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STATE-SPECIFIC ENERGY TRANSFER IN DIATOMIC RADICALS

August 1988

Final Report

By: David R. Crosley, Richard A. Copeland,
and Jay B. Jeffries

Prepared for:

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
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Building 410
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Quantum-state-specific collisional energy transfer has been studied in the N atoms, and the OH and NS diatomic radicals. Vibrational energy transfer (VET) in the $A^2\Sigma^+$ state of OH was found to depend on rotational level. Rotational energy transfer in A shows unusual propensities. The final vibrational level distribution following quenching of $A^2\Sigma^+$ is not governed by Franck-Condon considerations. VET in $X^2\Pi_i$ OH generally proceeds much faster than in A. $\Delta J = 1$ transfer is fastest among the spin-orbit components of the $3p^4D^o$ state of N. Quenching of $B^2\Pi$ NS varies with vibrational level differently depending on collider. The amount of $\Delta v = 2$ VET compared with $\Delta v = 1$ also depends on v and collider.

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CONTENTS

I INTRODUCTION

A. State-Specific Collisions

Many chemical and physical changes depend on the transfer of energy that occurs in an encounter between molecules. In recent years, new sophisticated experimental and theoretical techniques have addressed fundamental questions of energy transfer between individual quantum states in bimolecular collisions. Many processes are found to be state-specific, and the effects of different forms of energy are not equivalent. For example, some chemical reactions may be promoted more by vibrational than translational energy, or vice versa, and electronic state transfer may be more affected by rotation than by vibration.

Although some of these findings are readily understood in terms of simple pictures of collision dynamics, others are surprising and have not been explained. From a fundamental point of view, we do not know the regions on the potential surface that are responsible for different types of energy transfer. From a more applied standpoint, we are unable to predict details of energy transfer that might be needed to model the behavior of some practical system, outside the immediate regime of prior measurements.

Over the past three years, under support from the Directorate of Chemical and Atmospheric Sciences of the Air Force Office of Scientific Research, we have investigated energy transfer collisions of open-shell atoms and molecules on a state-specific basis. Lasers are used to select initial quantum states, and lasers or photon emission monitor final states after a collision. We choose species where we can simultaneously define several quantum states: rotational, spin and orbital angular momentum, vibration, electronic excitation, and orientation in both laboratory and molecular reference frames. By comparisons, and especially correlations, of simultaneous changes in two or more of these many quantum numbers, we obtain detailed insight into the collisional processes. Additionally, at least for the small hydrides and collision partners, the potential surfaces involved are amenable to realistic ab initio and approximate calculations.

B. Progress Summary

Several experiments were performed, most on the important and interesting OH radical. (These are described in more detail in Section II). We investigated the effect of rotational level J' on vibrational energy transfer (VET) and on electronic quenching of the $A^2\Sigma^+$ state of the OH radical. We found a strong dependence, which appears to sample the entrance region of the collision surface. The final-J distribution following VET samples the exit channel. Rotational energy transfer (RET) in the same state shows unexpected propensities, in particular a large amount of $\Delta J > 1$ transfer in collisions with He. The J' dependence, which is characteristic of both VET and total removal of the excited electronic state (quenching), can be interpreted in terms of an anisotropic potential. This concept, which we advocated qualitatively, has now been confirmed by independent ab initio results. The suprising magnitude of the $\Delta J > 1$ RET is also predicted by a similar theoretical calculation.

A subject of considerable interest and importance is the fate of the electronic energy when an excited state is quenched. This question has been studied in OH colliding with H_2O, using a two-laser pump-and-probe method. The results show that high vibrational (v) levels of OH are populated, contrary to the low-v levels that would correspond to previously assumed Franck-Condon-governed quenching collisions. In a different pump-probe experiment, VET and RET in ground electronic state ($X^2\Pi_i$) OH have been investigated. In the RET we are looking at correlation in the transfer among states with different rotation, spin-orbit, λ-doublet, and orientational quantum numbers. A crucial fundamental question concerning VET is the underlying cause of its faster rate in the A-state than in the X-state.

Fine structure transfer in the $3p^4D^o$ state of nitrogen atoms was studied in collisions with He. This system is also amenable to ab initio calculation for detailed comparison with these state-specific results. Individual J levels are populated following two-photon absorption of laser light, and the final states are monitored by wavelength-resolved fluorescence. The results show that $\Delta J = 1$ transfer is faster than $\Delta J = 2$ or 3 and that the m_J quantum number is not conserved in a J-changing collision.

C. Practical Significance

Our focus is on a fundamental understanding of the mechanism by which energy is transferred, in and between molecules in bimolecular collisions. Nonetheless, these results have practical importance as well, because of the many processes that rely on nonequilibrium energy transfer and reaction of gas-phase diatomic molecules.

An obvious and classic example is the search for new and powerful lasers, where energy transfer under different conditions is important in populating or depopulating crucial energy levels. In many cases, large computer models incorporating energy transfer rate coefficients are needed to assess new designs or to scale up to practical devices. These models often rely on parameterized descriptions of energy transfer (e.g., exponential gap laws) that are found lacking when examined on a state-specific basis. By addressing fundamental aspects of the collision phenomena, we hope to be able to place such models on a more sound basis, applicable over a wider range of untested conditions.

Other practical applications include the large variety of plasma processes that are likely to involve energy transfer in crucial steps. One example is the theoretically predicted billionfold enhancement of H_2 dissociative attachment with increased H_2 vibration, as needed for H^- production in powerful ion sources. High power switching may involve collisional redistribution, including excited state participation. The effects of deposition of energy by laser or particle beams in their passage through the atmosphere involve energy transfer. Nonequilibrium behavior in spark-initiated and shock-induced ignition (in turbines and energetic materials, respectively) necessarily incorporates the phenomenon.

Nonequilibrium energy transfer and reactions are also important in the emission of radiation from air heated by bow shock waves at high Mach numbers and altitudes above 50 km, where collisional relaxation is too slow to be complete. Diagnostic methods for trace species combustion, the atmosphere, and plasmas often rely on the emission of light, be it laser-based, collisionally generated, or chemiluminescent; in each case, state-specific energy transfer collision rates are needed to make the techniques quantitative. Emission of light in the upper atmosphere, e.g., Meinel bands of OH at 90 km leading to infrared background, involves collisional energy transfer between individual quantum states.

An area of renewed interest in which state-specific energy transfer and reactions of small diatomic molecules loom especially important is that of ultraviolet radiative emission from rocket plume exhausts. This problem, together with issues of fundamental interest, has been part of the selection of the proposed diatom-atom chemiluminescence and electronic-to-electronic transfer reactions. Ultraviolet detection of targets offers complementary advantages to operation in the infrared, including more sensitive detectors and a lower background. Of special importance is the much smaller spatial extent of the ultraviolet emission, located close to the exhaust port in contrast to the infrared radiation, which can extend over hundreds of meters or more. However, emission signatures in the ultraviolet region are not as easily characterized as those in the infrared because they arise from specific excited molecular species formed in the plumes by chemiluminescent reactions or energy transfer. These are nonthermal, nonequilibrium formation processes; energy transfer is also important in dictating the spectral distribution for a given emitter. Consequently, it is not surprising that ultraviolet signatures vary greatly with fuel and motor types, thrust, mixture ratio, and ambient atmospheric conditions. The ability to recognize the appropriate emission and therefore take advantage of this spectral region depends on an ability to understand the molecular mechanisms forming that emission.

An understanding of the participating state-specific reactions and energy transfer processes will permit the formulation of a soundly based computer model describing the phenomena over a large range of conditions. The reactions selected for study in the proposed project include some of the chemiluminescent and energy transfer processes suggested (though not proved) to be responsible for part of observed ultraviolet plume emission.

II RESEARCH PERFORMED

During the last 2-1/2 years, we have completed experiments on fine-structure transfer in nitrogen atoms, final states of OH quenching, and VET and RET in OH $A^2\Sigma^+$, energy transfer in OH $X^2\Pi_i$, and the collision dynamics of the NS free radical.

A. State-Specific Fine-Structure Transfer in Nitrogen Atoms

The $3p^4D^o$ state of nitrogen atoms has four separate fine-structure components, with total angular momentum J ranging from 1/2 to 7/2 and a total energy spread of 120 cm^{-1}. In these experiments, each individual J is excited by the laser, and fluorescence in the $3p^4D^o$-$3s^4P$ multiplet is resolved to provide state populations as a function of added He gas, furnishing state-specific cross sections.

The nitrogen atoms are formed in a low-pressure discharge; two-photon absorption[1] near 211 nm from the ground $^4S^o$ state elevates them to a specific J in $3p^4D^o$. The near infrared (870 nm) fluorescent emission is dispersed in a 0.35-m monochromator. A computer controls the wavelength scan and signal integration; long runs, up to two hours, are needed to capture a spectrum for these weak signals. The partial pressure of He is varied in the flow cell to alter the collision environment.

The spectra are fit to obtain populations of each fine-structure level for each initial J, using calculated line strengths. Polarization of the fluorescent emission is also measured and is accounted for in the analysis. These populations are then used to obtain state-to-state cross sections σ placed on an absolute basis by separate measurements of the radiative lifetime and quenching rates.[2]

The resulting σ are large, of the order of gas kinetic. Those for $\Delta J = 1$ are largest, but those for $\Delta J > 1$ are sizable, and the values drop for increasing ΔJ. There are decided propensities but no firm selection rules.

By monitoring the polarization of the fluorescence, we find that the m_J quantum number is not conserved in J-changing collisions between $J = 1/2$ and 3/2. This finding therefore questions the j_z-conserving approximation[3] used in theoretical descriptions of such collisions and provides results for comparison with more sophisticated close-coupled calculations, such as those performed for Mg-He.[4]

B. Final State of Quenching OH $A^2\Sigma^+$

Collisional quenching rates for electronically excited diatomics have often been measured, and OH $A^2\Sigma^+$ is one of the most extensively investigated. However, the fate of the removed electronic energy is seldom studied, and never for OH. We describe initial experiments performed to gain insight into the final-state distribution following quenching of this important and interesting hydride.

The OH is produced in a flowing discharge in H_2O vapor near 0.5 Torr, which serves as the OH source and collider species. One laser is used to pump $v' = 0$ of $A^2\Sigma^+$, which is then quenched by collisions in ~ 300 ns.[5] A second laser, time-delayed from the first, monitors the time evolution of populations in ground state v", using off-diagonal vibrational bands (e.g., 1, 4) in the A-X system.[6]

Thus far we have probed $v" = 1$, 2, and 4. A series of time-dependent populations is shown in Figure 1. Each signal rises and later falls, with characteristic times becoming faster as v" increases. The first feature shows that few if any molecules have been produced directly in these v" as a result of the quenching collision. This result is in contradiction to the view that this electronic-to-electronic transfer is governed by Franck-Condon overlap, which would yield 90:10:0 for ratios of populations in $v" = 0$, 1, and ≥ 2, respectively. Franck-Condon considerations appear important in e-to-e transfer in N_2^+ (Ref. 7) and CO^+ (Ref. 8), but not CN (Ref. 9). One theoretical treatment[10] suggests that Franck-Condon approximations should not be used, but these differences among molecules should provide important clues on this question.

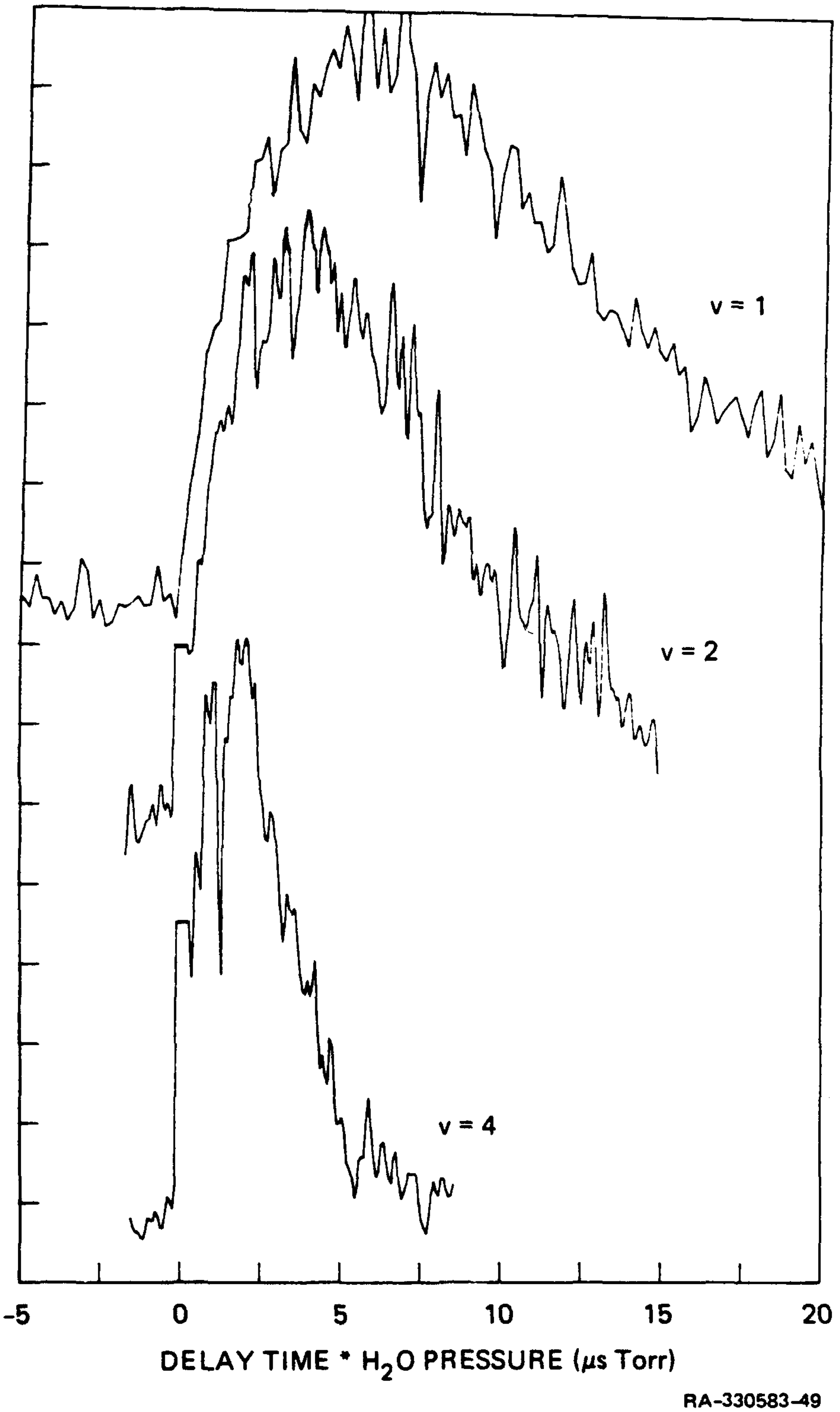

Figure 1. Time-dependent populations of vibrational levels v" = 1, 2, and 4 in OH $X^2\Pi_i$, following quenching of $A^2\Sigma^+$, v' = 0, by collisions with H_2O.

The second feature in Figure 1 is the time evolution of the populations. Each trace can be approximately represented by two exponentials, although the actual kinetic description is more complicated. The characteristic rates vary by a factor of 30, between v' = 4 filling and v' = 1 decay. A simple model involving only $\Delta v = 1$ transfer cannot fit these data; this suggests that multiquantum vibrational transfer is important in ground state OH relaxed by H_2O.

C. Vibrational Energy Transfer and Quenching in OH ($A^2\Sigma^+$, v' = 1)

These single-laser experiments use temporally and spectrally resolved laser-induced fluorescence (LIF) to measure both total removal rates (quenching plus VET) and VET alone from the v' = 1 level of excited OH, with several colliders. The apparatus is like that used for studying quenching of v' = 0[5], but with a spectrometer added; the OH is produced in a flow discharge in a differentially pumped cell. The total removal is faster than thermalization of rotational levels J', so the results are for the particular J' pumped by the laser.

The first result from these experiments with important mechanistic implications is the size of the total decay cross sections σ_D and comparison with quenching σ_Q for v' = 0. The σ_D range from 30 to 100 Å^2 for the eight colliders studied; such large values show that attractive forces are important. The colliders fall into three categories: (1) polar molecules (H_2O and NH_3), which quench efficiently but cause little VET; (2) CH_4, CO_2, and N_2O, which quench and cause VET with similar efficiency; (3) the colliders N_2, SF_6, and CF_4, which are efficient at VET but are poor quenchers. This result suggests that both VET and quenching occur on an attractive surface, forming a briefly lived collision complex. This suggestion was made earlier for quenching[5,11] and VET[12] separately, but it now appears that the same mechanism is responsible for both.

The second result is the J' dependence of σ_D. In going from N' = 0 to N' = 4 for the four colliders N_2, CO_2, CF_4 and SF_6, σ_D drops by 50%. This dependence has been observed for both σ_Q in v' = 0[5] and σ_{VET}.[12] Such behavior indicates collision dynamics governed by an entrance channel on an anisotropic attractive surface, whose efficiency is washed out by increasing rotation.[5,12] A recently calculated OH($A^2\Sigma^+$)-CO ab initio surface exhibits these very features.[13] Comparison among different colliders will indicate which regions of the surface are most important in determining the collision outcome.

The J distribution in the final v' = 0 level has also been measured by rotationally resolved fluorescence scans for N_2 collider. It may be described by a temperature hotter (750 K) than the gas temperature. The distribution appears independent of initial J in v' = 1. This result agrees with results seen earlier,[12] and because the OH loses all memory of its initial J, it indicates that this distribution samples the exit channel region on the potential surface.

D. Rotational Energy Transfer in OH ($A^2\Sigma^+$, v' = 1)

In these experiments, helium was used as the collider. Helium is poor at quenching and VET, but it can cause RET through R→T transfer, and it is an ideal candidate for the application of theories such as the infinite-order-sudden (IOS) model[14] or trajectory studies on realistic ab initio surfaces.[15] In these flow cell experiments, the laser populates an individual J in v' = 1, and rotationally resolved fluorescence spectra are taken. The spectra can be fit to obtain populations or fit directly to the rate constants from a model, for example, those in an IOS set.[15] Helium is a good choice of collider to test IOS, since it has a high relative velocity and its collisions are more sudden than for other colliders.

Spectra were taken pumping into the F_1 levels with J' = 1-1/2, 3-1/2, and 5-1/2. There is more rotational energy transfer for lower J than when exciting higher in the rotational manifold. Most intriguing is the result that collisions with $\Delta J \geq 2$ must be considered to have significant rates; the use of an IOS model with only $\Delta J = 1$ base rates provides a clearly inadequate description. This result is quite different from spectra taken in collisions with N_2.

Cross sections for rotational transfer in OH ($A^2\Sigma^+$) colliding with He have been calculated using a realistic ab initio surface.[15] These calculations show RET cross sections in which those for $\Delta J = 2$ are often greater than for $\Delta J = 1$, for this collider pair and certain ranges of initial J and collision energy. These experimental RET state-specific cross sections are thus at the level of detail to provide real tests of features of the interaction potential surface.

E. Rotational Energy Transfer in OH ($X^2\Pi_i$)

The objective of these experiments is to investigate RET and VET in ground state OH to answer two major questions: (1) How do collisional changes correlate for the several simultaneously observable quantum numbers in this open-shell diatomic? (2) How do RET and especially VET rates and mechanisms compare in ground and excited OH, for different colliders?

The experimental method is a two-laser pump-and-probe technique shown to be feasible for this purpose in an earlier preliminary experiment.[16] OH is produced in a water discharge, as in the final-states of quenching experiment. A tunable infrared (Raman-shifted dye) laser pumps OH ($v'' = 0$) to a specific level (rotational, spin-orbit fine structure, λ-doublet) in $v'' = 2$. An ultraviolet laser operating on an off-diagonal vibrational band in the A-X system is fired at a controlled time delay following the infrared pump. The laser is tuned to excite either the initially pumped level or other levels populated by collisional transfer. The time evolution of the population then furnishes the rates of energy transfer.

A new flow cell was constructed, and greatly improved laser, electronics, and computer control were installed.[16] An example of early RET data is shown in Figure 2. In this experiment, the $F_1(2)$ level in $v'' = 2$ is pumped with $R_1(1)$. The upper two traces show the decrease of population in $F_1(2)$, monitored by the $Q_1(2)$ line in the 1,2 band. The time scale of the top trace (a) is 0-9 μs after the infrared excitation, and the time scale for traces (b) through (d) is 240 nsec. The multiexponential decay evident in trace (a) is due first to filling the other λ-doublet component of this same rotational

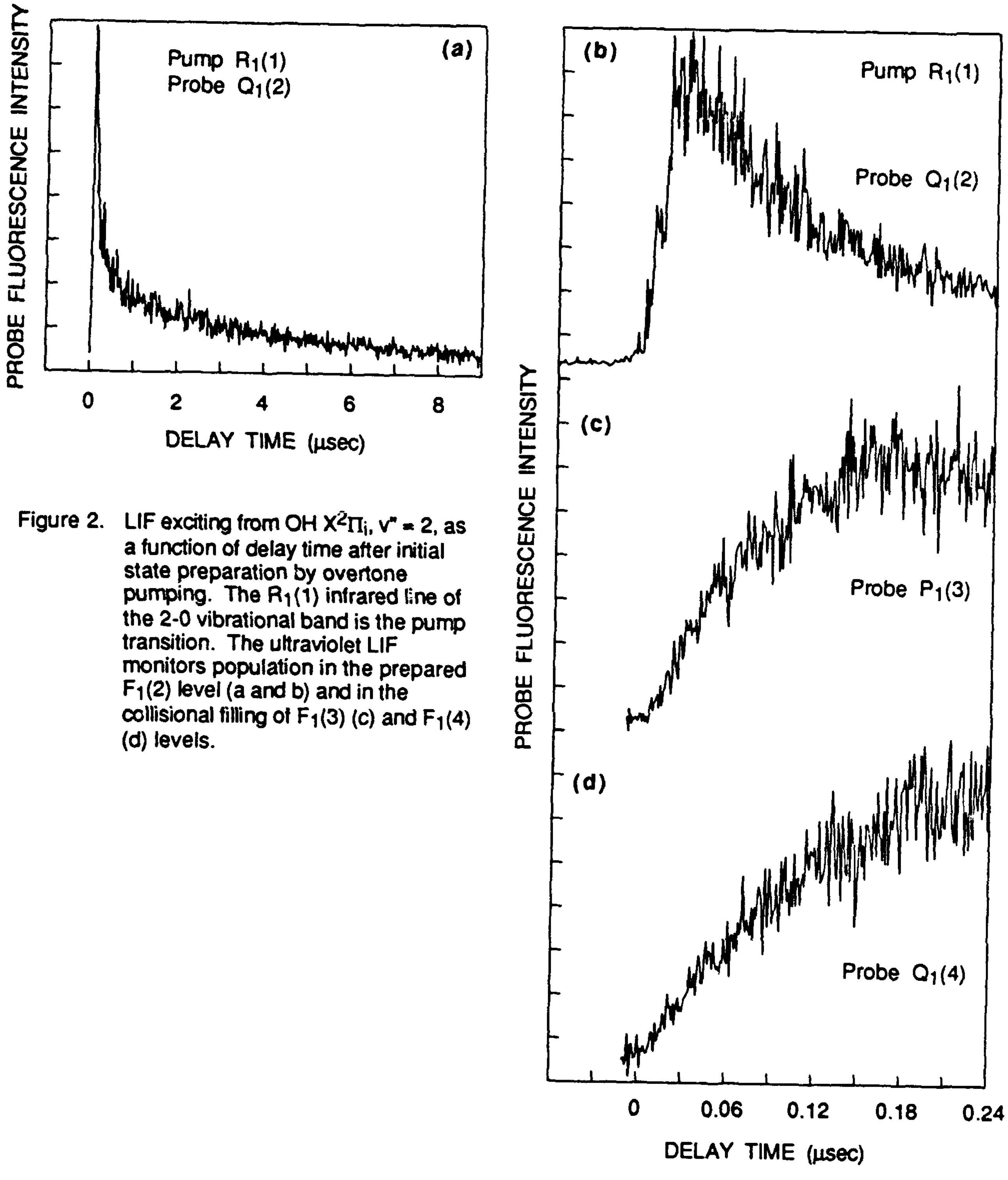

Figure 2. LIF exciting from OH $X^2\Pi_i$, v" = 2, as a function of delay time after initial state preparation by overtone pumping. The $R_1(1)$ infrared line of the 2-0 vibrational band is the pump transition. The ultraviolet LIF monitors population in the prepared $F_1(2)$ level (a and b) and in the collisional filling of $F_1(3)$ (c) and $F_1(4)$ (d) levels.

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level, then to transfer from the equilibrated λ-doublet pair into the remainder of rotational and spin-orbit levels; at the longest times shown, the signal decays owing to VET into v" = 1 and 0. Trace (c) shows the time evolution of the population in $F_1(3)$, which is populated by collisions from the initially excited $F_1(2)$. The bottom trace shows time evolution of population in $F_1(4)$, two rotational quanta above the initially excited $F_1(2)$. Note that the transfer to $F_1(4)$ is slower than to $F_1(3)$, and more data are required to determine if this time evolution can be fit by sequential $\Delta J = 1$ transfer, or if $\Delta J \geq 2$ transfer is also required. The signal levels are lower for these collisionally populated levels but are clearly adequate for state-to-state cross section measurements.

Preliminary runs have been made on He as a collision partner. Accurate theoretical results, potential energy surfaces, and trajectory calculations are possible for this small species together with OH. Most of the work has been a demonstration of the feasibility of performing RET studies with He under the conditions where the flow cell is operable (~0.05 to 10 Torr). At the lowest attainable pressures and delay times, we appear to be in a reasonable single collision limit. It is not yet obvious whether measurements on each excitation and a delay time sweep (as in Figure 2) or excitation scans at discrete delay times (as was done in Ref. 16) will be the better method for data analysis. It does appear that, in contrast to the results on $A^2\Sigma^+$ OH, $\Delta J = 1$ transfer is faster than $\Delta J = 2$ in $X^2\Pi_i$ OH.

F. Vibrational Energy Transfer in OH ($X^2\Pi_i$)

The same apparatus was used for studies of VET in the OH ground state. Here, much longer delay times were used, with measurements after the OH had attained rotational thermalization within v = 2. An example is shown in Figure 3. The sharp spike in the upper panel is the formation and relaxation of the initially pumped level; the slower decay is VET due to collisions with N_2. In the lower panel, the decay of a different rotational level (initially populated by RET from the pumped level) is shown. The VET decay time is the same in each case. Figure 4 shows a plot of decay constants vs. pressure for three different colliders. From the slope of this plot, we obtain the rate constant for vibrational relaxation of v = 2.

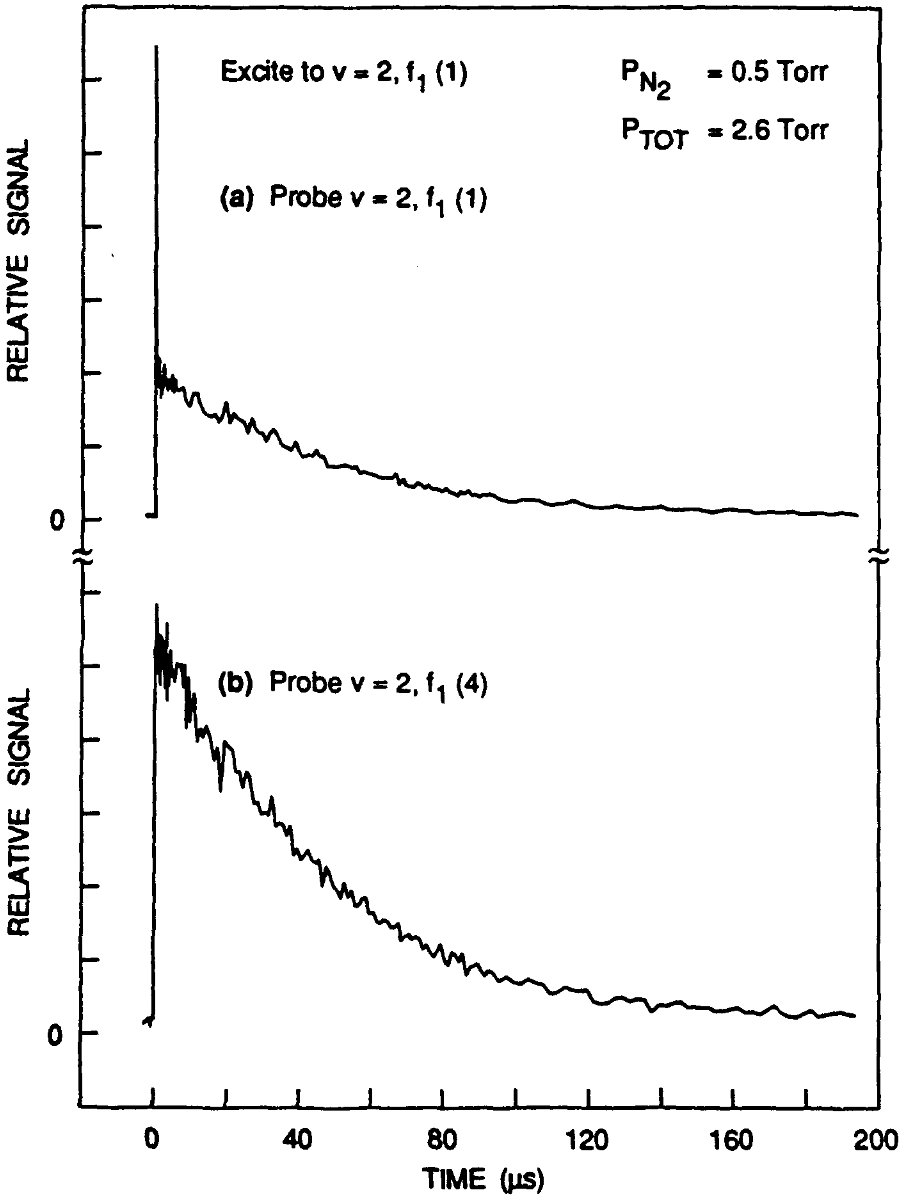

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Figure 3. Probe LIF signal from v = 2 in OH (X) vs. time delay after excitation of OH (X) v = 2, N = 1.

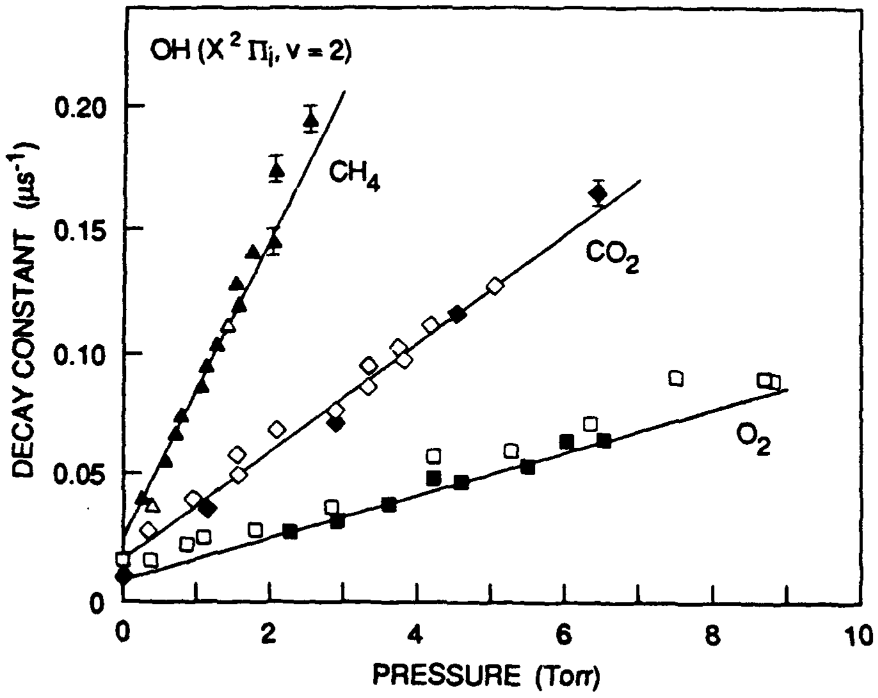

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Figure 4. Dependence of the v = 2 decay constant on the partial pressure of methane, carbon dioxide, and oxygen. The solid points are taken with helium carrier gas, and the open points with argon.

Rate constants and cross sections were measured for several colliders. The polar molecule NH_3 is a very rapid relaxer, with a cross section of 14 $Å^2$. Cross sections for the colliders CH_4, CO_2, N_2O, and O_2 were less than 0.2 $Å^2$ and fit well on an energy defect plot (that for NH_3 is 30 times larger than expected from the plot). Only upper limits have been deduced thus far for H_2 and N_2, much smaller than expected from an energy defect picture. The ammonia cross section is similar to that measured for $v = 1 \rightarrow 0$ transfer in OH $A^2\Sigma^+$; however, those for the other colliders are 100 to 1000 times smaller than in that excited state.

In one experiment, using NH_3 collider, the probe laser was tuned to detect $v = 1$, which is populated by VET from $v = 2$. The relative signal sizes indicate that about half the removal from $v = 2$ is via this $\Delta v = 1$ route ($\Delta v = 2$ and reaction are the other possible channels). Preliminary analysis indicates that $v = 1$ relaxes with about a quarter the rate of $v = 2$.

G. Quenching of NS $B^2\Pi$

The nitrogen sulfide free radical has two heavy atoms like the isovalent NO molecule. However, in contrast with NO, NS in the ground state has a large permanent dipole moment of 1.8D,[17] similar in magnitude to those of the hydride radicals OH, CH, and NH. Thus, collision studies with NS provide data to compare to both the hydrides and NO. In addition, NS in $B^2\Pi$ has several nearby excited electronic states. Perturbations by the $a^4\Pi$, $b^4\Sigma^-$, and $B'^2\Sigma^+$ have been catalogued by Jenouvrier and Pascat.[18] We measured the collisional removal and vibrational transfer rate constants for a series of vibrational levels of NS ($B^2\Pi$). The perturbed $v' = 3$ and 8 and the unperturbed $v' = 4$, 5, and 6 were studied in detail.

NS is produced from gas phase reactions in a low pressure discharge flow reactor. Helium with a few percent of added nitrogen at a pressure near 2 Torr flows through a microwave discharge to produce active nitrogen. A trace of $SC\ell_2$ is added downstream of the discharge, and NS is produced from subsequent chemical reactions. A specific rotational and vibrational level of the $B^2\Pi$ state is excited by the frequency doubled light from an excimer pumped dye laser. The total fluorescence is monitored with a filtered photomultiplier and the wavelength resolved fluorescence is detected through a monochromator. With the wavelength resolution adjusted to pass the light from an entire vibrational band, the LIF signal is time resolved. From the unperturbed levels, this signal is well described by a single exponential. Collider gas is added, and the pressure dependence of the decay constant from each single exponential fit provides the total removal rate constant for a given v level of $B^2\Pi$.

The measured removal rate constants are given in Table 1 (data on v' = 0 and 1 are from Ref. 19). The vibrational level dependence of the removal rate constants depends on collider. For CO_2, N_2O, SF_6, and N_2 as collision partners, the magnitude of the removal rate constants oscillates with vibrational level; there are minima at v' = 0, 4, and 6, and the fastest removal rate is from v' = 1. For O_2, H_2, He, and Ar the removal rate constants increase nearly monotonically with v'.

Vibrational relaxation rate constants in $B^2\Pi$ are obtained from the wavelength resolved LIF spectra. The wavelength resolution is increased to 0.5 nm from the 4 nm used for the time-resolved removal rate data where an entire band is collected, and the fluorescence is time integrated with a boxcar averager. The wavelength-resolved LIF spectra after exciting v' = 7 with and without CO_2 collider are shown in Figure 5. The vibrational relaxation within $B^2\Pi$ by the CO_2 is indicated by the appearance of fluorescence from v' = 6, 5, and 4. Both $\Delta v = 1$ cascade and direct $\Delta v = 2$ pathways are observed. From the ratio of the fluorescence intensities and the band emission strengths,[20] the ratio of populations in the different v levels is obtained. From these population ratios and the total removal rate constants, the vibrational relaxation rate constant is derived. A preliminary subset of the relaxation rate constants is presented in Table 2. Note that all the vibrational relaxation rate constants increase with v, and there is significant $\Delta v = 2$ transfer. Analysis of the relaxation from v' = 8, the $\Delta v = 2$ pathway for v' = 6, 7, and 8, and the data for He, Ar, N_2, O_2, and H_2 are not yet complete. Preliminary analysis shows these colliders are all

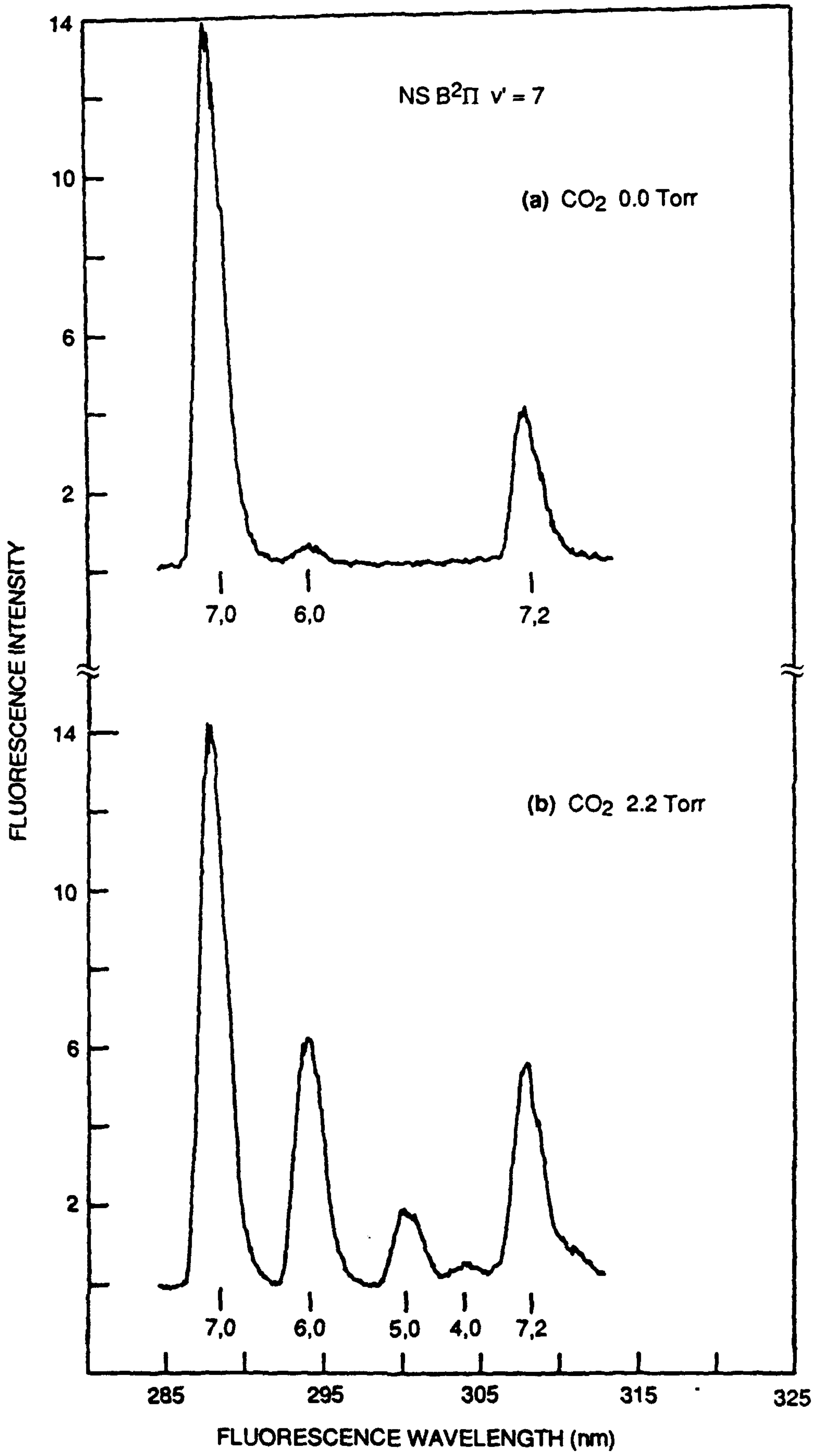

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Figure 5. Wavelength-resolved fluorescence following excitation to v' = 7 with and without added CO_2 collider.

Table 1

TOTAL REMOVAL RATE CONSTANTS FOR NS ($B^2\Pi$)

($10^{-11} cm^3 s^{-1}$)

	v'=0	v'=1	v'=4	v'=5	v'=6	v'=7	v'=8
CO_2		9.1	2.1	3.6	2.8	3.1	5.6
N_2O	4.7	8.2	1.3	2.6	1.9	2.0	
SF_6	0.9	3.1	0.9	1.8	1.5	2.2	
N_2	0.9	2.0	0.1	0.9	0.3	0.6	2.6
O_2	1.0	2.0	1.6	3.2	3.9	5.4	7.6
H_2		1.1	0.9	1.8	1.6	2.0	
He	0.04	0.1	0.3	0.3	0.2	0.3	0.1
Ar			0.07	0.5	0.2	0.4	

Table 2.

VIBRATIONAL RELAXATION RATE CONSTANTS FOR NS ($B^2\Pi$)

($10^{-11} cm^3 s^{-1}$)

	$\Delta v=1$				$\Delta v=2$
	$k_{4\rightarrow3}$	$k_{5\rightarrow4}$	$k_{6\rightarrow5}$	$k_{7\rightarrow6}$	$k_{5\rightarrow3}$
He		0.03	0.02	0.02	
H_2	0.5	1.0	1.3	1.3	
CO_2	0.6	1.3	1.6	2.1	0.6
N_2O	0.4	0.5	0.7	0.8	0.3
SF_6	0.4	0.9	1.1	1.2	0.4

inefficient, $<10^{-12}$ cm^3s^{-1}, at vibrational relaxation. Note that the vibrational relaxation for all the colliders in Table 2 is a significant fraction (~30%) of the total collisional removal shown in Table 1.

The v' = 8 level of $B^2\Pi$ is perturbed by $B'^2\Sigma^+$. If the B' state is excited, electronic-to-electonic state energy transfer is observed to the B state. We excited the B' state and observed the time-resolved B state fluorescence. The data are described by a double exponential where the rise is the energy transfer and the decay is the removal from the $B^2\Pi$. The rate constant for this transfer with N_2 is ~ $3 \times 10^{-10} cm^3s^{-1}$, which is approximately ten times faster than the collisional removal.

III PUBLICATIONS AND CONFERENCE PRESENTATIONS

The following publications have been supported by this contract:

1. R. A. Copeland, D. R. Crosley, and J. B. Jeffries, "State-Specific Collision Dynamics of OH Radicals and N Atoms," in Advances in Laser Science-I, W. C. Stwalley and M. Lapp, Eds., AIP Conference Proceedings 146, 545 (1986).

2. D. R. Crosley and R. A. Copeland, "Collisional Quenching and Energy Transfer in OH," in Laser Applications to Chemical Dynamics, M. A. El-Sayed, Ed., Proceedings of the Society of Photoinstrumentation Engineers 742, 6 (1987).

3. R. A. Copeland, M. L. Wise, and D. R. Crosley, "Vibrational Energy Transfer and Quenching of OH($A^2\Sigma^+$, v = 1)," J. Phys. Chem., in press.

4. K. J. Rensberger, J. B. Jeffries, and D. R. Crosley, "Vibrational Relaxation of OH($X^2\Pi_i$, v = 2)," submitted to J. Chem. Phys.

The following invited conference presentations have been partially supported by this contract:

1. R. A. Copeland and D. R. Crosley, "State-Specfic Collision Dynamics of the OH Radical," First International Laser Science Conference, Dallas, Texas, November 1985 [Bull. Amer. Phys. Soc. 30, 1851 (1985)].

2. D. R. Crosley, "Laser-Induced Fluorescence Measurement of Free Radical Intermediates," XVII Informal Conference on Photochemistry, Boulder, Colorado, June 1986.

3. R. A. Copeland and D. R. Crosley, "Collision Dynamics of the OH Radical," 192nd American Chemical Society National Meeting, Anaheim, California, September 1986.

4. D. R. Crosley and R. A. Copeland, "Collisional Quenching and Energy Transfer in OH," Society of Photoinstrumentation Engineers Meeting, Anaheim, California, January 1987.

5. D. R. Crosley, "State Selectivity in Light Emission from Flames," NATO Advanced Research Workshop on Selectivity in Chemical Reactions, Bowness-on-Windemere, England, September 1987.

6. D. R. Crosley, "Laser Detection of Reactive Intermediates in Combustion," Workshop on Processes in Premixed Gas Combustion Systems, Ein Gedi, Israel, February 1988.

7. D. R. Crosley, "Laser-Induced Fluorescence Measurements of Free Radical Intermediates," Materials Research Society Symposium, Reno, Nevada, April 1988.

8. D. R. Crosley, K. J. Rensberger, and J. B. Jeffries, "Vibrational and Rotational Energy Transfer in $X^2\Pi_i$ OH," Fourth International Laser Science Conference, Atlanta, Georgia, October 1988.

The following contributed conference presentations have been supported by this contract:

1. J. B. Jeffries, R. A. Copeland, and D. R. Crosley, "Collisions of the $2s^22p^23p$ $^4D_J{}^o$ State of Nitrogen Atoms," 191st American Chemical Society National Meeting, New York, April 1986.

2. R. A. Copeland, J. B. Jeffries, and D. R. Crosley, "Collision Dynamics of the $^4D^o$ Nitrogen Atom," Joint Meeting of the Division of Atomic, Molecular, and Optical Physics and the Division of Chemical Physics of the American Physical Society, Eugene, Oregon, June 1986 [Bull. Amer. Phys. Soc. 31, 939 (1986)].

3. J. B. Jeffries, R. A. Copeland, A. P. Hickman, and D. R. Crosley, "Collisions of Nitrogen Atoms in the 3p $^4D^o$ State," Spring Meeting of the American Physical Society, New York, March 1987 [Bull. Amer. Phys. Soc. 32, 736 (1987)].

4. R. A. Copeland, M. L. Wise, and D. R. Crosley, "Rotational Level Variation of Vibrational Energy Transfer in OH($A^2\Sigma^+$, $v' = 1$)," Conference on the Dynamics of Molecular Collisions, Wheeling, West Virginia, July 1987.

5. R. A. Copeland and D. R. Crosley, "Relaxation Rates and Pathways of Vibrationally Excited OH in $A^2\Sigma^+$ and $X^2\Pi_i$," 10th International Conference on Molecular Energy Transfer, Emmetten, Switzerland, August 1987.

6. K. J. Rensberger, J. B. Jeffries, and D. R. Crosley, "Vibrational Relaxation of OH ($X^2\Pi_i$, $v = 2$)," Twenty-Second Symposium (International) on Combustion, Seattle, Washington, August 1988.

7. K. J. Rensberger, J. B. Jeffries, and D. R. Crosley, "Vibrational Relaxation of OH ($X^2\Pi_i$, $v = 2$)," American Chemical Society Meeting, Los Angeles, California, September 1988.

8. I. J. Wysong, J. B. Jeffries, and D. R. Crosley, "Collisional Quenching and Energy Transfer of NS $B^2\Pi$," Fourth International Laser Science Conference, Atlanta, Georgia, October 1988.

The contract has also supported two contributed papers at the Gordon Conference on Atomic and Molecular Interactions, Plymouth, New Hampshire, August 1988.

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