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NO$_2$ PHOTODISSOCIATION DYNAMICS

Final Report

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The studies carried out under the present contract have all involved investigations of the photophysics and photochemistry of two nitrogen oxide molecules, NO and NO_2. As well as being intrinsically interesting, these molecules are important from the point of view of atmospheric chemistry, and the NO_2 molecule is a leading candidate as the emitting molecule that has been observed in the space shuttle glow. Major findings of these studies include the following observations: (1) Multiphoton dissociation of NO_2 by green light produces highly excited products, specifically, highly vibrationally excited O_2 and NO, and O(^{1}S). (2) Two-photon absorption of 268-280 nm radiation by NO results in production of the first excited state of the N-atom, N(^{2}D), an atmospherically important species that is difficult to produce by any other photodissociative technique. (3) the N(^{2}D) yield for two-photon absorption in NO is an effective probe for studying predissociative effects and identifying exit channels for Rydberg state decomposition. (4) the radiative lifetimes of vibrationally excited levels in the NO($B^2\Pi$) state have been accurately determined for the first time. These radiative lifetimes are found to be in good agreement with the most recent calculations and are compatible with earlier absorption studies, and the rotational and vibrational levels exhibit collisional behavior that relates to the placement of the levels of neighboring dark states. In addition, review articles have been prepared concerning the current state of knowledge of spacecraft and shuttle glow.

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INTRODUCTION

The molecules NO and NO_2, incorporating as they do the principal components of the atmosphere, are of importance in a variety of different environments. They are products of combustion and thus, their control is of concern, and their photochemistry is part of the overall chemistry of air pollution. Recent studies relating to the Antarctic ozone hole have demonstrated that their chemistry is atmospherically important on surfaces as well as homogeneously, and the catalytic destruction of ozone by odd nitrogen and other species is a subject that is again being brought to the fore not only because of ground-based pollution but also as a result of renewed interest in construction of a fleet of supersonic aircraft.

In recent years, it has been observed that spacecraft in low earth orbit are surrounded by a glowing halo, which has been shown to be due to interaction between the surfaces and the incoming particle flux, which bombards the vehicles at their orbital velocities, 8 km/s. This corresponds to 5 eV for the predominant species, O-atoms, and 9 eV for molecular nitrogen. Spectroscopic observations on the glow in the visible spectral region are most consistent with an identification of electronically excited NO_2, produced in a manner that involves fast particle interaction with the surfaces. There are other candidates for the glow in other spectral regions -- electronically excited nitrogen in the vacuum uv, and vibrationally excited OH in the infrared -- but the visible glow on the shuttle has been the most extensively investigated, and there is no molecule with a better claim to being the emitter than NO_2.

The studies carried out under this program have each involved different aspects of the photophysics and photochemistry of NO and NO_2. There have been four sets of laboratory measurements, involving various studies of NO_2 and NO photodissociation, and concomitant investigations of predissociative effects, transition probabilities, product yields, energy transfer, Rydberg state spectroscopy, production of highly vibrationally excited molecules, and development of new techniques for producing and detecting metastable atoms. In addition, the subject of spacecraft glow has been addressed in two review articles incorporating the most current information. Finally, two extensive papers on surface recombination of oxygen atoms and on surface destruction of excited oxygen molecules will be published, the work having been funded by an earlier AFOSR contract.

RESULTS

During the contract period, eight papers have been published or are in press; two of these are holdovers from the previous AFOSR contract. Summaries of the six studies from the present AFOSR contract follow.

1. "Multiphoton Dissociation in NO_2 at 532 nm and the Generation of Vibrationally Excited NO and O_2."

In this study, we followed up on a set of observations originally made by Tanaka and co-workers,[1] to the effect that focussed 500-550 nm radiation caused NO_2 to dissociate, producing highly vibrationally excited ground state O_2 with levels up to $v = 24$. They had proposed that the most likely source of the O_2 was unimolecular decomposition of highly excited NO_2 that had absorbed four photons of the laser radiation.

This source seemed improbable to us, and we felt a more likely explanation was that there was a reactive source of O_2(vib) in which multiphoton dissociation of NO_2 generated an excited oxygen atom, $O(^1D)$ or $O(^1S)$, which then reacted very exothermically with NO_2. Furthermore, it seemed reasonable to expect that the initial dissociation would lead to vibrationally excited NO, which had not been reported by Tanaka et al.[1]

We established that this reasoning was valid: vibrationally excited NO was indeed produced, and we found the pressure regimes favoring NO(vib) and O_2(vib) production to be different, the O_2(vib) appearing at higher pressures. In the meantime, Tanaka and co-workers[2] had changed their opinion of the reaction mechanism and in a second paper had proposed, on the basis of energetic considerations, that the O_2(vib) source was the reaction of $O(^1D)$ and NO_2.

We were able to demonstrate that such was *not* the case, by competitive quenching of $O(^1D)$ by NO_2 and N_2. In an excess of N_2, the O_2(vib) production rate should be strongly reduced if the source is $O(^1D) + NO_2$, since N_2 is an efficient $O(^1D)$ quencher. We observed negligible reduction of O_2(vib) production under these circumstances, from which we concluded that the $O(^1S) + NO_2$ reaction is the most likely O_2(vib) source. Subsequently, Tanaka and co-workers published yet a third paper,[3] which concurred with our reasoning. The important practical conclusions from this work are that with basic second harmonic Nd:YAG laser radiation at 532 nm, NO_2 is a potent source of three highly excited species, O_2(vib), NO(vib), and O(^{1}S).

2. "N(^{2}D) Production by Two-Photon NO Photodissociation."

In the course of studying the detection of the N(^{2}D) atom by multiphoton ionization,[4-6] we showed that two-photon dissociation of NO in the 268-280 nm spectral region was an efficient way of generating N(^{2}D). This atom is aeronomically important, and the only previously known photolytic source was vuv N_2O dissociation, which is an experimentally inconvenient system to use.

In the first of two papers on this topic we demonstrated how to measure the yield of N(^{2}D) by an overall five-photon scheme using two photons to dissociate the NO into an N(^{2}D) channel and three photons to ionize the N(^{2}D). The N(^{2}D) yield was shown to be quite variable, the variability reflecting the spectroscopy of the two-photon NO state, its predissociative lifetime, and the particular dissociation channel.

3. "N(^{2}D) Production from Predissociation of ns and nd Rydberg Levels in NO."

In the second paper on this topic, we identified the states in the 268-280 nm two-photon region that were predissociating to NO. Each was either an ns or nd Rydberg state, as expected for two-photon excitation, but interesting differences were found in the relative ionization and predissociation yields in each state and even sub-state. Although the work has concentrated only on the N(^{2}D) yields, it is clear that a lot can be learned by a complete characterization of the dissociation channels, of which there are three below the NO ionization limit : N(^{2}D) + O(^{3}P), N(^{4}S) + O(^{1}D), and N(^{4}S) + O(^{3}P). The same multiphoton ionization technique can be used to investigate each atom, and the excitation wavelengths for the relevant 2+1 processes are all within the 200-300 nm region. Extension of the technique to other molecules is obviously a possibility, and the resultant new dynamics dimension of multiphoton ionization spectroscopic studies should be generally utilized.

4. "Some Views on the Interpretation of Spacecraft Glows."

The Vehicle-Environment Interaction Workshop was held at Johns Hopkins University in February, 1989. Dr. Slanger was asked to give a review paper on the current status of the spectroscopic identification of spacecraft glows, which will appear in the proceedings of the meeting and is included as an appendix to this report.

5. "The Vehicle-Environment Interaction Workshop."

In addition to the above presentation, Dr. Slanger was asked to write a summary of the meeting, for publication as the cover story in the Sept. 26, 1989 issue of EOS. This summary is also included as an appendix.

6. "The Radiative Lifetime of the $B^2\Pi_r$ State of NO for v = 0-6."

This paper describes an extensive study of the NO($B^2\Pi$) radiative lifetime of the vibrational levels lying below the first dissociation threshold. The most significant conclusion is that these lifetimes, for a very important state of NO, have not previously been measured with any accuracy. Our results show that currently accepted values for the v = 0-6 range are inaccurate by factors of 1.5-3, the true transition strengths being stronger by these factors. The new values are being used to guide the extensive theoretical calculations currently being made by Langhoff and co-workers at NASA Ames, who have also concluded that the earlier experimental data were in error. They are refining their calculations to reflect the very strong coupling between the $B^2\Pi$ and $C^2\Pi$ states that accounts for the shortening in the observed lifetimes as these potentials approach each other.

With the aid of Langhoff's calculations, we have been able to show that our lifetime determinations are quite consistent with the measurements of absorption band strengths presented by Nicholls and co-workers in the early 1970s.[7,8] These values could not be converted into radiative lifetimes at the time, because of uncertainties about the form of the transition moment for the B-X system.

Although the lifetimes show a monotonic decrease with increasing vibrational level, the quenching behavior of the levels indicates that collisional coupling between the $B^2\Pi$ state and nearby dark states, either the ground state or the $a^4\Pi$ state, is quite variable, with the v = 0, 3, and 6 levels being quenched considerably faster than v = 1, 2, 4, and 5. Also of considerable interest is that in the most complicated level, v = 0 (as evidenced by its bi-exponential quenching behavior), individual rotational levels show variable quenching rates, although zero-pressure lifetimes are invariant. Such behavior is unexpected and is quite unusual for a diatomic non-hydride molecule. Ultimately, these observations will provide information concerning the positioning of the rotational energy levels of the coupling state; these energy levels are otherwise unavailable, since the B(0) level is isoenergetic with X(33) and a(8), neither of which is spectroscopically known. A preprint of this work is included in the appendices.

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PERSONNEL

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G. E. Gadd
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PUBLICATIONS PRODUCED WITH AFOSR SUPPORT

1. L. E. Jusinski, R. L. Sharpless, and T. G. Slanger, "Multiphoton Dissociation in NO_2 at 532 nm and the Generation of Vibrationally Excited NO and O_2," J. Chem. Phys. **86**, 5509 (1987).

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Appendix A

SOME VIEWS ON THE INTERPRETATION OF SPACECRAFT GLOWS

SOME VIEWS ON THE INTERPRETATION OF SPACECRAFT GLOWS

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ABSTRACT

Present indications concerning the identification of spacecraft glows are that different vehicles exhibit different glows. The spectrum of the shuttle surface glow is reasonably consistent with identification of the emitting molecule as NO_2, which is known to be produced in its ground state by the action of fast atmospheric particles on shuttle surfaces. The AE and DE satellites, on the other hand, observe a glow that may be associated with the OH molecule, and ground-based infrared observations of the shuttle indicate the presence of an OH wake. Observations in the far UV show intense emission from yet another molecule, N_2. The correlation between the space shuttle orientation and the areas exhibiting glow indicate that emission only originates from surfaces that are directly bombarded by the 5-10 eV particles of the incoming atmosphere. Neither scattered particles nor gas phase excitation contribute significantly to the observed emission. The glow associated with the thruster firings has not been spectrally analyzed, and it is not yet possible to say to what extent the shuttle glow is related to the residuum of the thruster effluents.

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INTRODUCTION

Since the glowing halo surrounding the space shuttle was first photographed, in 1982, there has been considerable interest, both scientific and public, in this phenomenon. Although seven years have passed since these initial observations, experiments to elucidate the source of this radiation have been quite limited. As a result, there has been considerable speculation concerning spectral identifications and mechanisms for excited state production. In this review of some of these issues, the present status of our understanding will be presented, biased to some extent by the author's views, and existing ambiguities in interpretation will be discussed. At the current level of our knowledge, there are more questions than answers.

The observation of glows associated with space vehicles is not new, and predates by a number of years the first reports of the glows recorded on film by the crew of STS-3 in 1982.[1] There are reports from rocket flights as long ago as 1957 in which extraneous emissions introduced by the rocket itself were noted,[2] and such observations have been made frequently in the intervening years, sometimes involving wake emissions, sometimes ram.[3-5] With the advent of the space shuttle and human observers, the documentation of these glows has improved, but there were Russian reports of satellite glows in the 1960's and 1970's, which were generally ignored by Western scientists.[6]

The data from the AE satellite[7] firmly established that there *is* a glow associated with satellites at orbital altitudes much higher than usual rocket apogees, that the intensity of the glow is altitude dependent, and appears to correlate with the O-atom density, and that the glow extends throughout the visible region of the spectrum but increases towards the red.

Subsequent measurements from the DE satellite[8] showed, with the aid of Fabry-Perot optics, that there appears to be some structure to the spectrum, and a case was made that particular rovibrational lines of OH, in the Meinel band system, could be distinguished. This is in line with the view that OH is a reasonable candidate for one of the emitting species.[9]

After the STS-3 observations, a number of camera studies were conducted by crew members of later missions.[10-12] It was established that the glow was strongest in the ram direction, that it was altitude, surface, and temperature dependent, and that the visible spectrum was continuous, peaking towards the red. This spectrum was attributed to NO_2, being similar to the so-called air afterglow, although shifted towards longer wavelengths.

With the implication that nitrogen and oxygen hitting the surface at the 8 km/s orbital velocity are responsible for the formation of the emitting molecule, possible mechanisms were investigated. Relevant to this question is the observation that N_2 LBH emission was detected at night from the S3-4 satellite.[13] Attempts were first made to find an LBH source in the nightglow, but since the emitting N_2 state could not be made from recombining N-atoms, it was finally realized that the source of the emission was the satellite surface.[14] Particularly interesting is the fact that the detectors on this satellite are nadir-viewing, which is to say that the glow is detected at 90 degrees from the ram direction, a quite unfavorable configuration. Clearly, intensities on the ram surfaces can be expected to be far higher than were observed. From the altitude dependence of the glow, a correlation with the cube of the N_2 density was obtained.

For military applications, the visibility of space vehicles is naturally of great concern. Ground-based tracking facilities have been used to detect the shuttle overhead.[15] IR observations in the 1-2 μm region have shown indications of an intense glow cloud enveloping the shuttle during the early parts of a mission,[16] and the spectra are consistent with OH as a principal emitter.[17]

DISCUSSION

Spacecraft glow is a collisional phenomenon that is a consequence of the velocity of the vehicle with respect to the quasi-stationary atmospheric atoms and molecules. In low earth orbit (LEO), the spacecraft velocity is 7.8 km/s, whereas the average velocity of an oxygen atom at 300 K is 0.55 km/s. The collisional energy is therefore mass dependent, and for the two most common atmospheric components at 200-300 km altitudes, O-atoms and N_2, the relative collisional energy is 5 ev and 9 eV, respectively. These energies are much higher than those encountered on rocket flights. For example, in a recent report on ram emission associated with a rocket having a very high apogee of 500 km,[4] the O-atom collisional energy at 90 km is only 0.6 eV.

In spite of these high energies in LEO, the potential energy transfer to the surface is insufficient to cause significant heating. At 130 km, the available energy is 0.5 watts/cm^2, and the shuttle skin shows little sign of frictional heating. Thus, spacecraft glows are unrelated to blackbody radiation.

The paper published by Heppner and Meredith[2] in 1958 is of historical interest not only because it appears to be the first evidence that rockets can interact with the atmosphere to generate excited atoms and/or molecules, but also because an attempt was made to identify the radiation. The glow, extending throughout the visible region, was found to be most intense as the rocket penetrated the peak of the O-atom layer at ~95 km, and from observations with multiple filters, it was concluded that the emission had a continuous spectrum, and was possibly due to NO_2. The data taken at the four wavelengths that were investigated are consistent with this identification, and are in fact quite similar to the shuttle spectrum of Swenson et al.[18] Nevertheless, the collisional energy regimes for the rocket and satellite observations are quite different.

GLOW IDENTIFICATION

Following the 1982 STS-3 mission, the initial interpretation[19] of the orange glow recorded on film was that it was likely to be due to excited O_2 molecules, since the predominant particle in LEO is the oxygen atom. The immediate problem attached to this explanation was that the glow appeared to be 10-20 cm in thickness, whereas the radiative lifetime of the O_2 metastable states originating from ground state atoms is quite long. For the shortest lived state, $O_2(A^3\Sigma_u^+)$, its lifetime of 150 ms means that in the absence of collisions, such a molecule leaving the surface at thermal velocities will travel 60 meters before radiating. Because the atmosphere that collects in front of the shuttle is much more dense than the typical 10^9 particles/cm^3 ambient condition, the mean free path is substantially reduced, to perhaps 5 meters. Even so, this figure is not compatible with the observed glow thickness.

It was then suggested that OH is a molecule that is probably produced in copious quantities from the interaction of O-atoms with contaminants on shuttle surfaces, such as water and organic materials.[9] Since the ground state of OH emits visible radiation, in high overtones of the Meinel system, it seemed reasonable to propose that OH was the emitting molecule, with much higher intensities being expected in the infrared spectral region than in the visible. Both the results of Yee and Abreu,[7] from the AE satellite, and those of Mende et al from the shuttle,[20] indicated that the radiation intensity increased towards longer wavelengths, and at that time (1983), resolved spectra did not exist.

At approximately the same time, ground based infrared observations of shuttle overflights were reported by Witteborn et al.[15] Measurements made at two wavelengths, 1.3 and 1.6 μm, and intensities considerably greater than what had been seen from the shuttle below 750 nm were reported, compatible with the OH hypothesis. However, it was also observed that the shuttle gave a more intense signature while departing than approaching, an indication that the radiation was not localized to the ram surfaces, but appeared to be more consistent with a glowing wake.

Soon after, Yee and Abreu reported the results of Fabry-Perot interferometric measurements from the DE satellite,[8] finding that the glow spectrum showed two lines (over a limited spectral region) at precisely the same positions as they appeared in the OH airglow, after corrections for the Doppler shift. This lent support to the OH hypothesis, but a short time later, Swenson et al. obtained a spectrum of the shuttle glow,[18] taken with 3.4 nm resolution, which indicated that the emission was continuous, and incompatible with any reasonable OH vibration-rotation distribution.

There are other differences between the AE/DE results and the shuttle observations, and it appears that the spectra are different. The deduced glow thickness on the satellites is much larger, typically 10 meters compared to 20 cm for the shuttle, and the satellite glows are an order of magnitude weaker.[7,8] In fact, the greater thickness of the satellite glows is compatible with a longer lifetime,[21] and the OH radiative lifetime is some two orders of magnitude longer than that of NO_2.

Another suggestion for the identity of the glow has been the First Positive system of N_2.[22] The basic problem here is that the emitter in this case, the $N_2(B^3\Pi_g)$ state, is not metastable, and radiates within 5 μs. This is much too short to be consistent with a 20 cm glow thickness, and it was suggested that a way around this impasse was for high-lying levels of the $N_2(A^3\Sigma_u^+)$ state to be initially formed, following collisional dissociation of incoming N_2. The $N_2(A\rightarrow B)$ radiative transition, although fully allowed, would take place rather slowly in the infrared, due to the ν^3 term in the radiative rate, and then the $B\rightarrow A$ transition, to low-lying $N_2(A)$ vibrational levels, would take place rapidly. The glow thickness would be determined by the slow infrared emission. The observation of continuous visible emission was inconsistent with this model of the shuttle glow.

In obtaining a spectrum at 3.4 nm resolution from STS-41 D, Swenson et al.[18] were able to conclude that the shuttle glow was not due to a diatomic molecule, as the emission appeared to be completely unstructured. Based only on the visible continuum, the best candidate for the emitter appears to be NO_2, although there is a red shift in the shuttle spectrum compared to the homogeneous air afterglow. This is not in itself surprising, since it is not unreasonable to find a difference in this direction if the nascent excited NO_2 molecule must use some of its internal energy to break away from the surface.

MECHANISMS AND LIFETIMES

More at issue is the question of the compatibility of the glow thickness and the NO_2 radiative lifetime. It has been shown, by film microdensitometer tracing,[21,23] that the e-folding distance of the glow is 20 cm. For this distance, and for the NO_2 molecule, there is a simple relationship between the translational energy of the molecule and its radiative lifetime, namely, $E(eV) = [100/\tau_R(\mu s)]^2$. Thus, with a radiative lifetime of 100 μs, the translational energy of the NO_2 molecule is 1 eV if it is to give a 20 cm thick glow. For a 32 μs lifetime, the translational energy must be 10 eV.

Since we do not understand the exact nature of the NO_2 formation mechanism, even if the NO_2 identification is correct, it is difficult to decide what recoil energies might be reasonable. If the NO_2 is formed when an NO molecule (formed by N + O recombination) encounters an O-atom during surface migration, through the Lindemann-Hinshelwood process, ejection of an *excited* NO_2 molecule with substantial kinetic energy would not be possible, since the 3 eV excitation energy is all that is available from recombination.

With the Ely-Rideal mechanism, in which an incoming O-atom pulls off a surface NO to form NO_2, conceivably some of the 5 eV kinetic energy of the O-atom could become

NO_2 kinetic energy, but more likely a large part of it is lost to the surface. Moreover, the fact that the NO_2 spectrum is red-shifted implies that *internal* energy is needed to break the surface bond, and that the O-atom collisional energy is not efficient in getting the NO_2 off the surface We take note that these arguments imply that O-atom kinetic energy may not be necessary in shuttle glow generation, a position with which we later disagree, on the basis of the appearance of shuttle glow photographs.

If we adopt the view that it is probable that the NO_2 translational energy is less than 1 eV, this requires that the NO_2 radiative lifetime be greater than 100 μs. There have been many measurements of τ_{NO_2},[24-29] and great variability has been exhibited, ranging from the 1 μs measured by Sackett and Yardley[24] to a range of 170-260 μs reported by Donnelly and Kaufman.[25] Many measurements are in the 30-60 μs region, corresponding to NO_2 translational energies of 3-10 eV. The system would be least surprising were the appropriate translational energy to be in the 0.3-1 eV range, with the radiative lifetime being 100-200 μs.

The issue of NO_2 generation has been addressed from another point of view, that of *total* NO_2 production, as observed mass spectrometrically. It is obviously important to establish that the flux of excited NO_2 observed in the glow does not exceed the total amount of NO_2 produced. Murad and von Zahn[30] have measured the amount of NO_2 generated at ram surfaces, and concluded that 10-100 times as much NO_2 was produced over that required to be in electronically excited states for glow generation. Engebretson[31] has also looked at this issue, concurring on the point that glow production need not be efficient, and noting that NO_2 is only generated effectively on surfaces exposed to the ram flux, i.e. thermalized atmospheric components are ineffective at generating thermalized NO_2, let alone excited NO_2.

FAST PARTICLE REQUIREMENTS

The question of the importance of particle velocity (as opposed to particle flux) in generating the shuttle glow can be addressed by studying the glow intensity as a function of the ram angle.[10,32] The point can be put forth that the glow intensity is highest when the surface is perpendicular to the velocity vector because the density enhancement is greatest when the surfaces are in a "sweep" mode. This would imply that the glow is generated in a *homogeneous* process, in a region of high density. Thus, as the surface turns away from the ram direction, the swept-up atmosphere leaks away, and the glow intensity thereby decreases. To counter this argument requires observation of a high pressure region where the surface is not subjected to ram particles.

This condition is met for the configuration shown in Figure 1, where there is a V-shaped region between the vertical stabilizer and the OMS pod. When the ram direction is parallel to the inside portion of the pod, the region marked A glows brightly,[32] but there is no glow on the inside of the pod itself. The V-shaped region is certainly an area where the atmosphere is swept up and the density is greatly increased above ambient. Furthermore, there is no reason not to expect that at areas A and B the atmospheric density will be comparable. Nevertheless, fast particles rushing by surface B do *not* cause a glow, whereas they do when they strike A. It may thereby be deduced that fast particles penetrating a region of high density do not cause gas phase excitation, whereas excitation does occur when the same particle flux hits a surface. It follows that the excited particles are produced *at* the surface, and are ejected into the gas phase, where they then decay.

A second conclusion to be drawn from these observations concerns the effect of thermalized particles. It is to be expected that the gas composition in the region of enhanced density is the same as that in the atmosphere, approximately 80% $O(^3P)$ and 20%

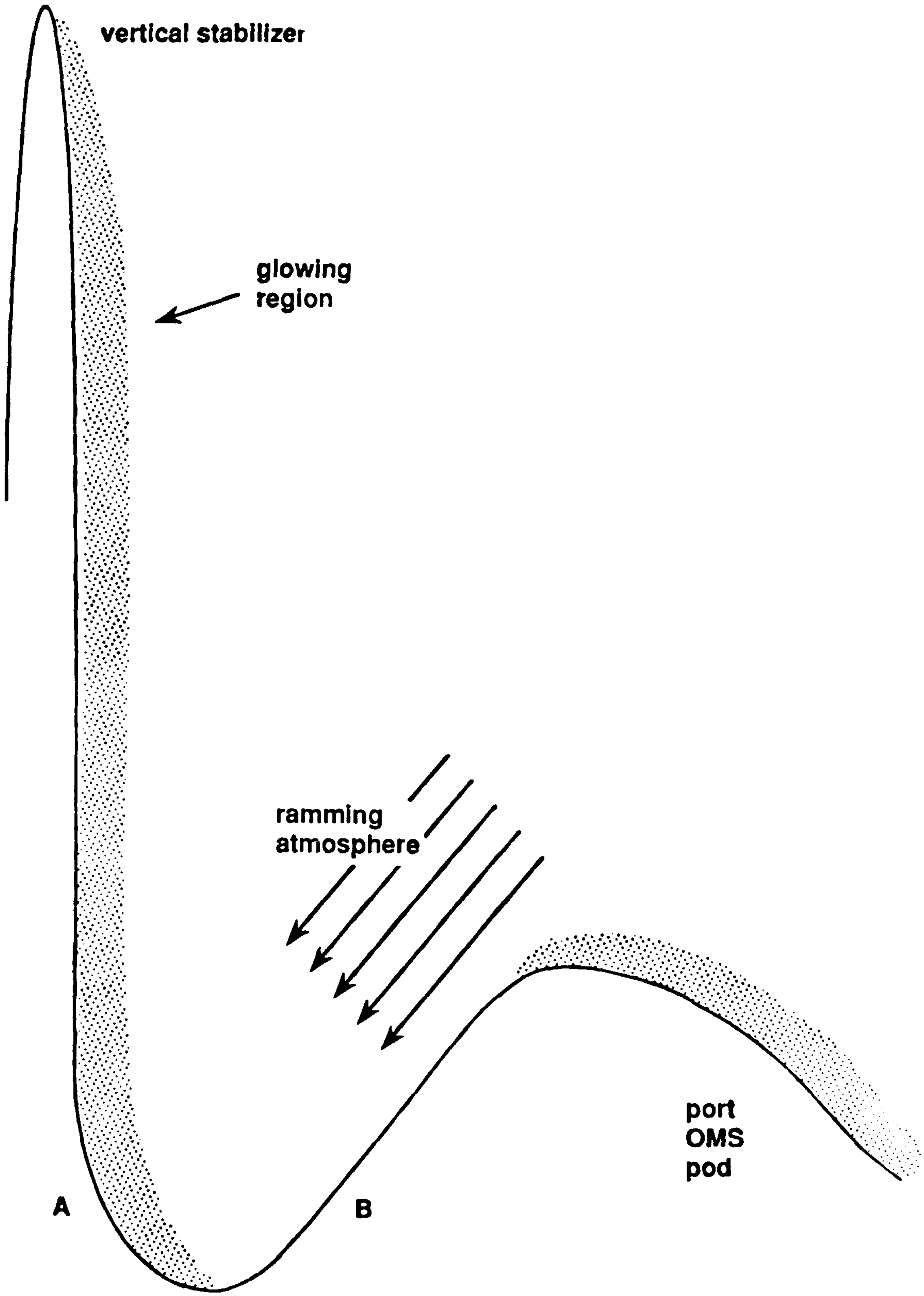

Figure 1. Spatial extent of glow for ram direction parallel to OMS pod interior surface.

N_2 at 250 km. This is because recombination of O-atoms on shuttle surfaces is probably quite slow, with an efficiency in the 10^{-4}-10^{-3} range[33] (however, see below). Therefore, in the V, where the mean free path is still on the order of meters, particles that have suffered only a single collision with surface A are bombarding surface B. Nevertheless, no glow is observed, an indication that "first bounce" glow is quite inefficient. First bounce glow has been proposed by Mende and Swenson[10] as an explanation for glow observed near shielded surfaces under much less favorable geometric conditions; on the basis of the above, this does not seem to be a likely explanation.

This discussion must be balanced by the point that "no glow" is determined by the film sensitivity characteristics. We have calculated elsewhere[32] that the detectability limit in region B is 14% of the intensity in region A. It is also true that most fast particles that hit shuttle surfaces do not suffer only one collision before leaving the surface. The shuttle tiles are extremely porous, and it is likely that an incoming particle penetrates well into the structure before finding its way out again. Thus, there are probably few particles that have lost only a portion of their translational energy; most will be completely accommodated to the surface temperature. By the same token, most NO_2 molecules will be translationally and electronically thermalized before leaving the surface; perhaps only those formed at the tips of the tile structure have a chance of carrying off substantial energy.

It is also important to consider the question of the effect of the surface porosity on the O-atom recombination rate. If the path of an atom is sufficiently convoluted after penetrating the surface structure, it may make sufficient collisions to recombine, and thus it is possible that the desorbing molecular oxygen flux is relatively high. As a consequence, the lack of a first bounce glow in Figure 1 could conceivably be due to a low flux of rebounding atoms.

LABORATORY STUDIES

There are some laboratory data that are relevant to the shuttle observations. Chu et al.[34] studied the effect of passing O(^{3}P) and NO simultaneously over a nickel surface, and discovered that an orange glow was generated, with spectral characteristics very similar to that observed on the shuttle, i.e. continuum emission that is red-shifted from the air afterglow spectrum. It was not possible to work at a pressure low enough for the (presumed) NO_2 to emit in the absence of collisions, but the extent of the glow, when corrected for the diffusional and quenching rates, implied a radiative lifetime of 80 μs. The same glow was observed when O_2 was part of the reaction mixture, but in that case the glow extended further from the surface, and it appeared that the kinetics became complicated by participation of an unidentified intermediate O_2 state. The presence of a glow from thermalized NO + O(^{3}P) on a nickel surface is not necessarily incompatible with the requirement that on a shuttle tile surface, collisional energy is needed. Nickel is a particularly effective surface for excited state generation,[35] and it may be that efficiencies would be higher yet with fast particles.

THRUSTER-INDUCED GLOW

It should be stated that there are at least two types of shuttle glow, although it is not possible to unequivocally distinguish between them. Up to this point, the discussion has assumed that there is a steady-state glow, caused by particle collisions with the surface, where the surface simply mediates the recombination of atoms and molecules that arrive from the ambient atmosphere. However, videotapes clearly show[36] that there is a very large increase in intensity of the glow when the attitude thrusters are fired. In addition to the surface glow there is also a gas phase glow, but the dominant feature of this phenomenon is that the surfaces that were glowing before the thruster firing are greatly enhanced in intensity, with little change in the geometric distribution of the radiation. In particular, the argument presented in relation to Figure 1 is still valid; the increased pressure and possibly changed environmental composition of the atmosphere following the thruster firing still does not cause significant glow without the incoming particles impinging on the surface. There are no existing spectra of the enhanced glow, so it is a major presumption that it is spectrally the same as what has been characterized. If this turns out to be true, it is very useful information, because a large component of the thruster effluent is NO.[37] Its absorption on the surfaces and subsequent stripping off by fast O-atoms presumably will lead to enhanced NO_2 production.

The enhanced pressure caused by the thruster firings is very transitory. Wulf and von Zahn have shown,[37] mass spectrometrically, that the typical time constant for reestablishment of ambient conditions is 0.2 s, but the persistence of the enhanced glow is considerably longer than this. Since there are no long periods without thruster firings, it is not possible to distinguish the thruster-induced glow from that related *only* to the ambient atmosphere. In other words, it has been assumed that recombination of NO and $O(^3P)$ is the NO_2 source, and that the NO arises either from absorption of ambient NO or from N + O recombination. It is possible that the *only* source of NO is in fact from the thruster firings, and that the time constant for its desorption is much longer than the 0.2 s measured for the gas density decay. It is interesting to note from Wulf and von Zahn's data that NO is the species that shows the greatest change in density following a thruster firing; it increases by a factor of 24, and becomes the third most common particle, after N_2 and H_2O (O-atoms were not measured). It would be very important to establish whether the surface is continually replenished by the thrusters, and whether there is indeed a background glow intensity level that is independent of the thruster contribution.

FAST PARTICLE BEAMS

The simulation of fast O-atom beams is an important area of research, and there are currently a large number of experiments in progress in which surface effects, including glow, are being investigated. Of great importance in such studies is the characterization of the beams in terms of the excited state content. Since oxygen and nitrogen metastable atoms and molecules are often very long-lived, and the beam generation may involve high-energy processes, there is a possibility that metastable concentrations are quite high. Bombarding surfaces under such conditions may in fact be a poor simulation of the space environment, where metastable concentrations, particularly in the absence of solar radiation, are negligible.

A new technique for detection of metastable particles is REMPI (resonance-enhanced multiphoton ionization), which can be used to investigate beam composition for all the particles present in nitrogen/oxygen systems. The technique has been worked out for ground-state N- and O-atoms[38] and for N(^{2}D)[39] and N(^{2}P),[40] and can be expected to be equally useful for O(^{1}D) and O(^{1}S), in addition to molecular metastables.

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Appendix B

VEHICLE-ENVIRONMENT INTERACTION WORKSHOP

THE VEHICLE-ENVIRONMENT INTERACTION WORKSHOP

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Introduction

On February 20-21, 1988, the Vehicle-Environment Interaction Workshop was held at the Applied Physics Laboratory at Johns Hopkins University. Its purpose was to evaluate the current understanding of the physical and chemical processes that occur when vehicles in low earth orbit (LEO) interact with the ambient atmosphere, the unique characteristic of this environment being the 8 km/s impact velocity of the incoming atoms and molecules. Most of the papers on the first day were devoted to the phenomenology and interpretation of space vehicle glows, whereas on the second day there were presentations of laboratory investigations, and discussions of charged particle interactions.

The unambiguous recognition of the phenomenon of spacecraft glows occurred when the astronauts on shuttle flight STS-3, in March, 1982, visually observed an orange glow on the shuttle surfaces visible from the flight deck [Banks et al., 1983]. Photographs showed that the glow was strongest on surfaces facing into the incoming atmosphere (the ram direction), and that it decayed with increasing distance from the surface, with a characteristic length on the order of 20 cm. The glow intensity was seen to be strongly enhanced when the rear attitude control thrusters were fired, when both surface-related and homogenous glows were observed.

Since that time, there have been numerous investigations of the glow phenomenon, and the STS-3 observations made plausible a variety of claims that had previously been put forth concerning near-field emissions from the surfaces of satellites and rockets, going back more than three decades. There is not necessarily a single mechanism involved in the effects that have been described, but it is abundantly clear that interaction between the vehicle and the ambient atmosphere is the first cause of the excitation of particles to radiating states.

In this workshop report, the individual contributions have been summarized. In some cases, consistent comparisons can be made between the phenomena observed by different investigators. More frequently, there are discrepancies that can only be resolved by further investigation. The field certainly warrants further study, because vehicle-atmosphere interactions, and in particular the glow observations, will be ubiquitous matters in the space age. Glowing halos around space objects obviously affect both their detectability and their ability to observe far-field emissions. It is to be hoped that funding agencies will respond accordingly.

Presented Papers

G. Swenson, one of the principal investigators in many of the space shuttle photographic studies, reviewed what has been deduced to date from observations on eight shuttle flights.

Following the initial photographs, showing a measurably thick orange glow concentrated in the ram direction, attempts were made to disperse the radiation to obtain a spectral signature. Hypotheses had been made that the glow might be the OH Meinel vibration-rotation bands [Slanger, 1983], the N_2 First Positive system [Green, 1984], and the NO_2 continuum, i.e. the air afterglow [Torr, 1983].

The best spectral resolution achieved so far in these investigations, 3.4 nm, has shown that on that scale there is no discernible structure [Swenson et al., 1985]. The spectrum seems to be continuous, commencing at ~400 nm, peaking at ~680 nm, with an indeterminate tailing-off at longer wavelengths that is not well-defined because of unexplained uncertainty concerning the transmission of the flight deck window. The observation of a continuous spectrum effectively eliminates OH and N_2 as the source of the visible space shuttle glow, but the spectrum of NO_2 is continuous in this region, although the peak intensity in the shuttle observations is shifted to somewhat longer wavelengths from that seen in the air afterglow.

The thickness of the glow provides information on the product of the velocity of the radiating particle and its radiative lifetime, given that the excited molecule is created at the surface, and that it is not collisionally quenched before emission. Mende and Swenson [1985] have shown that 20 cm is the e-folding distance, from which one can deduce either the velocity of the particle leaving the surface, or its radiative lifetime, given the other parameter.

Although NO_2 exhibits a large range of measured radiative lifetimes in the visible spectral region, 50 μs is a typical value [Bylicki et al., 1984]. In conjunction with the 20 cm thickness, the ejection velocity is then 4×10^5 cm/s, and the energy is 4 eV. Alternatively, if one assumes that the molecule leaves the surface at thermal velocity, $\sim 3 \times 10^4$ cm/s, then its radiative lifetime is calculated to be 700 μs. Neither of these extremes is likely to be valid, and thus further study is required to determine whether these restraints are consistent with the NO_2 identification.

Mass spectrometric studies have demonstrated that NO_2 is copiously produced on the shuttle by surface bombardment from the ram direction [von Zahn and Murad, 1986; Engebretson, 1985]. Such observations provide no information on the fraction of NO_2 that is electronically excited as it leaves the surface, but the amount necessary to account for the observed radiative flux is in fact quite small, <1%.

The model proposed by Swenson to explain NO_2 formation involves interaction of ambient 5 eV O-atoms with surface-adsorbed NO. The source of the latter is N+O surface recombination, with the N-atom source being somewhat uncertain. The ambient atmosphere contains both N and NO in small concentrations, but the suggestion has been made by Swenson and Meyerott [1988] that the N_2 halo which exists over the shuttle ram surfaces interacts with the fast oxygen atoms: $O^* + N_2 \rightarrow N + NO$. In this way, both N and NO may be produced locally close to the surface, conceivably with higher fluxes than provided by the incoming atmosphere.

Swenson et al. [1986] investigated the effect of shuttle surface temperature on glow intensity, and found an indication that the glow is enhanced when surfaces are cold. If NO surface coverage is a critical parameter in the mechanism, this correlation is to be expected.

A set of experiments that preceded those on the shuttle was described by J. H. Yee. These were made from the AE satellite [Yee and Abreu, 1983], and demonstrated a ram directional glow with a filtered photometer. Since the satellite operates over a range of altitudes, it was possible to determine the manner in which the glow intensity varied with atmospheric density. It was found that at two wavelengths, 656 and 732 nm, there was a strong functional dependence of intensity with density, the data exhibiting a linear relationship to the oxygen atom density above ~180 km, and to the molecular densities below this altitude. These studies confirmed earlier data from the AE satellite [Torr, et al. 1977] which indicated the presence of a ram-enhanced surface glow.

With five different filters, ranging from 280 to 732 nm, it was observed that the glow intensity increased sharply from about 500 nm towards longer wavelengths, consistent with the shuttle observations. However, it is claimed that the satellite glow thickness is on the order of meters rather than tens of centimeters, and that the intensity exhibits a different angular dependence with ram direction. Moreover, experiments carried out from the DE satellite, using Fabry-Perot optics, suggest that in the 732 nm region there is structure [Abreu et al., 1983]. By viewing the OH Meinel band emission lower in the atmosphere, and then carrying out a Doppler correction, the conclusion was reached that the observed surface glow near 732 nm and the atmospheric OH emission were the same, based on two lines in the instrumental bandpass. There is therefore evidence that the surface glows on the shuttle and the AE and DE satellites are different, and further work is needed to resolve this issue. It is interesting to note that the satellite surfaces should have been well outgassed compared to the shuttle surface, and that therefore emissions involving OH or H_2O should be more easily observable on the latter, contrary to the present interpretation of the data.

It was subsequently mentioned by P. Banks that there are ground-based IR data of a shuttle overflight, obtained by F. Witteborn in Hawaii. These show that there is strong emission at 1.3-1.8 μm, in the first overtone region of the OH Meinel system. However, it is not clear that this phenomenon is related to the visible shuttle glow, as the measurements are more indicative of a glowing cloud, rather than a relatively thin halo. It should be noted that the early AE data [Torr, et al. 1977] showed evidence of enhanced glow in the wake as well as the ram direction, a possible indication of a longer-lived emitter than encountered on the shuttle flights.

Yet another glow observation was reported by R. Conway, made from the S3-4 satellite. In this case, earlier reports of N_2 LBH emission at night [Huffman et al., 1980] were reinterpreted as a near-field surface phenomenon [Conway et al., 1987]. The instruments used were nadir-viewing photometers and spectrometers, providing a very unfavorable geometry for studying a ram-related glow. Had a comparison been possible between ram- and anti-ram intensities, it would have immediately been evident that the observations were surface-related.

The vibrational distribution of the upper state of the N_2 LBH system, $a^1\Pi_g$, was examined, and it was observed that it was different from either the distribution seen in the dayglow, from electron excitation, or that seen in the laboratory from homogenous N-atom recombination. These processes are both dominated by $N_2(a^1\Pi_g)$ generation in relatively high vibrational levels (v=2-6), whereas the surface process favors substantially greater yields in v=0,1.

The eccentric satellite orbit permitted the determination of the altitude dependence of the LBH intensity. It was found possible to fit the data with an $[N_2]^3$, or possibly $[N_2]^2[O]$, relationship. Thus, there is certainly evidence for a multistep mechanism. It was pointed out that the generation of $N_2(a^1\Pi_g)$ in low vibrational levels was consistent with a radiative cascade mechanism, whereby the 10 eV collisional energy of N_2 was in some manner converted to electronic excitation of the molecule to a high Rydberg state, which then radiates to v=0,1 in the $a^1\Pi_g$ state.

VUV spectra where also measured from the shuttle on Spacelab 1, as described by D. Torr. He identified, by spectral simulation, a variety of surface-related emissions, including the N_2 Vegard-Kaplan (A-X) system, and the NO(A-X) γ and NO(D-X) ε bands, as well as N_2 LBH. In the 160-180 nm region, it was concluded that the N_2 Vegard-Kaplan and LBH emissions are comparable in intensity, although Conway did not report N_2 VK emission from the S3-4 satellite in the same spectral region. However, in the latter case ram measurements were not made, which would imply that N_2 LBH emission extends further from the surface than N_2 VK, so that viewing towards the nadir permits observation of one but not the other. It should be noted that the $N_2(A)$ radiative lifetime is some four orders of magnitude longer than that for $N_2(a)$, so that it is more likely for $N_2(A)$ to generate a far-field glow if both $N_2(A)$ and $N_2(a)$ are surface-produced. However, it is Torr's opinion that $N_2(a)$ is <u>collisionally</u> produced from $N_2(A)$, which would explain N_2 LBH emission being discernible in a nadir-viewing experiment.

An alternative mechanism for $N_2(a)$ production was discussed by G. Swenson, in which it was proposed that the surfaces are bombarded by fast N-atoms that are the consequence of homogenous atom exchange between fast N_2 molecules with O-atoms, or fast O-atoms with N_2. The N-atoms produced in such processes may have excess translational energy, and it is suggested that the interaction of these fast atoms with adsorbed N-atoms will generate highly-excited N_2 states, which are inaccessible by normal

N-atom recombination. These states, $N_2(c_4'{}^1\Sigma_u^+)$ being typical, then radiatively relax over a very short time scale, to the $N_2(a)$ state. It follows that the spatial extent of the $N_2(a)$ envelope will be related to its 100 μs lifetime, and thus there should be no far-field glow. The difference between this mechanism and that described by Torr remains to be resolved. Confirmation of the mechanism described by Swenson would involve detection of emission from the high Rydberg levels, either in R→X or R→a bands. The former, lying in the extreme UV below 100 nm, would be much more intense. Both types of emission would occur directly at the surface, but resonant scattering from atmospheric N_2 could cause a far-field fluorescence at 90° to the vehicle velocity vector.

A general review was given by P. Banks, stressing observed and expected IR emissions from atmospheric-surface interactions. He described the variety of homogenous and surface-mediated processes that may be significant in the space environment, including those involving O_x, HO_x, NO_x, and combinations thereof. With the available kinetic and chemical energies, newly produced and/or excited molecules will in general be infrared active. Thus, much useful information should be available from IR observations. Banks discused the 1.4-1.8 μm ground-based observations of Spacelab 2, showing emission peaks at 1.52 and 1.68 μm, and presented IR data from shuttle flight 51-F. It is evident that water is an important glow component, since there is very marked outgassing at the beginning of shuttle flights, as shown both mass spectrometrically, and by the behavior of the IR glow cloud detected from the ground. It was pointed out that the visible glows induced by the thrusters are very intense, and persist much longer that the gas release itself. Thus, the surfaces adsorb the combustion products - NO, H_2, N_2, CO_2, CO - as well as unburned monomethyl hydrazine, suggesting that ultimately a large variety of emissions will be identified.

A review was presented by the author in which a number of current problems concerning vehicle glows were discussed. It was pointed out that there have been reports dealing with vehicle glows almost as long as optical experiments have been carried out from rockets. These vary in character, and except for rockets with very high apogees, are likely to differ from LEO glows because of the much smaller collisional energies involved. Nevertheless, it is worth considering the earlier literature - the paper by Heppner and Meredith [1958] suggested NO_2 as a possible source of the glow that they observed more than 30 years ago!

There have been suggestions that the source of the shuttle surface glow is the interaction between the atmospheric cushion that builds up on ram surfaces, where densities are typically two orders of magnitude greater than ambient, and the incoming fast particles. Were this the case, the 20 cm e-folding distance would be related not to velocities or radiative lifetimes, but to the density gradient. It was pointed out that photographs of the surface glow taken as the shuttle rotates around the body axis are inconsistent with any substantial visible glow component due to homogenous interactions [Slanger, 1986]. When the thrusters are fired, videotapes show that a glow is produced homogenously, but it is much weaker than the glow that simultaneously originates at the surface.

The same photographs indicate that there is no evidence that atoms or molecules scattered from the surfaces generate a glow at nearby surfaces that are not bombarded by fast particles. Either these scattered particles have lost enough energy upon collision to fall below some threshold for glow generation, or else the flux of singly scattered particles is a small fraction of the total flux of reflected particles. The latter is likely to be true, because the microsurface of the shuttle tiles is extremely rough, and the average particle probably makes a number of collisions before it is able to leave the surface. Thus, there is reason to believe that departing O-atoms are thermally accommodated to the surface.

There have been a number of laboratory experiments that demonstrate the enhancement of homogenous glows in the presence of a surface. Of particular interest are those in which NO is added to O-atom streams; strong intensity increases of continuum glows are observed upon the introduction of nickel surfaces [Chu et al., 1986]. The spectra of these glows show red shifts from the homogenous NO_2 air afterglows, an indication that some of the NO_2 excitation energy is used in breaking surface bonds. It is important to note that the spectral distribution is comparable to that of the shuttle glow, implying that, if the glows are in fact the same, that the collisional energy of the particles causing the shuttle glow does not contribute to the excitation energy of the product NO_2. This is of course contrary to the statement in the previous paragraph, and demonstrates the difficulty in making such comparisons; it may well be that these phenomena are quite different on nickel and on silica (shuttle tile) surfaces.

Although USSR cosmonauts have logged more hours in space than have American astronauts, there do not appear to have been any reports in the literature concerning their glow observations. The author has learned [V. A. Krasnopolsky, private communication] that a specific attempt was made in 1985 to observe the glow, at an altitude of 220 km, with negative results. This may be due to differences in construction material between the space shuttle and the Russian spacecraft.

W. Raitt presented extensive calculations on the formation and geometric extent of outgas clouds around the shuttle. Water is the principal component of such clouds, and calculations showed that the water cloud extends some 8 km in front of the shuttle, moving at a relative velocity of 1-2 km/s. At the beginning of a flight, water concentrations near the shuttle actually exceed those of N_2 and O-atoms, the main constituents of the ramming atmosphere.

The interaction of fast O-atoms with H_2O was considered, and calculations were presented of excitation rates, as a function of relative velocity, in the 000-010 transition at 6.27 μm. Known kinetics for water cloud chemistry were used to determine profiles for various neutral and charged species.

N. Tolk discussed different aspects of erosion caused by bombardment of surfaces by electrons, charged particles, and photons. One practical importance of such processes is that structures in permanent earth orbit, such as a space station, can lose a large fraction of their mass over the proposed system lifetime. The presentation stressed processes in which electronically excited particles are generated during the interactions, although total erosion rates are presumably much greater than exemplified by the DIET process (Desorption Induced by Electronic Transitions).

A number of examples were given of systems generating excited products. It was shown that electron bombardment of NaCl and NaF generates the Na doublet at 589 nm, whereas irradiation of LiF gives strong Li emission at 671 nm. The Li emission is the principal feature when LiF is irradiated with either γ-rays, 9 keV Ar^+, or 300 eV electrons. Electron irradiation of NaCl as a function of surface temperature shows that the generation of excited Na is not at all an instantaneous process, but requires some surface rearrangement before the Na* is ejected. At 310 K, the Na* decay time after cessation of excitation is ~0.5 ms, whereas at 373 K it is an order of magnitude faster.

The effect of gas adsorption on surfaces can be quite dramatic. It was shown that electron irradiation of KCl generates K* emission at 770 nm, which is completely suppressed by introduction of an H_2 partial pressure of 2×10^{-8} torr, and replaced by much stronger H and even OH emission. Time-of-flight experiments show that the H-atoms possess 3.5 eV translational energy.

In other experiments on KCl, it was shown that the effects of surface impurities can overwhelm emissions from the substrate. Electron irradiation of KCl shows strong emission from CN, and a series of bands between 220 and 350 nm has been tentatively identified as originating from CN^-. The vibrational band progression shows no indication of rotational structure. The generation of the CN^- state is another slow process, with a decay time following production cessation of ~200 ms. Photon irradiation also results in

CN^- emission, with a threshold energy of 6.8 eV, only slightly higher than the 5.6 eV energy of the first CN^- band. It was noted that KCl surface erosion was minimized when CN^- emission was observed, showing that the fluorescent process acts as an energy dissipation channel.

Tolk also reported on yields of excited Al and Li from Al/Li alloys subject to N^+ bombardment. It was observed that the Li* yield monotonically increased with N^+ energy up to 200 eV, whereas the Al* yield is found to have a broad minimum at 50-80 eV. At higher energies, the Al* yield increases monotonically to 2 keV, whereas the Li* yield reaches a broad maximum at 1.2-1.6 keV.

B. D. Green discussed the status of fast O-atom sources in general and the apparatus at PSI in particular. There is now a plethora of fast oxygen atom sources, utilizing a variety of principles, including high temperature electrical discharges, ion beam neutralization, photodetachment, laser-sustained plasma discharges, and beam-surface interactions. Not all of these techniques have produced useable atomic beams, the issues being a) sufficient energy (5 eV) to simulate LEO, b) comparable flux to that in LEO, typically 10^{15} cm^{-2}, and c) compositional purity, since many sources are likely to give excited O-atom states and relatively high O_2/O ratios.

In the PSI system, a pulse of O_2 is introduced into a hypersonic expansion nozzle, and a highly focused CO_2 laser beam is used to dissociate and heat the O_2 to 20000 K. The gas expansion results in an intense high-velocity O-atom beam. Beam velocities are dependent on laser power, and have been measured at 5-13 km/s, giving an energy range of 2-13 eV, with $3x10^{18}$ O-atoms being obtained in a pulse. The beam is relatively wide, with a radius on the order of 10 cm at a distance from the nozzle of 40 cm.

Infrared emissions have been measured for fast O-atom interactions with a variety of collision partners. With CO, vibrational levels up to v=13 have so far been observed, and fast O_2 on CO has excited CO up to v=21. With fast O-atoms on CO_2, both CO and

CO_2 emissions are seen in the IR. With CH_4, low yields of CH_4 in the v_3 mode are seen, and the process is apparently favored over the reactive channel to give OH(v). Calculations were presented for IR irradiance surrounding the space station, compared to the zodiacal light background, and the expectation is that the background will be exceeded at 1.0-3.6 μm and 4.6-5.5 μm.

The charged particles and fields surrounding spacecraft were discussed by four speakers. W. R. Patterson described experiments with the Plasma Diagnostic Package (PDP), a free-flying unit released from the shuttle. Measurements of ions, electrons, magnetic fields, and plasma waves were made within ~400 m of the shuttle. During the Spacelab 2 mission, the PDP made observations while 1 keV electrons were generated aboard the shuttle with an electron gun. The PDP measured the return current flowing back to the shuttle, finding it to be confined to a current sheet about 20 meters wide, with a length of at least 170 meters. Within this sheet, electron temperatures on the order of 100 eV were measured.

An ion tail was detected by the PDP, primarily containing molecules associated with shuttle outgassing, including H_2O^+, H_3O^+, and O^+. This ion cloud was used to infer an H_2O density some 50 meters from the shuttle of approximately 10^9 cm^{-3}, comparable to the ambient atmospheric density.

H. C. Koons discussed electric field and plasma wave measurements on satellite and rocket flights. Many of these studies were made with a Langmuir probe, and included observations during chemical releases, effects due to electron beam generation, and DC and AC electric field measurements.

The electron beam studies showed that several factors influence beam propagation, including beam-plasma discharges, local vehicle discharges, beam neutralization, and the beam pitch angle. A return current is induced by the electron beam, and electrical and radio noise can be detected at considerable distances. The same is true for N_2^+ emissions that are generated by high energy electron beams.

I. Katz discussed the spacecraft charging phenomenon, in which potentials as high as 20 keV are developed through the interaction of the vehicle with naturally occurring fluxes of high energy electrons. Studies have involved satellites in geosynchronous orbit as well as lower altitude satellites in polar orbit. Limits to the charging are achieved as the vehicle collects positive ions, and the flux of electrons at sufficiently high energies to overcome the negative potential are reduced. Numerical models were described for predicting charging effects, which depend on satellite geometries and materials, and the specific environment (solar flux, electron and ion densities, electron and ion energy distributions, etc.).

C. K. Goertz discussed charged particle heating in neutral gas-plasma interactions. He showed that numerical simulations of a magnetized plasma moving through a neutral gas cloud (analogous to the space shuttle outgas cloud moving through the ionosphere) show the development of a relative drift between the ions and electrons, as a consequence of ion-neutral collisions. The electrostatic waves that are thereby generated can be quite effective at heating the electrons, and the resultant increase in ionization rates can cause large increases in the plasma density.

Summary

This workshop was useful in bringing together people with various perspectives on vehicle-atmosphere interactions, and establishing a benchmark for what is currently known about optical effects relating to the passage of high velocity vehicles through tenuous atmospheres.

It is evident that spacecraft glow is a general phenomenon, and that the least ambiguous way to study it is from the space shuttle. Considering the many uncertainties associated with previous measurements from satellites and rockets, and the difficulties associated with separating near- and far-field emissions, the visual observations from the space shuttle, limited though they have been, provide the clearest picture of the nature of the process. In this respect, the manned shuttle has been successful in a way that an unmanned vehicle could not be. The STS-3 observations were made with no preconceived notions about glowing surfaces, yet were instantly recognized as a new phenomenon, while on unmanned platforms such as the various satellites, unambiguous recognition of the glow, which was always present in the optical channels, literally took years.

That spacecraft emit light throughout the 120-350 km altitude region, where surface heating effects are negligible, is a fact that is important for any type of optical system. Whether space telescopes glow in orbit is a matter of concern. Whether vehicles in space are surrounded by glowing infrared clouds needs to be established, and is certainly a matter of interest to military establishments of any country with a space program.

It is quite surprising to see that in the seven years that have passed since the glow was first detected on STS-3, there has been relatively little follow-up work, due to very low levels of funding. Although there is obviously great pressure from many scientific disciplines to fly experiments on the shuttle, it is amazing that basic questions have not yet been answered, considering that a large fraction of studies, both from the scientific and military standpoints, are of an optical nature. It is to be hoped that with the shuttle program back in business, that more emphasis can be given to investigating a phenomenon the study of which was first made accessible by the shuttle flights themselves.

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Appendix C

THE RADIATIVE LIFETIME OF THE $B^2\Pi_r$ STATE OF NO FOR v = 0-6.

NO($B^2\Pi$) RADIATIVE LIFETIMES; v = 0-6

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ABSTRACT

The zero-pressure radiative lifetime of the NO($B^2\Pi$) state has been measured over the vibrational level range v = 0-6. Laser-induced fluorescence was the technique chosen for this study, using two different sources of ground state NO. In one case, photodissociation of NO_2 at 193 nm was used to obtain a range of ground state vibrational levels, from which selected rotational levels were then pumped to the $B^2\Pi$ state, while in the second case, NO in v = 0 was directly pumped. The two methods of preparing the excited state gave identical lifetime results. The data show a linearly decreasing lifetime with increasing vibrational level, and to a good approximation the lifetimes are given by $\tau(\mu s) = 2.00 - 0.193v$. Recent calculations for the B-X system show excellent agreement with experiment at low v, and an increasing discrepancy with increasing vibrational level, the experimental lifetimes decreasing more rapidly than the calculated ones. The lifetime values fall within the 0.85-2.0 μs range for v = 0-6, and are substantially different from the 2-3 μs values that are currently quoted. Comparison of the new values with data derived from absorption studies shows good agreement even for the high vibrational levels. Absolute Einstein A-factors are presented for the v' = 6 progression.

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INTRODUCTION

The $B^2\Pi$ state is the lowest excited doublet valence state of NO, and is found in a number of environments, including air afterglows and shock-heated air. Along with the NO(A) state, it is the longest wavelength NO absorption system, and there have been numerous measurements made of the absorption oscillator strengths.[1-3] Figure 1 shows the NO potentials relevant to this study.

A very important parameter is the radiative lifetime of this state, because of its relationship to the absorption strength and to the balance between radiative and quenching effects. It is somewhat surprising to find a lack of consensus concerning the radiative lifetime,[4-8] and this is related to the fact that clean preparation of the $B^2\Pi$ state is not as simple as that for the Rydberg states, such as $A^2\Sigma^+$, $C^2\Pi$, and $D^2\Sigma^+$. The reason is that the relatively large displacement of the ground state and B state potentials means that optical pumping of $B^2\Pi$ from $v = 0$ of the ground state has very small Franck-Condon factors to the lowest $B^2\Pi$ vibrational levels, and for the higher levels, the transition wavelengths are inconveniently short for one-photon LIF experiments. However, there have been studies of the $B^2\Pi(v = 6,7)$ levels using tuneable vuv lasers[9-11], and it also happens that the B-X 7-0 transition overlaps, at high rotational levels, the ArF laser line at 193 nm, and advantage has been taken of this fact.[8,12] Two-photon LIF or MPI experiments have to a large extent been limited to accessing the Rydberg states.

The NO dissociation limit lies at $B^2\Pi_{1/2}$, $v = 7$, $J = 7.5$, in the same region as absorption to the $C^2\Pi$ state begins. Although interaction with the $C^2\Pi$ state is presumably responsible for the rapidly decreasing lifetimes that we observe as the v = 7 level is approached, it is only at the energy of the latter that spectral interpretations become complicated. We have therefore limited the present study to v = 0-6, and will report on the rotational dependence of the v = 7 lifetimes separately.

In earlier direct lifetime studies electron excitation has been used, and the generally quoted lifetimes are based on these studies.[5,6] However, high energy electrons do not provide as precise a method of excitation as optical pumping, and we will show that this disadvantage has apparently led to measured lifetimes that are too long.

The recombination of N-atoms with O-atoms, as is also true for N-atom recombination, incorporates certain problems that have not yet been fully resolved. The principal issue is the mechanism for the production of radiation that accompanies three-body association. For NO, there are five different band systems that are observed - $C^2\Pi$-$A^2\Sigma^+$, $C^2\Pi$-$X^2\Pi$(δ-bands), $A^2\Sigma^+$-$X^2\Pi$ (γ-bands), $B^2\Pi$-$X^2\Pi$ (β-bands), and $b^4\Sigma^-$ -$a^4\Pi$ (Ogawa bands).

For the production of the $C^2\Pi$ state, the v = 0 level of which is located close to the first dissociation limit, it is generally accepted that there is strong interaction with the $a^4\Pi$ state, which both crosses the $C^2\Pi$ state at v = 0 and has an energetic turning point there.[13,14] Thus, radiation from $C^2\Pi$(v = 0) is produced, and the very strong C-A 0-0 emission populates the v = 0 level of the A state. This mechanism thus accounts for three of the band systems - emission from C(v = 0) to A(v = 0) and to a range of levels in the ground state, and emission from A(v = 0) to the ground state.

What is less well understood is the mechanism for population of the $B^2\Pi$ and $b^4\Sigma^-$ states. The latter has not been extensively studied, but there are many publications devoted to understanding the source of $B^2\Pi$ state excitation.[15-18] One of the clearest characteristics of the β-band emission is that population of the v = 0 level of the $B^2\Pi$ state is strongly favored, with the next most populated level being v = 3. This has been reported a number of times, and another demonstration of the uniqueness of the v = 0 and 3 levels appears in the work of Campbell and Mason,[18] who measured the quenching rates of v = 0-3 with a number of species. They showed that v = 0 is invariably quenched most rapidly, followed by v = 3, with v = 1 and 2 substantially slower. Such behavior is unusual, and as it is indiscriminate with respect to the quencher, it suggests that there is some unique interaction within the NO molecule that distinguishes these particular vibrational levels.

EXPERIMENTAL

The experiments were carried out with a relatively standard arrangement for an LIF study. For the measurements in which NO_2 was photodissociated to provide vibrationally excited NO for subsequent pumping to the $NO(B^2\Pi)$ state, a Lumonics 861-T excimer laser was operated with an Ar/F_2 mixture to generate 193 nm ArF radiation. No attempt was made to characterize the vibrational distribution of NO from such a source, but we were able to obtain excitation spectra from ground state levels in
$v'' = 4$-10.

A Quantel Nd:YAG/dye laser combination run at 10 Hz was used to pump the vibrationally excited NO to the desired $B^2\Pi$ levels, from which emission was then observed. A delay of 10 µs was used between the two lasers, and the lifetime of the desired $B^2\Pi$ vibrational level was obtained by feeding the PMT signal directly to a Lecroy 9400 digitizing 120 MHz scope, fitted with the WP01 waveform processing option. 1000-2000 decay traces were then taken and averaged to give a decay curve, usually spanning 5-10 µs with a point every 10 ns. The signal amplitude resolution was 0.001% of full scale.

The averaged trace was transferred from the scope to a VAX computer system for analysis and plotting. A curve fitting program was used to derive the single- and bi-exponential constants from the decay traces.

The LIF signals were observed with a phototube having an S-20 surface, equipped with a suitable interference filter (7-11 nm half bandwidth) to limit extraneous radiation.

Table 1 lists the bands that were pumped to access the v' = 0-6 levels in the NO(B) state, and the bands that were selected for observation.

In the same manner, NO pumping was used as a source, except in this case no excimer radiation was necessary for photodissociation. The two NO(B) levels pumped in this case, v' = 2,6, were excited from v" = 0, and the detected wavelengths are listed in Table 1.

Generation of the dye laser radiation for the NO_2 experiments only involved doubling the radiation from 532 nm-pumped fluorescein, at 545-575 nm. For NO-pumping much shorter wavelengths are required. To produce radiation for pumping the 6-0 transition at 195 nm, it was necessary to use the fourth anti-Stokes Raman line from 576 nm radiation (from R590 and R610 dyes in ethanol) doubled in KDP, then scattered in high-pressure H_2. For the 2-0 band, the third anti-Stokes transition was used, starting with 568 nm dye laser radiation. Laser power in these instances was on the order of 10 μj/pulse.

A 0.3 meter Heath monochromator, equipped with a phototube with an S-20 response, was used to obtain fluorescent spectra, for the purpose of ascertaining that the detected emission was what we assumed. At low pressures, the observed vibrational progressions were those expected. For the v' = 6 progression, the band intensities were carefully measured so as to obtain relative A-factors. Rather than using a standard lamp for instrumental calibration, the 300-400 nm region being difficult to cover with either a D_2 lamp or a tungsten lamp, we performed the spectral calibration with the aid of the observed band intensities of the v' = 3 progression in the NO γ-system, using A-factors supplied by Langhoff.[19]

NO_2 was added as a 1% NO_2/He mixture, and was used without further purification, whereas the NO mixture, 5% NO/He, was passed through an Ascarite trap to remove NO_2. This is because in the NO experiments, the doubled dye laser radiation might dissociate NO_2 and excite the resulting vibrationally excited NO.

RESULTS

The data that were sought for the purposes of the study reported here are the zero-pressure lifetimes of individual vibrational levels in the $B^2\Pi$ state. In the course of the investigation, we made a variety of other observations which will be described in subsequent publications. These include studies of the $B^2\Pi(v = 7)$ level, the variability of quenching rate coefficients of the $B^2\Pi$ vibrational levels with NO_2 and He, and the rotational level dependence of NO_2/He quenching in the $B^2\Pi(v = 0)$ level.

The lifetime studies were carried out in a conventional manner, using laser-induced fluorescence (LIF) on individual rotational levels. Excitation spectra were taken to identify the accessed levels, with detection of the fluorescence at much longer wavelengths than the pump wavelength. For example, for $B(v = 0)$ the 0-5 band at 275.2 nm was pumped and the 0-11 band at 379.6 nm was detected. Observations at long wavelength have the advantage both of being far from scattered light from the laser, and of being spectrally removed from other NO transitions, where NO A-X radiation is of greatest concern.

Excitation of $NO(B^2\Pi)$ from cold NO for $v' = 0$-6 occurs in the 220-195 nm range. For the 0-0 band, the published Franck-Condon (FC) factor[20] is 2.27×10^{-5}, increasing to 0.0184 for the 6-0 band. For excitation from high-lying vibrational levels of the ground state, the laser wavelengths are more convenient, and the FC factors are generally larger, at least for low v' levels. For example, to access $v' = 0$, one can utilize the 0-5 band at 275 nm, with an FC factor of 0.058, while for $v' = 6$, the 6-9 band at 281.8 nm, with an FC factor of 0.0121, is a reasonable choice.

To take advantage of the improved accessibility of the $B^2\Pi$ state from vibrationally excited ground state NO, a source of the latter is required. This is available from NO_2 photodissociation, where we have previously demonstrated extensive vibrational distributions from KrF (248 nm)[21] and F_2 (157 nm)[22] laser dissociation, with vibrational levels up to the thermodynamic limit of v" = 8 being detected in the former case, and up to v" = 21 in the latter. In the present instance, we have utilized ArF (193 nm) NO_2 photodissociation, which provides an intermediate range of vibrational levels, sufficient for our purposes.

NO_2 can dissociate at 193 nm (6.42 eV) to produce ground state NO and either $O(^3P)$ or $O(^1D)$. If the oxygen atom is in the ^3P ground state, the excess available energy is equivalent to NO vibrational excitation up to v" = 16. For the $O(^1D)$ product, only excitation to v" = 6 is possible. The highest level from which we have pumped in these experiments is v" = 10, which indicates that the NO(X) + $O(^3P)$ dissociation channel is significant, the same conclusion that was reached in the case of dissociation at 157 nm.

Most of the measurements were made with NO_2 as the source molecule, because of the simplified laser frequency generation. However, we felt the problem to be sufficiently important that we also used direct pumping from NO(v" = 0), to show that a different system would give the same results; the v = 2 and v = 6 levels of $NO(B^2\Pi)$ were investigated in this manner.

An example of an excitation spectrum is shown in Figure 2 for the B-X 6-9 band, where detection is made on the 6-17 band at 429.3 nm, the unresolved $P_1(5)$-$R_1(9)$ line pair being pumped for the decay measurements. As mentioned above, the B(6) level was also investigated by pumping the 6-0 band, and Figure 3 shows a low pressure fluorescence spectrum that was obtained in this case, demonstrating that all the bands are part of the 6-v" progression. Increasing the pressure causes the appearance of other bands, as has been discussed elsewhere.[12] Shown in Figure 4 is a fluorescence scan of the

NO(A-X) 3-v" progression, lying in the same spectral region. These two spectra were subsequently used to obtain absolute Einstein A-factors for the B-X 6-v" progression, as described below.

The LIF signals obtained from pumping the v' = 0-6 levels of the NO(B) state show interesting differences. In Figure 5 we contrast the behavior of decay from the v' = 0 and v' = 1 levels, at equal total pressures of 1% NO_2/He. It is evident that the v' = 1 temporal decay is fit by a single exponential, whereas the v' = 0 level has more complex behavior, with the preponderant fast decay being more rapid than that for v' = 1, whereas the slow component is slower. This difference is consistent with the observations made by Campbell and Mason on these two levels generated by N + O recombination.[18] The non-exponential behavior of the v' = 0 level is pressure-dependent; below 2 torr, the data can be fit with a single decay component, as radiation becomes the dominant loss mode.

The temporal behavior of other levels fall into two categories - they either look like v' = 0 or v' = 1 decay. Figure 6 shows plots of decay rate vs pressure for v' = 1,2,4,5, demonstrating the similarity in slopes. In each of these cases, the decays are clean single exponentials. It is important to note that the quencher is an NO_2/He mixture, so that these plots do not differentiate between the two components. The data for v' = 2 were taken by means of LIF on the B-X 2-0 band, whereas in the other three cases, vibrationally excited NO from NO_2 photodissociation is the source, as noted. Thus, the v' = 2 data are displaced downward, to remove the contribution of the NO quenching of NO(B), which does not affect the NO_2/He quenching slope. Several different rotational lines were pumped on these four B-X transitions, but no significant differences in extrapolated lifetime or quenching slope were observed for a given level.

The data for the v' = 0,3,6 levels are quite different, the most obvious change being an increased quenching rate with NO_2/He. The v' = 0 level stands out in particular, because with increasing pressure, its decay becomes increasingly nonexponential, which is not the case for v' = 1,2,4,5. Figure 6 shows how well the decay trace for v' = 0 can be fit by inclusion of a second slower exponential decay in the analysis. On the assumption that the slower decay is related to collisional coupling between the $B^2\Pi$ state and a non-radiating state, either the ground state or the $a^4\Pi$ state, the faster decay is taken as the one that is needed for the zero-pressure extrapolation.

To demonstrate the precision and reproducibility of the lifetime measurements, Table 2 presents values obtained from twelve different lines belonging to the v' = 0 level. Not only is it necessary to remove the slower component from the data to perform the extrapolation, but the quenching slopes are rotational level dependent, as will be discussed in a subsequent paper. Nevertheless, the lifetimes are seen to be very reproducible, and we can assign a precision of ± 3.8% to the data.

In Figure 8 the v' = 0 decay rates are plotted against NO_2/He pressure, with the data below 2 torr requiring no adjustment for a slower exponential. Clearly the two regions merge well, giving a quenching slope more than twice as large as found for the v' = 1,2,4,5 data set in Figure 6.

The data for v' = 3 also show a double exponential, but the slow component is a substantially smaller fraction of the total than is the case for the v' = 0 level. The results of quenching experiments are plotted in Figure 8, with the slower exponential removed from the emission decay analysis at pressures above 2 torr. Figure 8 also shows the data for the v' = 6 level, for which the decays are single exponential at all pressures, but we classify it as part of the v' = 0,3 data set because of its fast quenching. The v' = 6 level was produced both by laser pumping of v" = 9, following NO_2 photodissociation, and by pumping of v" = 0, from a 5% NO/He mixture.

A reprentative set of data for quenching slopes and intercepts are collected in Table 3, which show the similarity in quenching slopes for the members of the two sets, v' = 0,3,6 and v' = 1,2,4,5. The intercepts, which are the collision-free radiative lifetimes, show no evidence of these groupings, and are monotonic functions of vibrational level. The two methods of generating v' = 6 give essentially the same results.

In Figure 9 the zero-pressure lifetime data are plotted from the intercepts of all quenching plots, using both NO and NO_2 as parent gases. The variances of the least squares fits on the intercepts are quite small, typically 1-3%. The differences between individual plots for a given vibrational level are somewhat larger. Since the data were obtained by pumping different rotational levels, it is possible that the variations are real, i.e., that different rotational levels exhibit slightly different lifetimes. In any case, the variations are not great, and the linear least squares fit to the data of Figure 9, $\tau(\mu s) = 2.00 - 0.193v$, is a good representation. It is evident that if the line had been constructed from only the v' = 1,2,4,5,6 data, which required no adjustment for multiexponential behavior, then the predicted values for v' = 0,3 would be precisely those extracted from the fast component of the decays. It is interesting to note that an extrapolation of the line to v' = 7 gives a value of 0.64 µs, compared to reported literature values,[9,10] for rotational levels below the dissociation limit, of 0.39-0.54 µs.

With a value for the sum of the Einstein A-factors for the v' = 6 level (the reciprocal of the radiative lifetime) of 1.18×10^6 s^{-1}, it is then possible to use the relative band areas in the B-X 6-v" progression of Figure 3 to obtain absolute A-factors for the individual bands. Depending as these do on the Franck-Condon factors and the transition moment function, such a set of data can be used as a benchmark for subsequent theoretical calculations on the $B^2\Pi$ state. For this purpose, it is necessary to calibrate the optical system, and we have done this by comparison with the v' = 3 progression of the NO γ-system, shown in Figure 4, which samples the same spectral region as the B-X 6-v" progression.

Langhoff, et al[23] have calculated the transition moment function and A-factors for the A-X system, for v' = 0-2. Comparison with the careful measurements of McGee et al[24,25] for v' = 0,1 show excellent agreement, lending confidence to the calculations, which have been extended to the v' = 3 progression.[19] The band areas in the A(v' = 3) progression, Figure 4, when divided by the A-X 3-v" A-factors, provide wavelength-dependent system sensitivity factors. These factors are then applied to the band areas for the B-X 6-v" progression in Figure 3, resulting in a relative set of A-factors, which must sum to 1.18×10^6 sec^{-1}. The final set of values is given in Table 4.

DISCUSSION

The most extensive set of lifetime measurements reported for the $B^2\Pi$ state are those of Brzozowski et al.,[6] spanning the same range of vibrational levels as the present work. The agreement with the earlier work of Jeunehomme and Duncan[4] was considered adequate, and it is these two sets of data that are generally quoted for the $B^2\Pi$ lifetimes. However, we note that the work of Brzozowski et al. was preceded by another set of measurements,[5] and the earlier lifetime values are not quoted in the subsequent paper. It is to be presumed that the previous work was thereby rejected in favor of the later data.

Table 5 compares these two sets of lifetimes with our measurements and those of others, and it may be seen that the earlier data of Brzozowski et al.[5] are in excellent agreement, particularly for v' = 0 and v' = 1, with the current measurements.

The two sets of measurements of Brzozowski et al.[5,6] also include data on the $A^2\Sigma^+$, $D^2\Sigma^+$, and $B'^2\Delta$ states. The $A^2\Sigma^+$ and $D^2\Sigma^+$ data are reproducible, and agree with other studies, including our own. The data for the $B'^2\Delta$ state differs, however, and it has been subsequently shown that the data in the second paper are the more correct.[26,27] The experimental results therefore seem to be rather unpredictable, and lacking a discussion of these effects by the authors, it is not evident what weight to give the data.

When lifetimes that are too long are measured in an electron excitation experiment, cascading transitions are often an explanation. However, the $B^2\Pi$ state is one of the longest-lived of the NO states, and the only known cascading transition, $B'^2\Delta$-$B^2\Pi$, has an upper state lifetime of only 110-140 ns,[26,27] and therefore cannot be responsible for a lengthening of the lifetimes. The fact remains that it is the 1976 study which has found general acceptance for the $B^2\Pi$ lifetimes, and it is clearly at odds with our present investigation, with the most recent calculations,[19] and particularly with data on the $B^2\Pi(v = 7)$ level.[9,11,12]

Interactions between the $^2\Pi$ states in NO are extremely strong, and it is to be expected that such states with an intrinsically long radiative lifetime will be affected by nearby states having a short lifetime. This is the case for the $B^2\Pi$ and the $C^2\Pi$ states, which is manifested both by the greatly shortened radiative lifetimes of the $B^2\Pi(v = 7)$ level, which lies very close to $C^2\Pi(v = 0)$, and by the irregularities in the absorption strengths of the B-X v'-0 progression above v' = 7, where calculated Franck-Condon factors are unrelated to the observed band strengths.[28] Since the radiative lifetimes of the C(v = 0) and B(v = 0) levels differ by approximately two orders of magnitude, it is hardly surprising to find a substantial effect of the strong C-X transition on the much weaker B-X. Gallusser and Dressler[29] *have calculated the vibronic coupling between* $^2\Pi$ *states in NO,* and concluded that effects should not be limited to the $B^2\Pi$ vibrational levels lying at or above $C^2\Pi(v = 0)$, i.e. $v \geq 7$, but should extend downwards to at least $B^2\Pi$ (v = 4).

Langhoff and co-workers[19] have recently investigated the NO(B-X) system from the point of view of obtaining an accurate transition moment. They had previously shown that their SCF(MRCI) technique provides excellent agreement with experimental data for the NO(A-X) system.[23] A comparison between our results and lifetimes derived from their calculation is given in Figure 10, showing good agreement for the lowest vibrational levels, *but increasing divergence for higher levels.* Their calculation invokes the $B^2\Pi/C^2\Pi$ coupling, and to the extent that the experimental data are accurate, suggests that the coupling is still underestimated.

Another data set over a range of vibrational levels for the B-X transition can be found in the work of Nicholls and co-workers,[2,3] who measured the absorption band strengths for the v'-0 progressions in v' = 0-5 (two different experiments were involved, in which v' = 0-4 and v' = 3-5 were studied). They extracted Einstein A-factors for these bands, from which one can obtain a radiative lifetime if it is possible to estimate what fraction of the summation of v'-v" A-factors is represented by the measured v'-0 A-factors. For this purpose, we have used an A-factor array calculated by Langhoff[19]. In spite of the discrepancy between our experimental results and the calculations for the radiative lifetimes, use of this array to obtain the $A_{v'-0}/\Sigma(A_{v'-v''})$ ratio should not be seriously in error, since the ratio is not proportional to the absolute value of the transition moment, but is more closely related to the Franck-Condon factors. Comparison of our results with those derived from Nicholls and co-workers[2,3] is shown in Figure 10, indicating that agreement with their data, particularly for the v' = 0-4 study, is quite satisfactory. Thus, direct lifetime measurements and integrated absorption cross sections give compatible results.

Langhoff's calculations[19] include the branching ratios for the v' = 0-6 progressions. In Figure 11 we compare our branching ratios for v' = 6, from Table 3, with his values, and find the agreement to be in general quite good. The discrepancies may well reflect the fact that the calculations have not yet been refined to the point where the radiative lifetimes are in agreement, particularly for this high v' level. We note that literature values of the Franck-Condon factors,[20] do not correlate particularly well with the data in Figure 11, which is hardly surprising since the earlier calculations did not take into account the perturbations of the $B^2\Pi$ potential caused by the presence of the $C^2\Pi$ state. For instance, Ory et al[20] calculate that the Franck-Condon factor for the B-X 6-4 band is 30% larger than for the 6-3 band, which is quite a different result than our observations (Figure 3) or the calculations.[19]

With the greatly increased transition strength [almost a factor of 3 for $B^2\Pi(v = 6)$] for the B-X system, compared to that implied by the earlier studies,[5,6] one may ask if the NO β-bands should appear in the airglow, as do other NO systems. After all, the 850 ns lifetime of the B(v = 6) level is only a factor of four longer than that of the NO(A) state, the source of the NO γ-bands.

The issue is one of sensitivity; certainly NO(B) is produced, but with what intensity compared to, for example, the γ-bands? In a recombination system, the A and B lifetime similarity is irrelevant, because NO(A) is produced in a more direct manner than NO(B). The principal NO(A) source is cascading from NO(C), which is formed by curve crossing between the C state and the recombinant $a^4\Pi$ state (Figure 1), the NO(C-A)/NO(C-X) branching ratio being 0.21.[30]

For solar pumping of NO, the decreased lifetime of NO(B) makes its excitation a more efficient process than previously assumed, but it is still weak compared to NO(A) excitation, principally as a result of NO(A) being a Rydberg state, while NO(B) is a valence state. Although the states have almost equal energy, the Franck-Condon factors favor excitation of the lowest levels of the A state (1-0 is the strongest v" = 0 band), whereas for the B state, low v' levels are very inefficiently excited from v" = 0 (our rationale for using NO_2 as a source of vibrationally excited NO). For the B-X v" = 0 progression, the maximum Franck-Condon factor (ignoring the $C^2\Pi$ interaction) is found for v' = 13.[20] Thus, the maximum excitation into the B state will occur at substantially shorter wavelengths than for the most efficient A state excitation.

The absorption data of Bethke demonstrate this effect[1] at 195 nm the ratio of the integrated absorption coefficients for the A-X 3-0 and B-X 6-0 bands is approximately 8 (favoring A-X), whereas at 204 nm the ratio for the A-X 2-0 and B-X 4-0 bands is 50. The solar intensity ratio for these two wavelengths, I(204)/I(195), is ~ 1.5,[31] also favoring NO(A) excitation. Furthermore, emission from the higher levels of the B state will be spread out over a substantially greater number of bands than A state emission from low vibrational levels, so here again detection of the A-X bands is favored. It is for this combination of reasons that solar-pumped B-X bands have much lower detectability than A-X bands, in spite of the new lifetime measurements which indicate only a factor of four difference between the A state and the highest levels of the B state.

CONCLUSIONS

We have carried out direct measurements of the NO($B^2\Pi$) radiative lifetime for v' = 0-6, using the LIF technique, and employing both NO and NO_2 as source molecules. We find that the generally accepted lifetime values must be revised sharply downwards, by factors of 1.5-3. The lifetimes are found to be a linearly decreasing function of vibrational level, attributable to increasing $C^2\Pi$-$B^2\Pi$ interaction as the $C^2\Pi$ potential is approached.

Comparison with recent extensive calculations on the B-X system show excellent agreement for the lifetimes of the lowest $B^2\Pi$ vibrational levels, with an increasing discrepancy for higher vibrational levels. Comparison with lifetimes derived from absorption measurements over the v' = 0-5 range show good agreement, even for high vibrational levels.

For the v'= 6 progression of NO(B), absolute Einstein A-factors have been obtained from calibrated fluorescence spectra.

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TABLE 1

NO($B^2\Pi$) VIBRATIONAL LEVELS PUMPED AND DETECTED

v'	Band Pumped	Wavelength (nm)	Band Detected	Wavelength (nm) (filter)
0	0-5	275	0-11	380 nm
1	1-6	281	1-12	390
2	2-0	210	2-14	420
3	3-7	278	3-16	460
4	4-8	284	4-17	470
5	5-8	276	5-16	420
6	6-9/6-0	282/195	6-17	430

TABLE 2

VARIATION OF ZERO-PRESSURE LIFETIME WITH ROTATIONAL LINE FOR v' = 0

Line	Lifetime (μs)
R_1(head)	2.021 ± 0.037
R_1(3)	2.023 ± 0.075
R_1(4)	2.068 ± 0.057
R_1(5)	2.029 ± 0.064
R_1(7)	2.033 ± 0.056
R_1(8)	2.088 ± 0.064
R_1(9)	1.926 ± 0.046
R_1(10)	2.058 ± 0.098
R_1(11)	1.903 ± 0.080
P_1(11)	1.977 ± 0.055
R_1(12)	2.086 ± 0.135
R_1(13)	1.912 ± 0.099
R_1(14)	2.138 ± 0.135
P_2(5)	2.001 ± 0.062
Ave	2.019 ± 0.076

TABLE 3

QUENCHING OF NO(B) IN v = 0-6 BY 1% NO_2/He

Vibrational Level	Slope [μs^{-1}/torr]	Intercept [μs^{-1}]
0	0.177	0.511
1	0.0754	0.582
2	0.101*	0.655*
3	0.203	0.686
4	0.112	0.831
5	0.0875	0.932
6	0.209	1.154
6	0.191*	1.219*

* These entries were obtained by adding 1% NO_2/He to 5% NO/He for the slopes, and in 5% NO/He alone for the intercepts. All other data were obtained in 1% NO_2/He.

TABLE 4

EINSTEIN A-COEFFICIENTS FOR B-X v' = 6 PROGRESSION

v"	A-coefficient (s^{-1})
0	1.05(5)
1	3.14(5)
2	2.93(5)
3	6.14(4)
4	2.12(4)
5	1.01(5)
6	5.55(4)
7	1.11(4)
8	7.43(4)
9	2.83(4)
10	7.79(3)
11	5.07(4)
12	1.65(4)
13	5.78(3)
14	1.89(4)
15	9.00(3)
16	2.95(3)

TABLE 5

EXPERIMENTAL NO($B^2\Pi$) RADIATIVE LIFETIMES (μs); v = 0-6

v'	A	B	C	D	E
0	2.00	3.10	1.99	3.10	1.4-1.7
1	1.82	2.86	1.78	2.26	
2	1.52	2.77	--	2.18	
3	1.46	2.63	--		
4	1.19	2.53	1.65		
5	1.07	2.34			
6	0.85	2.29			

A	present work
B	ref. 6
C	ref. 5
D	ref. 4
E	ref. 7 (undifferentiated vibrational levels)

FIGURES

1. NO potentials

2. Excitation spectrum of NO B-X 6-9 band; pressure = 8.6 torr 1% NO_2/He.

3. NO B-X 6-v" fluorescence spectrum; 6-0 band pumped, pressure = 0.55 torr 5% NO/He.

4. NO A-X 3-v" fluorescence spectrum; 3-0 band pumped, pressure = 0.25 torr 5% NO/He.

5. Decay of $B^2\Pi$ v' = 0, 1 levels. For v' = 0, 0-5 band pumped at R_1 head; 7.7 torr 1% NO_2/He. For v' = 1, 1-6 band pumped at $P_1(9)$; 8.0 torr 1% NO_2/He.

6. Decay rate vs pressure for v' = 1, 2, 4, 5

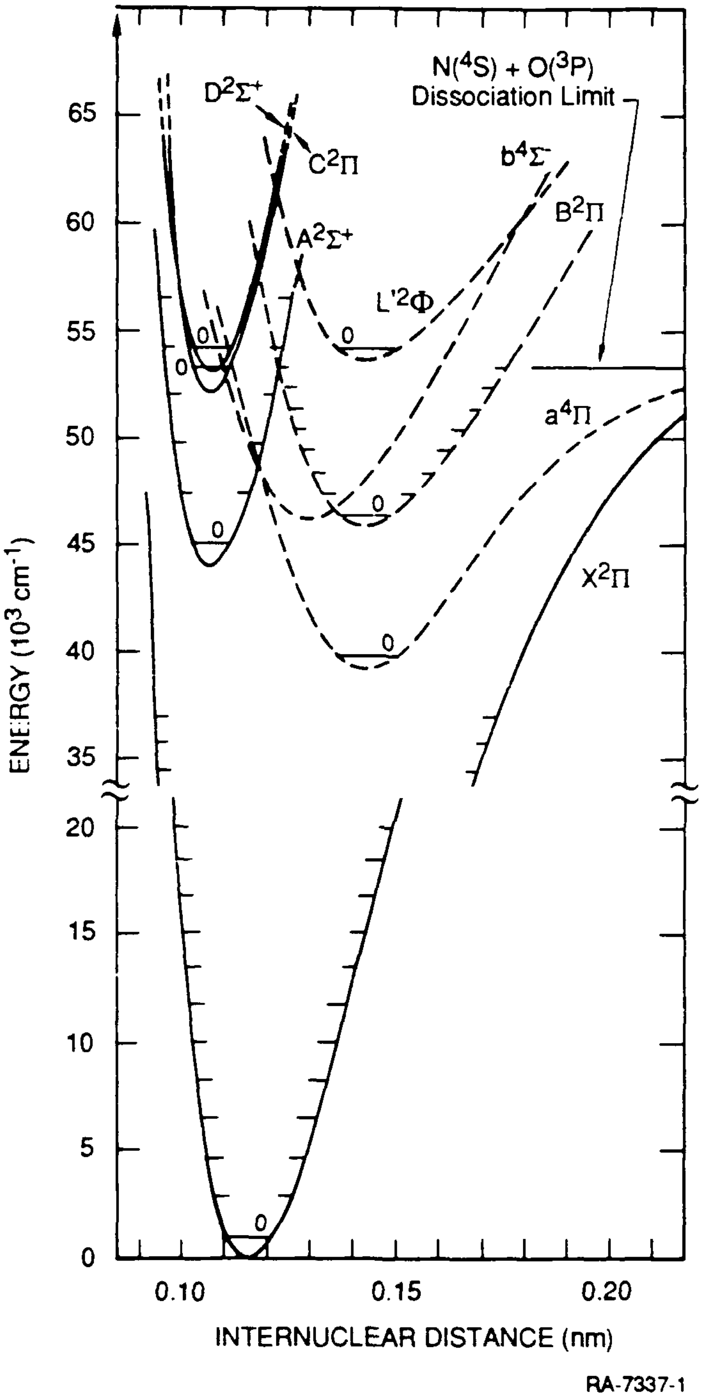
7. Two-exponential fit of v' = 0 decay; pressure = 7.5 torr 1% NO_2/He.

8. Decay rate vs pressure for v' = 0, 3, 6

9. NO(B) radiative lifetime vs vibrational level

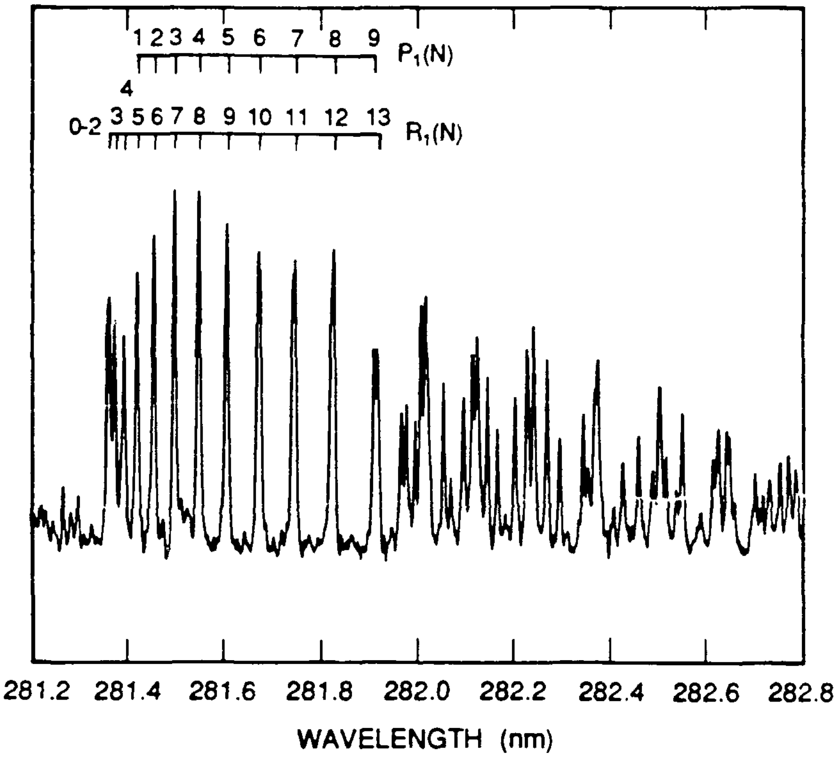
10. Comparison of current radiative lifetime measurements (dashed line) with the calculations of Langhoff[19] (solid line) and the absorption measurements of Nicholls and co-workers.[2,3]

11. NO(B-X) v' = 6 progression branching ratios, and comparison to calculations of Langhoff.[19]



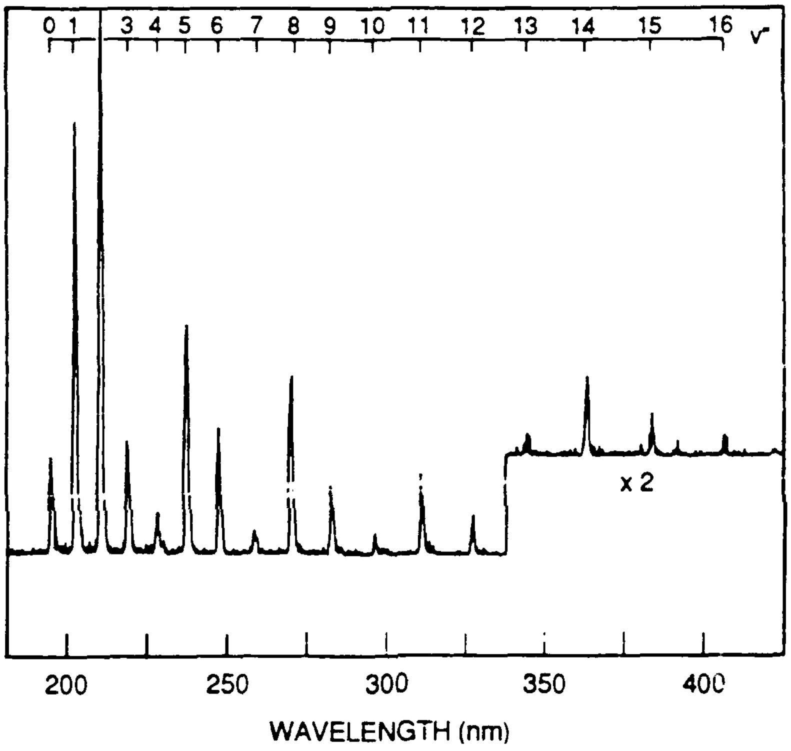
N(^{4}S) + O(^{3}P)
Dissociation Limit
$D^2\Sigma^+$
$C^2\Pi$
$b^4\Sigma^-$
$B^2\Pi$
$A^2\Sigma^+$
$L'^2\Phi$
$a^4\Pi$
$X^2\Pi$
0
0
0
0
0
0
0
65
60
55
50
45
40
35
20
15
10
5
0
ENERGY (10^3 cm^{-1})
0.10
0.15
0.20
INTERNUCLEAR DISTANCE (nm)
RA-7337-1

FIGURE 1



RA-7337-2

FIGURE 2



RA-7337-3

FIGURE 3

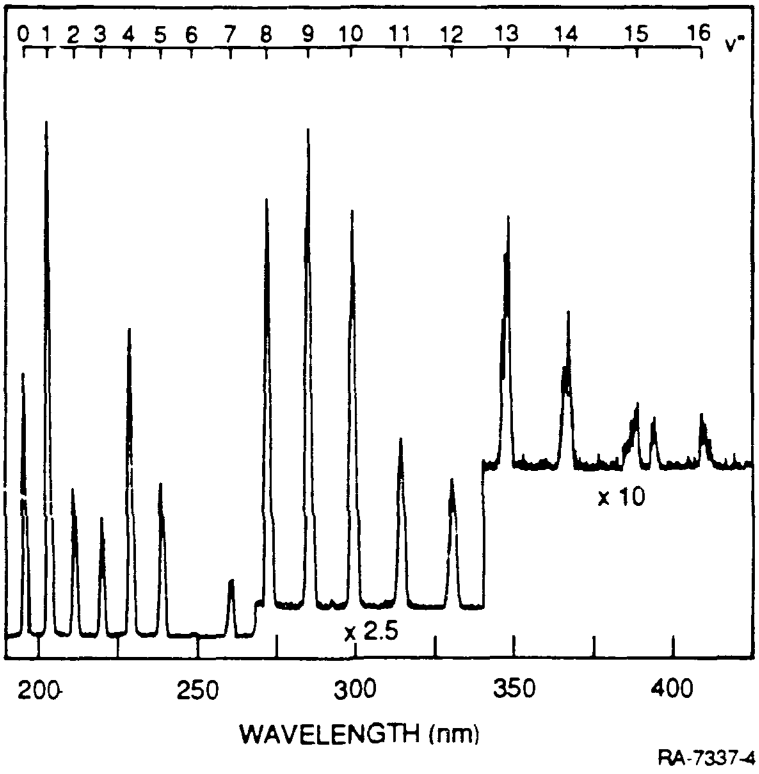
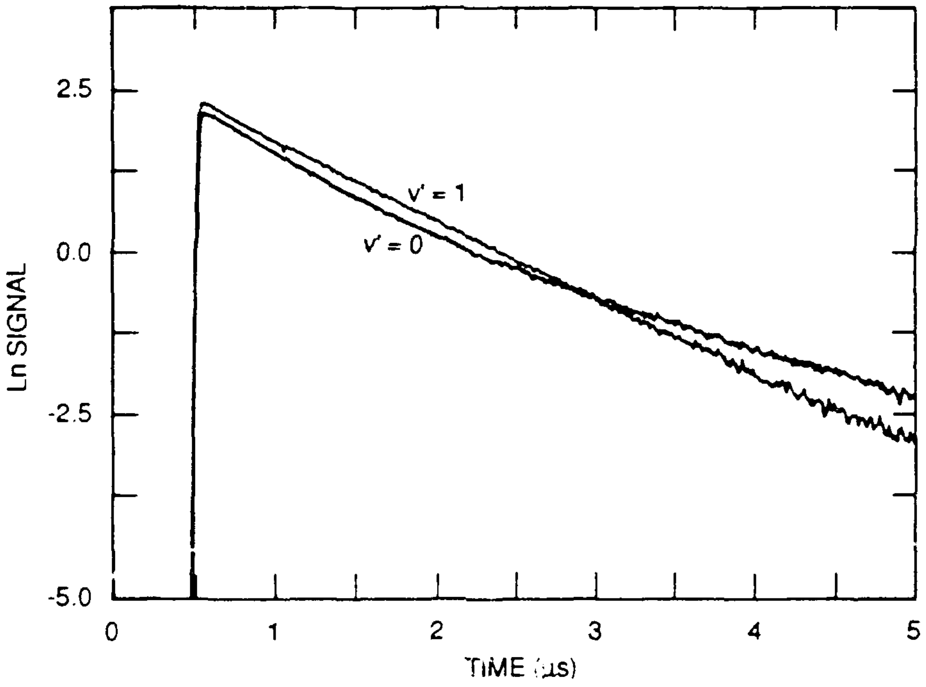
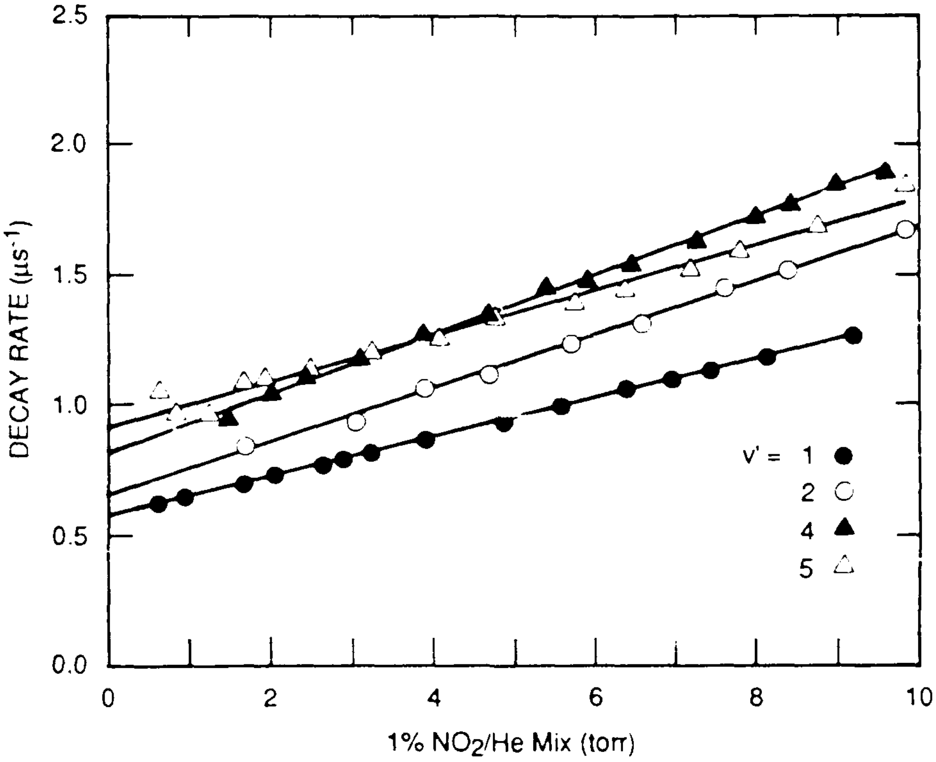

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 v"
x 10
x 2.5
200
250
300
350
400
WAVELENGTH (nm)
RA-7337-4

FIGURE 4



RA-7337-5

FIGURE 5



RA-7337-6

FIGURE 6

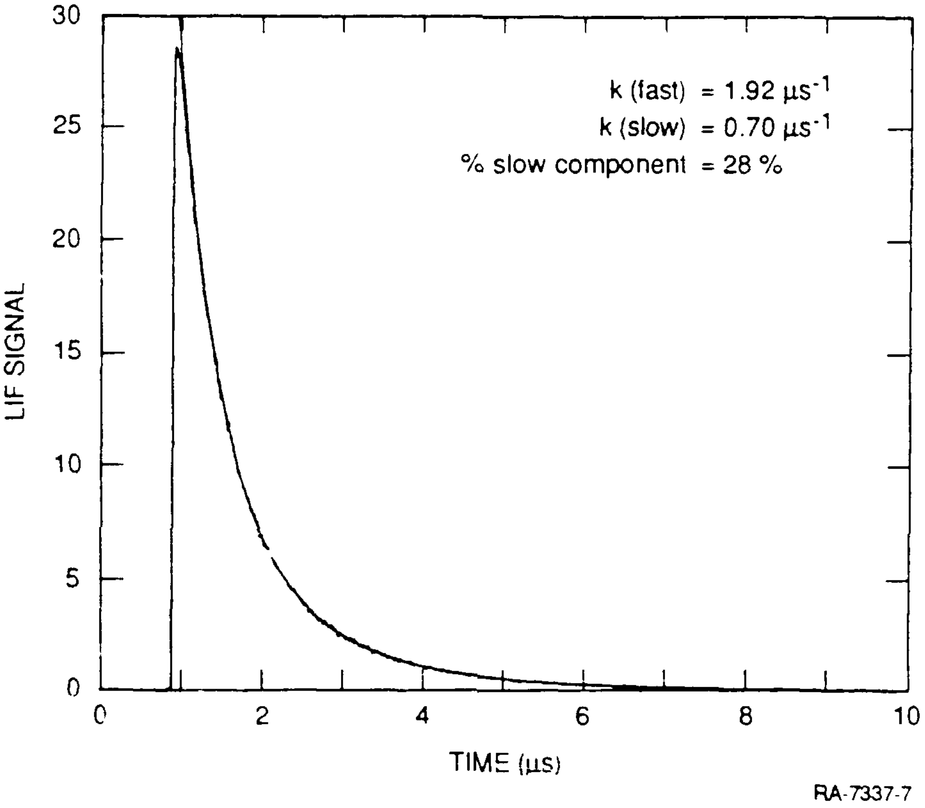
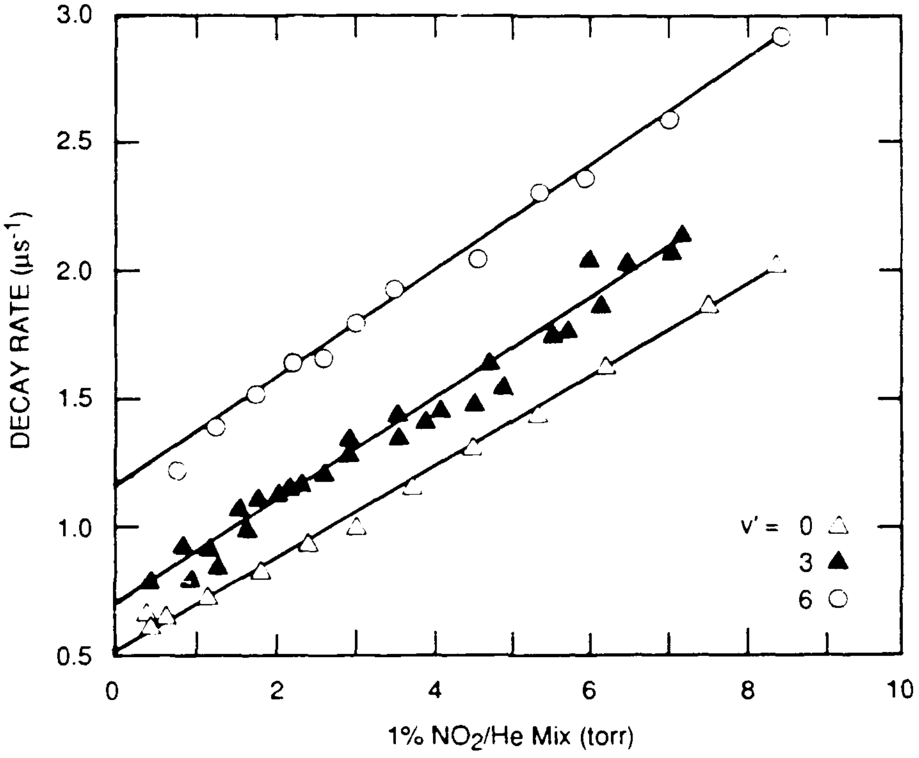

30
25
20
15
10
5
0
LIF SIGNAL
0
2
4
6
8
10
TIME (µs)
k (fast) = 1.92 µs-1
k (slow) = 0.70 µs-1
% slow component = 28 %
RA-7337-7

FIGURE 7



RA-7337-8

FIGURE 8

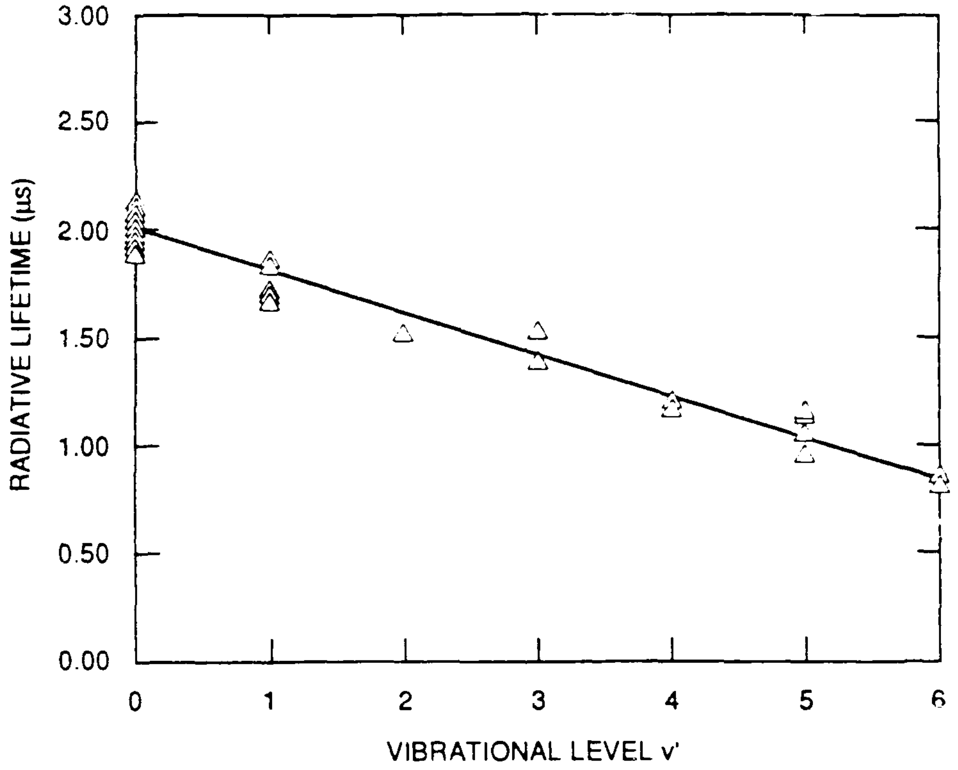
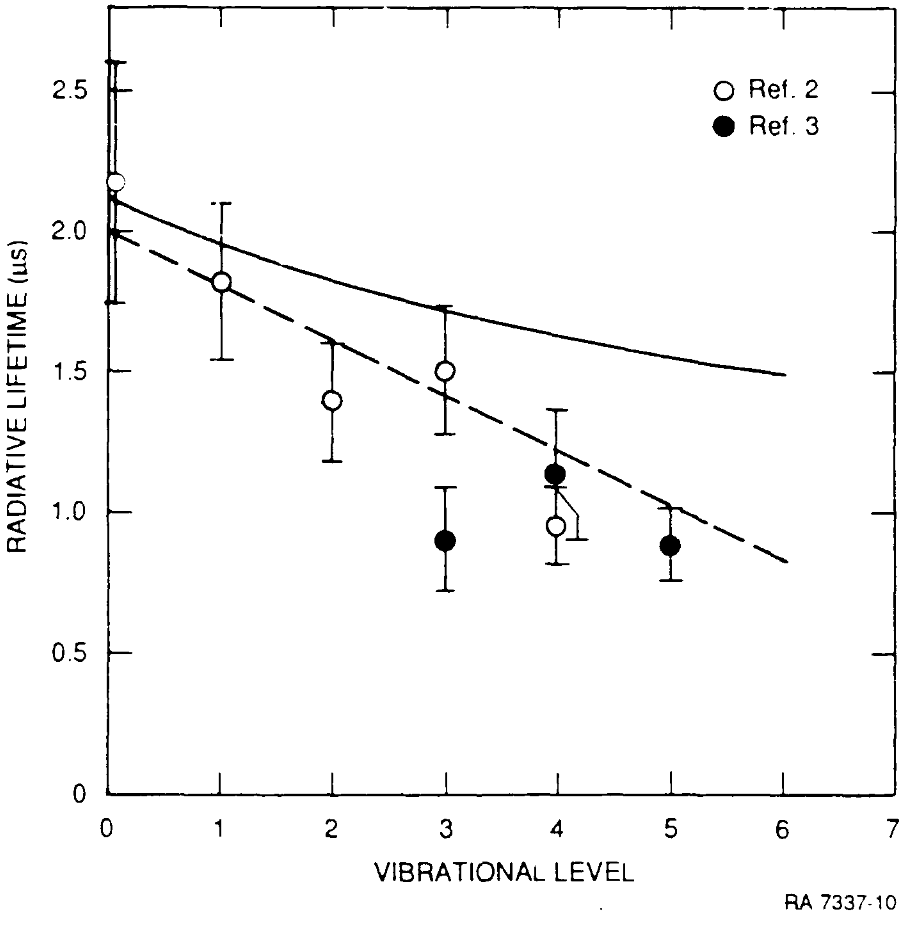
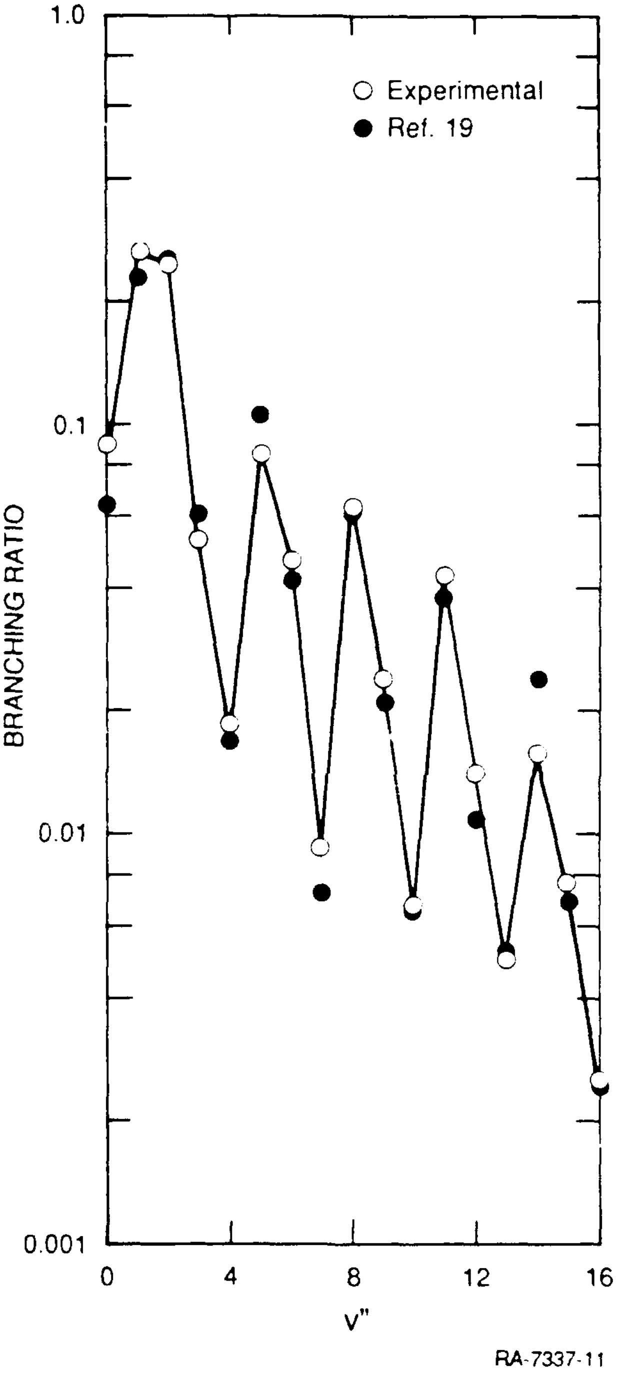

3.00
2.50
2.00
1.50
1.00
0.50
0.00
RADIATIVE LIFETIME (µs)
0
1
2
3
4
5
6
VIBRATIONAL LEVEL v'

FIGURE 9



2.5
2.0
1.5
1.0
0.5
0
RADIATIVE LIFETIME (µs)
0
1
2
3
4
5
6
7
VIBRATIONAL LEVEL
○ Ref. 2
● Ref. 3
RA 7337-10

FIGURE 10



1.0
0.1
0.01
0.001
BRANCHING RATIO
0
4
8
12
16
V"
○ Experimental
● Ref. 19
RA-7337-11

FIGURE II