration was assigned by measuring the loss of $[\text{SO}_2]$ when the microwave discharge was operating. The dissociative excitation-transfer reaction^{1,2} between $\text{Ar}(^3\text{P}_{0,2})$ and SO_2 generates SO(A) , but reaction of $\text{Ar}(^3\text{P}_{2,0})$ with SO(X) does not generate SO(A) ; therefore, from the difference of the SO(A-X) emission intensity (under first order conditions of the $\text{Ar}^* + \text{SO}_2$ reaction) with the microwave discharge on and off, we established the fractional SO_2 decomposition. For a microwave discharge power of 70 W, about 40% of the SO_2 was decomposed. According to Clyne and co-workers⁶, one-half of the SO_2 that is decomposed gives SO(X) . In our work we think the fraction is higher for the reasons just given and we used 80% to relate the loss of $[\text{SO}_2]$ to formation of $[\text{SO}]$ in our $\text{N}_2(\text{A})$ reactor. Even after many days of operation there were no sulfur deposits in the flow reactor or the SO flow line; and for our conditions there is no appreciable loss of S_r to the walls.

The S_2 was generated from a microwave discharge in dilute $\text{S}_2\text{Cl}_2/\text{Ar}$ mixtures. The fractional dissociation was monitored from the decrease in the ArCl(C-A) emission intensity¹⁵ at $\sim 200 \text{ nm}$ from the $\text{Ar}(^3\text{P}_{0,2}) + \text{S}_2\text{Cl}_2$ reaction when the microwave discharge was activated. The dissociation was about 75% and we assumed that the loss of $[\text{S}_2\text{Cl}_2]$ was equal to the formation of $[\text{S}_2]$.

The $\text{N}_2(\text{A})$ molecule is quenched by encounters with the walls and the parabolic flow formulation should be used to convert flow distance to reaction time, providing the flow distance is sufficiently long that parabolic flow develops. The necessary length is calculated using the following formula:^{13,16} ($l = 0.113d\text{Re}$); d is the diameter of flow tube, Re is Reynolds number. ($\text{Re} = 2M\dot{Q}_m/\pi\eta R T d$) with M being the molecular weight, $\dot{Q}_m$ is the carrier gas flow in liter (STP) sec^{-1} and η is the carrier gas

viscosity in poise. In our experiment Re is about 75 and l is about 25 cm. The distance from the argon discharge zone (which was located in a tube of about the same diameter as the flow reactor) to the observation window is 35 cm. Even though there are reagent inlets, and one right angle bend (with light trap), we consider that the gas flow has a fully developed parabolic flow. Therefore, our measured rate constants include the factor of 1.6 for conversion from plug to parabolic flow velocity.

The emission spectra was observed with a 0.75 m Jarrell Ash monochromator equipped with a cooled 9558QB EMI photomultiplier tube and SSR photon counter. The wavelength response of the detection system was calibrated with standard lamps. For excitation rate constant measurements the NO , S_2 and SO emission spectra were acquired by computer and stored on tape for subsequent integration to obtain total relative intensities.

EXPERIMENTAL RESULTS

We used the fixed point method to measure the total quenching rate constants of $N_2(A)$ by SO , SO_2 and other reagents. The differential rate law for decay of $N_2(A)$ in presence of reagent Q is

$$d[N_2(A)]/dt = -(k_W + k_Q[Q])[N_2(A)] \quad (3)$$

and from this equation and for pseudo-first-order conditions we obtain the integrated first order rate law,

$$\frac{[N_2(A)]}{[N_2(A)]_0} = \exp^{-(k_W + k_Q[Q])\Delta t} \quad (4)$$

For our flow speeds and $[N_2]$, about 20% of the $N_2(A)$ molecules were in $v'=1$ and we will consider the quenching to be entirely for $N_2(A, v=0)$. Previous work^{13,17} has established that the total $N_2(A)$ concentration is $\sim 10^{10}$ molecules cm^{-3} . There are two methods to measure the decay of $N_2(A-X)$ for

fixed Δt . If the $N_2(A-X)$ emission is strong, we can directly measure the $N_2(A)$ emission intensity at different concentration of reagent. If the emission of $N_2(A)$ is not strong, we can add NO into the flow tube and use the $NO(A-X)$ emission intensity to monitor $[N_2(A)]$ because $I_{NO} = k_{NO}[NO][N_2(A)]$. The slope of a plot of I_{NO} vs $[Q]$ for fixed $[NO]$ is the same as direct monitoring of $[N_2(A)]$, providing that the concentration of $N_2(A, v'=1)$ is not significant. In our experiments the distance between the point of the addition of reagent and observation of $[N_2(A)]$ is 20 cm. We take 3 cm as the mixing distance and these experiments correspond to a reaction time of 10.6 ms. Tests were made for the reliability of the decay kinetics of our flow reactor by measuring the rate constants for O_2 and C_2H_4 , which have well documented^{16,17} rate constants (0.23 and 12×10^{-11} cm^3 molecule $^{-1}$ s $^{-1}$). We obtained $0.31 \pm 0.05 \times 10^{-11}$ and $12 \pm 2 \times 10^{-11}$ cm^3 molecule $^{-1}$ s $^{-1}$ for O_2 and C_2H_4 , respectively.

We measured the total quenching rate constants for $N_2(A)$ by SO and SO_2 using both direct $N_2(A)$ detection and with addition of NO. The results (shown in Table 1 and Figure 1) were nearly equal for the two methods. The quenching rate constant for SO is large, $12 \pm 2 \times 10^{-11}$ cm^3 molecule $^{-1}$ s $^{-1}$, whereas that for SO_2 is much smaller, $2.8 \pm 0.5 \times 10^{-11}$ cm^3 molecule $^{-1}$ s $^{-1}$. The SO_2 result is from an average of several experiments, and the present result is in good agreement with earlier measurements.¹⁷ The SO_2 emission from excitation-transfer with $N_2(A)$ is too weak to be of interest, and most of the quenching by SO_2 may give dissociation. The quenching rate constant plot for S_2 also is shown Figure 1. By coincidence, the rate constants for quenching by S_2 and S_2F_{12} are equal. The rate constants tabulated in Table 1 are the average of three or more independent experiments. In addition to the statistical uncertainty in the rate constant measurements there is the

possibility of systematic error associated with the uncertainty of $[S_2]$ or $[SO]$.

The rate constant for Cl_2 , Br_2 , I_2 and $SOCl_2$ also are listed in Table 1. Specific tests were made to search for Cl_2^* , Br_2^* and I_2^* emissions, including the $D'-A'$ transitions. Even for $[Cl_2]$ and $[Br_2]$ sufficiently high to achieve half-quenching of $[N_2(A)]$ within the observation zone, i.e. 3 cm reaction distance, no $Cl_2(D'-A')$ or $Br_2(D'-A')$ emission could be observed and the suggestion that excitation transfer from $N_2(A)$ to Cl_2 and Br_2 under 300K Boltzmann reaction conditions can give $Cl_2(D')$ or $Br_2(D')$ is incorrect.²⁰ Our measurements would not rule out a very minor $Br_2(D')$ formation channel.²¹ The quenching by I_2 does give some $I_2(D'-A')$ emission, but the branching fraction, measured relative to reaction (2), is only ~0.02%.

The $SO(A-X)$ emission from addition of $SO(X)$ to the $N_2(A)$ flow was very bright, and a spectrum is shown in Fig. 2. At higher resolution, a small $SO(B-X)$ emission component in the 280 to 340 nm range can be observed, but this only contributes 5% to the total emission intensity. The $SO(A)$ formation rate constant was measured using the NO reference reaction technique^{13,14}. The NO and SO were introduced successively to the reaction zone and the wavelength integrated $SO(A-X)$ and $NO(A-X)$ relative intensities were measured just beyond the mixing zone under conditions such that both intensities were first order in reagent concentration, see Fig. 3. The value for the $SO(A)$ excitation rate constant was obtained from the relative slopes of the plots and the $NO(A)$ formation rate constant¹⁹ ($k_{NO^*} = 0.80 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). As the average of several experiments, we find $k(SO(A)) = 5.0 \pm 0.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Since this measurement is made for $[SO_2] \leq 10^{13} \text{ molecule cm}^{-3}$, there can be no quenching by SO_2 even for the long lifetime (~15 μs) of $SO(A)$. Variation of the Ar and N_2

pressures showed no SO(A) quenching. The vibrational distribution of SO(A) at ~ 3 torr was calculated directly from the SO(A-X) emission spectrum by summing all transitions from a given v' level. The results are $v_0:v_1:v_2:v_3:v_4:v_5:v_6 = 1.0: 1.14: 1.21: 1.16: 0.97: 0.68: 0.32$. This distribution can be compared to the vibrational distribution of SO(A) generated in the dissociative excitation reaction of SO_2 with $\text{Ar}(^3\text{P}_{0.2})$, $v_0:v_1:v_2:v_3:v_4:v_5:v_6 = 1.0: 0.65: 0.80: 0.77: 0.57: 0.43: 0.20$, which declines with increasing v . In both cases we have assumed that the decay is dominated by radiative decay and not quenching. Therefore, the observed steady-state intensities correspond to the initial distribution. Experiments were done from 1-8 torr to check for vibrational relaxation. Only minor relaxation was observed below 3 torr; however, at a higher pressures there is some vibrational relaxation.

Experiments also were done for the $\text{N}_2(\text{A}) + \text{S}_2$ reaction to establish the product formation rate constants. The emission spectrum $\text{S}_2(\text{B}^3\text{E}_u^- - \text{X}^3\text{E}_g^-)$ shown in Fig. 4 consists of the $(\text{B}^3\text{E}_u^-, v'=0-8 + \text{X}^3\text{E}_g^-)$ transitions. Although the $\text{S}_2(\text{B-X})$ emission is easily observed, the intensity seems to be approximately an order of magnitude weaker than from $\text{SO}(\text{A-X})$ for the same SO and S_2 concentrations. Measurements of the $\text{S}_2(\text{B})$ formation rate constants gives $1.7 \pm 0.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; however, the total quenching rate constant ($\sim 6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) also is smaller than for SO. Thus, the observed branching fraction for $\text{S}_2(\text{B})$ formation is ~ 0.3. Based upon work²² which shows that some levels of $\text{S}_2(\text{B})$ are coupled to reservoir S_2^* states, it seems likely that other S_2^* states are produced from $\text{N}_2(\text{A})$ quenching. The $\text{S}_2(\text{B})$ vibrational distribution is $v_0:v_1:v_2:v_3:v_4:v_5:v_6:v_7:v_8 = 1.0:1.2:1.5:1.9:2.3:2.1:1.8:1.6:0.9$.

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CONCLUSIONS

The excitation-transfer reactions between $N_2(A)$ and S_2 or SO give relatively efficient formation of $S_2(B^3I_u^-)$ and $SO(A^3I^-)$ states. Based upon comparison with the NO reaction, which still has some uncertainty in rate constant,^{17,19} the branching fractions for $S_2(B)$ and $SO(A)$ formation are in the range of 0.3 and 0.5, respectively. The large quenching total rate constant for $SO(X)$ makes it the more interesting candidate for efficient energy conversion from $N_2(A)$, i.e. for an ultra violet laser based upon excitation-transfer from $N_2(A)$. The large rate constant for quenching of $N_2(A)$ by SO is consistent with a model which requires good Franck-Condon factors for both molecules.

The quenching rate constants for the sulfur halide and the diatomic halogen molecules are all in the $5 - 20 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ range. Unfortunately, the quenching of $N_2(A)$ by Cl , Br_2 and I_2 do not give significant branching fraction formation for states that subsequently emit photons. All molecules have suitable acceptor states for dissociative excitation transfer and this seems to be the main quenching pathway of $N_2(A)$. The Br_2 and I_2 cases require some comment since our total quenching rate constants are considerably larger than the measurement by Mandl and Ewing²³ for I_2 ($6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and Coombe and Lan²¹ for Br_2 ($5 \pm 2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). In their work Mandl and Ewing reported a rate constant $4.5 \pm 0.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for quenching by NO that also is low relative to currently accepted values and there must have been some systematic error in their measurements. Coombe and Lan followed the time dependence of the $Br_2(D')$ emission following photolysis of BrN_3 and associated the decay time with the quenching of $N_2(A)$. Evidently the

excitation in that system is not for 300K Boltzmann $N_2(A)$ and $Br_2(X)$ reactants.

Acknowledgments

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Table 1. Total Quenching Rate Constants for $N_2(A^3E_u^+)$

Reagent	Rate constant ($10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Comments
SO	12 ± 2	direct observation of $N_2(A, v'=0)$
	15 ± 2	Nitric oxide tracer for $N_2(A)$
SO ₂	2.8 ± 0.5	direct observation of $N_2(A, v'=0)$
	3.2 ± 0.5	nitric oxide tracer for $N_2(A)$
SOCl ₂	$8.7 \pm 1.$	direct observation of $N_2(A, v'=0)$
S ₂	6.0 ± 2.0	direct observation of $N_2(A, v'=0)$
S ₂ Cl ₂	6.0 ± 1.0	direct observation of $N_2(A, v'=0)$
Cl ₂ ^b	7.8 ± 1.5	direct observation of $N_2(A, v'=0)$
Br ₂ ^b	12 ± 2	direct observation of $N_2(A, v'=0)$
I ₂ ^b	23 ± 5	direct observation of $N_2(A, v'=0)$
NO	8.0 ± 2.0	From reference 17; ($k_{NO^*} = k_Q$) ^a

a. The NO(A) formation rate constant was set equal to the NO(X) quenching rate constant. 17,19

b. No Br₂^{*} or Cl₂^{*} emission observable from quenching of $N_2(A)$; the I₂ (B'-A') emission was observed but it is a minor component for quenching.

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Fig. 1 Decay of $[N_2(A)]$ versus reagent concentration for fixed reaction time of 10 ms.

o SO with $[N_2(A)]$ directly observed from $N_2(A \rightarrow X)$ emission intensity;

Δ SO with $[N_2(A)]$ from monitoring by the $NO(A \rightarrow X)$ emission intensity; the decay plots for $SO_2(O)$, $S_2(X)$ and $Cl_2(O)$ were obtained with direct $N_2(A)$ observation.

Fig. 2 Emission spectrum of $SO(A)$ from the reaction of $N_2(A) + SO(X)$ for $[SO] = 5 \times 10^{12}$ molecule cm^{-3} and total pressure of ~ 3 torr (20% N_2).

There are traces of $SO(B)$ and SO_2^* emission in the 280 to 340 nm region.

Fig. 3 Plot of $NO^*(A \rightarrow X)$ and $SO^*(A \rightarrow X)$ emission intensities from the reaction with $N_2(A)$ vs $[SO]$ and $[NO]$ for the same $[N_2(A)]$. Observations of the intensities were made 3 cm downstream from the reagent mixing inlet.

Fig. 4 The $S_2(B \rightarrow X)$ emission spectrum from reaction of $N_2(A) + S_2(X)$ for a $[S_2]$ of 1×10^{13} molecule cm^{-3} and total pressure of 3 torr (20% N_2).

$A^3\Pi_0$

$S_2(B-X)$

QUARTERLY REPORTS FROM KANSAS STATE UNIVERSITY
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Lawrence Livermore Labs
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REACTIONS OF $\text{H}_2(\text{A}^3\Sigma_u^+)$ AND CANDIDATES FOR
SHORT WAVELENGTH LASERS

Subcontract No: 4636105

Principal Investigator: D. W. Setser

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Manhattan, KS 66506

Scientific Officer: Dr. Ken Fehsenfeld

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Quarterly Progress Report (Fourth Report)

Report Period: Dec. 1, 1984 - Feb. 27, 1985

Fourth Quarterly Report (Dec. 1 (1984) - Feb. 28(1985))

Mr. De-Zhao Cao continued full time postdoctoral work on the project. The manuscript describing the $N_2(A)$ excitation-transfer reactions to SO and S_2 has been accepted by Chem. Phys. Lett. In addition to studying the S_2 and SO reactions, experiments to characterize the total quenching rate constants of $N_2(A)$ by the precursor molecules for SO and S_2 and the molecular halogens are included in the manuscript.

Experiments have been done to search for new $N_2(A)$ excitation-transfer systems using the flowing-afterglow apparatus. We have examined cases that are formally isoelectronic with SO, in particular PF and PCl. Although the $A^3\Pi - X^3\Sigma^-$ emission systems are known for these molecules, reaction of $N_2(A)$ with mixtures of Ar/ PCl_3 and Ar/ PF_3 that have been passed through a microwave discharge did not give these PF* or PCl* transitions. Instead other weak band systems of unknown origin were found. Inspection of the PF(A) and PCl(A) potentials suggests that the favored Franck-Condon excitation events may lead to formation of PF(A) and PCl(A) above their dissociation limits. The PF(A) state appears particularly interesting for laser applications if an adequate excitation means could be found. Mr. Cao also has investigated microwave discharges of Ar/ $SOCl_2$ and Ar/ SOF_2 mixtures as an alternative to a discharge in Ar/ SO_2 mixtures as sources for SO molecules. During the next quarter, Mr. Cao will write a general manuscript describing his excitation-transfer studies with $N_2(A)$. Fortunately he will stay at KSU a second year and continue work on this project.

The original budget had money for support of one postdoctoral person. However, Mr. Cao, a visitor from China, requested a salary somewhat less than the "normal" postdoctoral salary. With the extra money a 2nd year student was appointed for the third and fourth quarters. Mr. Glenn Le has

built a laser cell for a pulsed source of $N_2(A)$ for kinetic studies. Such a laser based technique would be complementary to the discharge-flow technique. Experiments are in progress to investigate the possibility of two-photon laser excitation of NO followed by transfer to N_2 as a $N_2(A)$ system for kinetic studies. Mr. Lo has made moderately good progress and test experiments indicating the presence of $N_2(A)$ have been done during the final quarter. However, the signal averaging and data acquisition package for the new digitizer and new computer needs further work before reliable kinetic data can be obtained. We also will investigate the two-photon laser excitation of $Ne(6p[1/2]_0)$ followed by collisional transfer to N_2 as a pulsed $N_2(A)$ source. The same apparatus can be used for both experiments. Mr. Lo will continue work on the project through the summer.