We can also compare the ratio of $k_2$ to $k_1$. In this case, all of the determined ratios are in fair agreement. Our ratio of 9.0 compares well to Pilling (8.3), Temps (11.2), and Laufer (10.7). Vinckier, who measured these rates relative to O + $^3$CH$_2$O, obtains a value of 12.5, which is somewhat farther from our value.

A number of determinations of $k_3$ have been made. The earlier works by Vinckier et al., Homann et al., and Laufer et al. indicated $k_3$ to be on the order of $1 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. This value is substantially larger than one might expect based on conventional triplet carbene reactivity. More recent determinations of $k_3$ by Walsh et al. gave a much smaller value for this rate constant. Utilizing a laser flash photolysis gas chromatographic end product analysis, they derived an upper limit of $1 \times 10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Finally, Bohland et al. in a direct measurement of CH$_2$ in an LMR/flow system recently have reported that $k_3$ is less than $8 \times 10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Our direct observation of $k_3 < 1.4 \times 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ by an independent method conclusively verifies that $k_3$ is much smaller than earlier thought.

Conclusion
In this study we have used infrared diode laser absorption flash kinetic spectroscopy to measure the reaction rates of $^1$CH$_2$ with O$_2$, NO, and C$_2$H$_2$. Our measured rates are generally in good agreement with other direct measurements of these rates and in disagreement with the results of indirect studies.

In these experiments we have seen that, in the absence of added reactant gases, $^3$CH$_2$ is eventually consumed in a recombination reaction. In principle, then, we should have a measure of the recombination rate of $^1$CH$_2$ through analysis of decays in the absence of reactive gases. However, the recombination of CH$_2$ is described by second-order reaction kinetics. Since second-order kinetic processes require that the absolute concentration of $^1$CH$_2$ radicals be known, unfortunately, in these experiments we do not believe we can precisely define the density of $^1$CH$_2$ species in our probe volume. We are currently proceeding with a measurement of this recombination rate. We also have not addressed important questions with respect to the products of the reactions studied. With the flexibility in tunability of our diode laser spectrometer system, we should be able to study the rises of any molecular products (except homonuclear diatomics) by direct time-resolved absorption. Studies of this nature are also in progress.

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Rate Coefficient for the H + NF(a$^1\Delta$) Reaction

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We have measured the rate coefficient of the reaction between atomic hydrogen and NF(a$^1\Delta$) in a discharge-flow reactor by monitoring the decay of NF(a$^1\Delta$) in excess hydrogen atoms. Reacting H$_2$ with the effluents of a low-power discharge through NF$_2$/Ar mixtures produced the NF(a). It was monitored in fluorescence at 874 nm. A thermally stabilized discharge in H$_2$/Ar mixtures generated the atomic hydrogen. The chemiluminescent titration of H with NOCl determined H atom number densities. The measured value is $(3.1 \pm 0.6) \times 10^{13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. These results are necessary to evaluate the potential efficiency of a proposed scheme for generating metastable nitrogen beginning with the addition of atomic hydrogen to NF$_2$.

Introduction
The lowest lying metastable state of N$_2$, A$^3\Sigma^+$, is a well-known energy reservoir (~6 eV) which has potential as an energy storage candidate for use in short-wavelength laser systems. As such, knowing the means to generate this species efficiently and understanding its energy-transfer kinetics in the lasing medium are essential requirements for laser device design. Several laboratory investigations have identified methods for forming N$_2$(A) chemically. Two methods, in particular, may be capable of producing N$_2$(A) in sufficient quantities to drive a transfer laser. The first method consists of a set of reactions initiated by the reaction of atomic hydrogen with NF$_2$ and appears to involve the metastables NF(a$^1\Delta$) and N(2D) as key intermediate species. An intriguing second method is the bimolecular disproportionation of the highly energetic azide radical, N$_3$. The former method has a potentially high efficiency per unit mass, but it requires the handling of the hazardous species N$_2$F$_4$ (the thermal source of NF$_2$) and may present serious kinetic complications upon scale-up from laboratory experiments. The latter method, which uses ionic metal azides such as NaN$_3$ as thermal sources of N$_3$ radicals, is also potentially mass efficient.

This paper is concerned with one aspect of excited molecular nitrogen production from the H + NF$_2$ reaction sequence. This reaction has been the subject of several previous studies, and its history in the literature is intriguing. The first report was by Clyne and White in 1970. They observed that the reaction of H + NF$_2$ produced NF(a$^1\Delta$), NF(2$^2\Sigma^+$), and N$_2$(B$^1\Pi_q$). They thought that recombination of N(4$^3\Sigma^+$) atoms was the source of N$_2$(B) (1).


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In 1973 Herbelin and Cohen\(^7\) performed a similar chemiluminescence study and suggested the following mechanism:

\[
H + \text{NF}_2 \rightarrow \text{NF}(a) + \text{HF} \quad (1)
\]

\[
H + \text{NF}(a) \rightarrow N(^2D) + \text{HF} \quad (2)
\]

\[
N(^2D) + \text{NF}(a) \rightarrow N_2(B) + F \quad (3)
\]

Although they could not prove this model, they presented indirect evidence for its validity and argued that spin and angular momentum conservation would be major determinants in reaction product channel availability. In particular, they emphasized that the reaction of H with NF\((a)\) would produce N\((^2D)\) exclusively if these correlation rules held rigorously. In spite of these early observations, the reaction mechanism for this potentially important source of N\(_2^{2D}\) has remained unclear.

In the early 1980s Clyne and co-workers published a series of detailed experiments designed to clarify this interesting reaction sequence.\(^8\)\(^9\) Using sensitive diagnostic techniques, they observed that N\((^2D)\) apparently was the primary product of reaction 2 and concluded that Herbelin and Cohen's proposed mechanism probably was correct. In addition, they determined a rate coefficient for reaction 1 (H atom removal by NF\(_3\) or \((1.5 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\)) and estimated the rate coefficients of reactions 2 and 3 to be \(2.5 \times 10^{-11}\) and \(7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\), respectively. Subsequent investigations by Malins and Setser\(^10\) found a total rate coefficient for reaction 1 of \(1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) by observing the formation of the HF product. They also found that \(90\%\) of the reaction resulted in NF\((a^1\Delta)\) formation and established a radiative lifetime for NF\((a)\) of 5.6 s. This latter value agrees with recent theoretical calculations.\(^10\)\(^11\)

This paper describes measurements of the rate coefficient for reaction 2. A subsequent paper\(^11\) will describe measurements of the rate coefficient for reaction 3 and will show our results provide further evidence in favor of Herbelin and Cohen's model.

**Experimental Section**

**Flow Tube Description.** A new, modular, fast-flow reactor was constructed specifically for these experiments and is shown, schematically, in Figure 1. It is similar in most respects to another discharge-flow reactor we have described in detail.\(^11\)\(^13\) The flow tube is constructed from 5-cm-i.d. Pyrex, and the observation region is 5-cm-i.d. stainless steel chamber coated with Teflon (DuPont Poly TFE No. 852-201). Prior to Teflon coating the entire observation chamber was painted with a flat black primer. The black primer/Teflon combination serves two functions. The primer reduces scattered light which facilitates all spectroscopic observations while the Teflon coating reduces wall reactions and recombinations.

NF\((a^1\Delta)\) is produced in the upstream end of the reactor by mixing the effluents of a weak microwave discharge (~6 W) of NF\(_3\) dilute in argon with a substantial flow of molecular hydrogen (vide infra). Further downstream, H atoms, produced in a microwave discharge (~50 W) through a flow of H\(_2\) and argon in a side arm, are injected into the flow. Still further downstream, the number densities of NF\((a)\) and H are monitored by observing NF\((a-X)\) emission at 874 nm and HNO emission at 693 nm (when NO is added to the reactor), respectively.

All gas flows are monitored by electronic mass flowmeters. The flowmeters were calibrated by measuring the change in pressure versus time of gas flows into a standard volume (6.5- or 12.0-L flasks). The pressure change was measured with a Validyne pressure transducer that had been calibrated against a mercury or oil manometer. Typical flow rates included 2000 and 400 pmol s\(^{-1}\) for the \(\text{NF}_3\), 200 pmol s\(^{-1}\) for the \(\text{NF}_2\), 200 \(\mu\)mol s\(^{-1}\) for the \(\text{H}_2\) mixed with the \(\text{NF}_3\) discharge effluent, and 0-100 \(\mu\)mol s\(^{-1}\) for the \(\text{H}_2\) through the H atom discharge.

The pressure in the flow tube is measured with a Baratron 0-10-Torr capacitance manometer. Typical flow tube pressures ranged from 0.13 to 2.5 Torr. Flow velocities varied from 500 to 5300 cm s\(^{-1}\).

The present configuration uses two ports for optical detection. Visible and near-infrared chemiluminescence is monitored with a 0.3-m McPherson monochromator and a thermoelectrically cooled Hamamatsu GaAs photomultiplier tube. The other port has a filtered photometer for monitoring HNO emission which is used to calibrate H atom number densities (described below).

**NF\((a^1\Delta)\) Production.** We used the reaction of hydrogen with the products of a weak microwave discharge of NF\(_3\) dilute in Ar to produce NF\((a^1\Delta)\). Initial runs showed that the emitting species produced by the NF\(_3\) discharge consisted almost exclusively of NF\((b-X)\) and NF\((a-X)\) emissions at 528 and 874 nm, respectively. Weak N\(_2(B\rightarrow A)\) first-positive emission was also observed, but since the radiative lifetime for N\(_2(B)\) is orders of magnitude shorter than those for NF\((a)\) and NF\((b)\), N\(_2(B)\) is a minor product.

Upon addition of molecular hydrogen to the effluents of the NF\(_3\) discharge, the NF\((a,b)\) emissions increased approximately an order of magnitude and the emission from N\(_2(B)\) decreased, vanishing at high H\(_2\) flow rates. Observing enhanced NF\((a)\)

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emission from H$_2$ was added to the discharge effluents indicates that, in addition to NF(a,b), both NF and F are products of the NF$_3$/Ar microwave discharge. Rapid reaction of F with added H$_2$ produces atomic hydrogen which then reacts with NF$_2$, via the abstraction reaction (1), to generate more NF(a). These conditions of high H$_2$ flow rate obtained in our kinetic measurements. The motivation for adding a large excess of H$_2$ with respect to NF$_2$ was to react away any free F and NF$_2$ produced in the discharge. In addition, by injection of a large excess of H$_2$ in the formation region of NF(a), subsequent addition of smaller amounts of undissociated H$_2$ further downstream would have minimal affect on the NF(a) number density. All removal then could be attributed to H atoms. The point in Figure 2 at which the [NF(a)] reaches a plateau, which is independent of further increases in H$_2$, is most likely the point at which all F generated in the discharge has been consumed, i.e., [H$_2$]$_0$ = [F]$_0$. In this case the discharge produces approximately four F atoms for every five NF$_3$ molecules introduced to the discharge. We estimated [NF$_2$] from kinetic modeling of profiles of NF(a), N(5D), and N$_2$(B).\(^{(11)}\) We found the ratio [NF$_2$]/[F]$_0$ ~ 0.5, from which we infer a yield of NF$_2$ from NF$_3$ of about 40%. Note that the discharge runs at low power, <10 W. Increasing the discharge power to 30 W drastically reduces [NF(a)], indicating dissociation of NF$_2$ at the higher microwave powers. Another indication of this enhanced dissociation is our observation of N(5S) generation at the higher microwave powers.

Our approach appears to provide a relatively safe and efficient source of NF(a) for kinetic studies. Habdas et al.\(^{(16)}\) recently showed that adding NF$_2$ to excess F atoms also provides a good chemical source for NF(a) kinetic studies. The advantage of our approach over that of Habdas et al. or that from direct addition of H to NF$_2$ is the elimination of handling hazardous chemicals such as HN$_3$ or N$_2$F$_4$.

**H Atom Calibration Procedure.** The chemiluminescent titration of H by NO was used to measure H atom number densities. The recombinaton reaction of H + NO produces HNO emission with four characteristic features at 627.2, 692.5, 762.5, and 796.5 nm.\(^{(17)}\) We monitored the 692.5-nm peak with a Hamamatsu R955 photomultiplier tube (PMT) restricted to a 9-nm band-pass by an interference filter centered at 690.5 nm.

Clyne and Thrush\(^{(18)}\) have shown that the HNO$_2$ emission intensity resulting from the three-body recombination H + NO + M → HNO$_2$ + M is described by

$$I_{HNO} = K[H][NO]$$

and is independent of total pressure over the range of 1–2.5 Torr. The proportionality constant, $K$, is determined by titrating H with NOCl as originally described by Clyne and Stedman.\(^{(18)}\)

The reaction sequence is

$$H + NOCl → HCl + NO$$

followed by radiative emission from HNO$_2$. When [H] > [NOCl], unreacted H combines with NO to produce the HNO$_2$ → HNO + he red afterglow.\(^{(17)}\) When [NOCl] > [H], the glow is extinguished. To use this titration, one adds a metered flow of NOCl to an unknown flow of H while monitoring the HNO$_2$ emission. Equation 4 shows that $I/[NOCl]$ is proportional to [H]. Thus, in the calibration experiment, $I/[NOCl]$ added is also proportional to [H].

Note that [H] = [H]$_0$ - [NOCl]$_{added}$ where [H]$_0$ is the atomic hydrogen number density in the absence of added NOCl. Therefore

$$I = K([H]_0 - [NOCl])$$

A plot of $I/[NOCl]$ versus [NOCl] will be linear with a slope of $K$ and an intercept on the abscissa of $[H]_0$. With $K$ for our PMT/filter combination determined by this method, H atom number densities can be measured by adding known number densities of NO to the unknown H flow and monitoring the resultant HNO$_2$ chemiluminescence.

Although straightforward in principle, the NOCl calibration proved to be tedious with several subtle problems. Initial calibration plots were nonlinear with irreproducible $K$ values. This problem apparently results from wall reactions. Clyne and Stedman\(^{(18)}\) reported similar behavior on bare Pyrex walls. They postulated the following reaction sequence to explain this behavior:

H + NOCl → HCl + NO

H + NO + M → HNO$_2$ + M

H + HCl → H$_2$ + Cl

Cl + Cl → Cl$_2$

H + Cl$_2$ → HCl + Cl

The catalytic recombination of Cl on the wall forms Cl$_2$ which then consumes H via the rapid H + Cl$_2$ reaction. By treating their flow tube walls with phosphoric acid, which inhibits wall recombination of Cl, Clyne and Stedman's results became reproducible.

A section of our flow tube was uncoated Pyrex. This design permitted visual examination of chemiluminescence in the flow tube. Subsequent coating of this section with Teflon resulted in the calibration plots of $I/[NOCl]$ versus [NOCl] which were linear and which gave reproducible $K$'s. Although the NOCl titration technique proved to be more difficult to use than anticipated, the titrations performed in the Teflon-coated flow tube gave satisfactory results.

Figure 3 shows a typical plot of $I/[NOCl]$ as a function of added [NOCl] using the fully coated reactor. An average of five calibration runs at various conditions yielded a proportionality constant $K = 0.43 \times 10^{-7}$ A mTorr$^{-2}$ with a standard deviation of 15%. With a known $K$ one can add a known concentration of NO to the flow and determine [H] from $[H] = I_{HNO}/K[NOCl]$. One problem encountered was that the H atom production at a given microwave power and at a constant Ar/H$_2$ flow rate varied in time. Heating of the microwave cavity and discharge tube appears to have been the cause of this problem. The flow of compressed air which was forced through the cavity apparently provided insufficient cooling for uniform H atom production. Flowing the cooling air through an ice bath prior to introduction into the microwave cavity alleviated this difficulty. H atom production remained constant for at least a minute at any microwave power. Since only a few seconds was sufficient to measure both the NF(a→X) and HNO$_2$ emission intensities, this remedy was satisfactory. A further improvement might be realized using...
the design of Ding et al., who used a fluid as a coolant.

In practice, the microwave power was held fixed and [H] variations were obtained by changing the H₂ flow rate. The hydrogen dissociation efficiency, however, diminished as [H₂] increased. This fact and the previously described dependence of H atom production on the temperature of the microwave cavity make it imperative that [H] be measured for each H₂ flow. One cannot rely upon comparable conditions to give the same [HI.

**Results**

The rate equation for NF(a) decay in the flow tube is given by

\[
d[NF(a)]/dt = -(k₂[H] + k₄[NF(a)]
\]

where quenching of NF(a) by NF₂, HF, and undissociated NF₃ is neglected. The rate coefficient for NF(a) self-quenching is a matter of some current controversy. Koffend et al. saw no evidence of self-quenching in their experiments and concluded the rate coefficient for this process was less than \(10^{-13}\) cm³ molecule⁻¹ s⁻¹. Quiñones et al. on the other hand observed a decay at high [NF(a)] in their discharge-flow study which led them to assign a rate coefficient of \(2.2 \times 10^{-13}\) cm³ molecule⁻¹ s⁻¹ for this process. At the low number densities of NF(a) in these studies, \(\leq 10^{-12}\) molecules cm⁻³, self-quenching should be unimportant whether or not it is fast. No one has measured a rate coefficient for the reaction between ground-state NF and NF(a), but spin and angular momentum conservation rules indicate that the favored channel is endoergic. Koffend et al. report that the rate coefficient between NF(a) and NF₂ is slow, \(k = 2.7 \times 10^{-16}\) cm³ molecules⁻¹ s⁻¹, and Quiñones et al. measured a value of \(3.0 \times 10^{-15}\) cm³ molecules⁻¹ s⁻¹ for the quenching of NF(a) by HF (ν=0). Those two species, therefore, can be neglected safely. Vibrationally hot HF does quench NF(a) somewhat more efficiently, but the large number densities of H₂ in the reactor will quench out all HF vibrational energy in the upstream region of the flow reactor prior to the reaction zone. The rate coefficient for NF₃ quenching of NF(a) is unknown, but generally NF₃ is an inefficient electronic quencher. Experimentally, we keep the initial NF₃ concentration low (<\(10^{13}\) molecules cm⁻³) and constant for each run. Thus, even if some quenching by NF₃ or discharge-produced species were present, it will be independent of changes in [H]. Neglecting wall collisions, the integrated rate equation (under pseudo-first-order conditions, [H] >> [NF(a)]) becomes

\[
[NF(a)]/[NF(a)]₀ = e^{-k₂[M⁺(t/τ)]}
\]

where \(τ\) is the distance from the injector to the observation port and \(d\) is the bulk gas velocity in the flow tube. If the number density of H is much greater than that of NF(a), plots of ln [NF(a)] chemiluminescence intensity as a function of [H] (z/τ) yield \(k₄\), the desired rate coefficient. Because NF₃(a) is relatively inert to wall deactivation, it will have a planar radial number density gradient. The plug-flow approximation used here, therefore, is appropriate.

The [NF(a)] was monitored, therefore, as a function of added discharged H₂, holding all other flows constant. No detectable change in [NF(a)] was observed for any secondary H₂ flow without the discharge. Large changes (approximately an order of magnitude) could be observed when the secondary H₂ discharge was initiated. Typical H atom number densities were \(\geq 10^{11}\) atoms cm⁻³ while the undischarged [NF₃] which represents the maximum possible [NF(a)] was \(10^{12}-10^{13}\) molecules cm⁻³. Thus, the pseudo-first-

**Discussion**

Our experimental value, \((3.1 \pm 0.6) \times 10^{-13}\) cm³ molecule⁻¹ s⁻¹, agrees quite well with the estimate of Cheah et al. of \(2.5 \times 10^{-13}\) cm³ molecule⁻¹ s⁻¹. Their value is based upon computer modeling of temporal profiles of H in a flow containing H₂, H, and NF and carried a substantial uncertainty regarding the electronic state of NF involved in the reaction. Subsequent modeling by Cheah and Clyne of temporal profiles of N(²D), N(⁴S), and NF(a) resulted in estimated rate coefficients for reaction 2 of \(9 \times 10^{-13}\) cm³ molecule⁻¹ s⁻¹ assuming the bimolecular disproportionation of NF(a)

\[
NF(a) + NF(a) \rightarrow N₂ + 2F
\]
had a rate coefficient of $7 \times 10^{-11}$ and $4.5 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ assuming reaction 13 to be negligibly slow. As we have already pointed out, whether or not reaction 13 proceeds facilely is subject to some controversy. Even Quifiones et al.'s$^{21}$ value for this rate coefficient, however, is substantially lower than the upper limit used in Cheah and Clyne's model calculations, so we might tend to support their smaller value for $k_2$. Given that Cheah and Clyne's calibration of their resonance lamp used to determine $N(2D)$ number densities was indirect, their estimated value for $k_2$ of $(4-6) \times 10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ also agrees adequately with our findings. Our measurement is a direct determination and should be preferred.

Throughout these studies [NF(a)] was always independent of [H$_2$] added. No decrease in [NF(a)] could be seen even though sensitivity was more than adequate to see a 10% degradation. These observations establish an upper limit for H$_2$ quenching of NF(a) of $1 \times 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. This can be compared to an earlier measurement of D$_2$ quenching of NF(a) by Kwok et al.$^{21}$ who reported a value of $k < 7 \times 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, and the recent measurements of Quifiones et al.$^{21}$ who obtained $k = 6.4 \times 10^{-16}$ and $3.2 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for NF(a) quenching by H$_2$ and D$_2$, respectively.

Using vacuum-UV resonance fluorescence to monitor N(2D) and N(4S), we have observed initial formation only of N(2D), with N(4S) appearing only later in the reaction, presumably as a result of N(2D) quenching. Cheah and Clyne$^{21}$ made similar observations and suggested that the primary product channel was to make N(4D). Absolute photometric measurements we have made of NF(a), N(4D), and N$_2$(B) temporal profiles resulting from reactions 1 through 3, and which we shall report soon,$^{11}$ are fully consistent with a branching ratio for N(4D) formation in reaction 2 of unity. This is the result predicted by spin and orbital angular momentum correlation rules. 22

Given that N(4D) is a key precursor for N$_2$(A) formation via reaction 3, reaction 2 presents a kinetic bottleneck for this N$_2$(A) generation scheme. Due to its relatively small rate coefficient, large H and NF(a) concentrations will be required in a generator to produce enough N(4D) to drive reaction 3. This is further exacerbated by the reactivity of N(4D) with generator surfaces and with other generation species such as NF$_2$, NF, H$_2$, and HF. However, the small value of $k_2$ at room temperature suggests the presence of an energy barrier, such that either elevated temperature or modest vibrational excitation of the NF(a) might provide a means for accelerating the reaction rate substantially.

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Laser-Induced Fluorescence Spectroscopy of the B$^2\Pi$, A$^2\Delta$, and C$^2\Sigma^+$ States of the NS Radical

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Laser-induced fluorescence has been used to study the B$^2\Pi$, A$^2\Delta$, and C$^2\Sigma^+$ excited states of the NS free radical in a low-pressure discharge flow system. Excitation scans were recorded exciting $v' = 0-12$ in B, $v' = 0$ and 1 in A, and $v' = 0$ in C. Numerous perturbations appear in excitation scans to the B state through anomalous A-doublet splittings and line intensities. Fluorescence spectra have been recorded through $v'' = 26$ in X$^2\Pi$ and have been used to determine vibrational term values in the ground state. Vibrational band transition probabilities have been measured for 236 bands in the B-X system, 10 bands in A-X, and 5 in C-X. The electronic transition moment for the B-X system is constant with internuclear distance, while that for C-X decreases with increasing distance.

Introduction

The NS radical possesses a large number of excited electronic states in the energy region 30 000-45 000 cm$^{-1}$ above the ground X$^2\Pi$ state. These include both valence and Rydberg doublet states, as well as quartet states whose presence and spectroscopic constants have been inferred from perturbations of the doublets. This overall state structure has features in common with the more familiar, isolated NS molecule, although in NS the valence states lie significantly lower in energy.

These states in NS are readily accessible to detection by laser-induced fluorescence (LIF) using tunable lasers together with standard nonlinear frequency conversion techniques. The NS radical is thereby amenable to two types of useful studies. The first type is collisional energy transfer, both internal ($\nu_i, \Omega_i$) transfer within an electronic state, and state-specific quenching (total removal) and electronic-to-electronic transfer. For example, we have used the time dependence of LIF signals to investigate vibrational-level-specific total decay rates of the B$^2\Pi$ state. 1 The $\nu'$ dependence of the decay rate varied with collision partner in both direction (increasing or decreasing) and magnitude, indicating interesting dynamic effects tied to the structure of the collider. In similar experiments on higher lying vibrational levels of B$^2\Pi$, the effects of perturbations on the collision-free decay and on collisional removal by N$_2$ were studied.2 The many nearby electronically excited states in NS, having different electronic structure, and each accessible by laser excitation and fluorescence studies, make this radical a fertile ground for such collision studies.

The other type of study is the detection of NS in practical systems where it may play a chemical role. An example of this is the important area of combustion chemistry.3 The radical had not previously been considered in this context, but we recently detected it in simulated coal flames,4 that is, methane burning in oxygen with minor amounts (a few percent) of added NH$_3$ and H$_2$S. The detection was by LIF in the C-X system, and the absolute radical concentrations were deduced by using spectro-