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FINAL REPORT

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STUDIES OF NON-RADIATING SPECIES IN METAL + OXIDANT CHEMILUMINESCENT FLAMES

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Chemical production of metastable states of barium oxide in the gas phase have been studied under low pressure flow and molecular beam relaxation free conditions. Optical-optical double resonance excitation of ground state barium oxide has allowed measurements of excited state radiative lifetimes,

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electronic transition moments and a variety of energy transfer processes. The reactions of Barium with nitrous oxide and nitric oxide are found to produce mostly ground electronic state products, with some production of metastable triplet and singlet states. Electronic transition moments cannot be explained by simple atomic orbital descriptions of molecular states. Rotational relaxation in the first excited singlet pi state of barium oxide is found to be faster than gas kinetic and also exceeds the relaxation rate between lambda components of the pi state.

STUDIES OF NON-RADIATING SPECIES IN METAL + OXIDANT CHEMILUMINESCENT FLAMES.

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Introduction

Metal atom oxidation reactions have been of interest for several years, primarily due to the efforts to understand their luminescent behavior.[1] Measurements of photon yields under both molecular beam and flow conditions yielded valuable information on the kinetic production of visible light for these systems. Those chemiluminescent studies renewed the interest of spectroscopists to understand complex perturbed spectra of the metal oxides and metal halides, and helped them to develop new multiple laser techniques to probe the complicated spectroscopy.

This report documents several additional areas of progress in understanding the behavior of these chemiluminescent reactions.[2-7] These studies have established the electronic and vibrational state identities of the primary reaction products of the reactions of Ba with N_2O and NO_2, measured absolute electronic transition moments among excited electronic states of BaO, catalogued several new excited electronic states of BaO in the 4-6 eV range which show promise for accessing low lying Δ states around 2 eV, and measured directly the rotational relaxation and parity

relaxation rates in the acknowledged chemiluminescent gateway state ($A'^1\pi$) of BaO.

Results

We have concentrated on the two reactions Ba + N_2O and Ba + NO_2. Our first results on Ba + N_2O showed that under flow conditions, "dark" states of the reaction can be easily observed using laser induced fluorescence and we were able to observe ground state populations of vibrational levels that were iso-energetic with several of the low lying excited electronic states.[2] We also saw significant population in the metastable b $^3\pi$ state but were unable to interpret its population relative to the ground state due to a lack of electronic transition moment data.

To overcome that obstacle we initiated a series of single and double resonance experiments to accurately measure radiative lifetimes and electronic transition moments among the excited states of BaO.[3] These measurements were made under a variety of experimental conditions. Absolute radiative lifetimes were measured using nanosecond resolved fluorescence decay following pulsed optical double resonance excitation of various vibration-rotation levels of the BaO $C^1\Sigma^+$ state. The BaO $A^1\Sigma^+$ state was used as an intermediate state in these experiments, but only fluorescence with wavelengths shorter than 400 nm was observed, so that no interference from A state fluorescence occurred. The BaO was produced under molecular beam conditions using the reaction Ba + CO_2 to insure measurement of a collision free lifetime. Collisional effects were observed at higher pressures

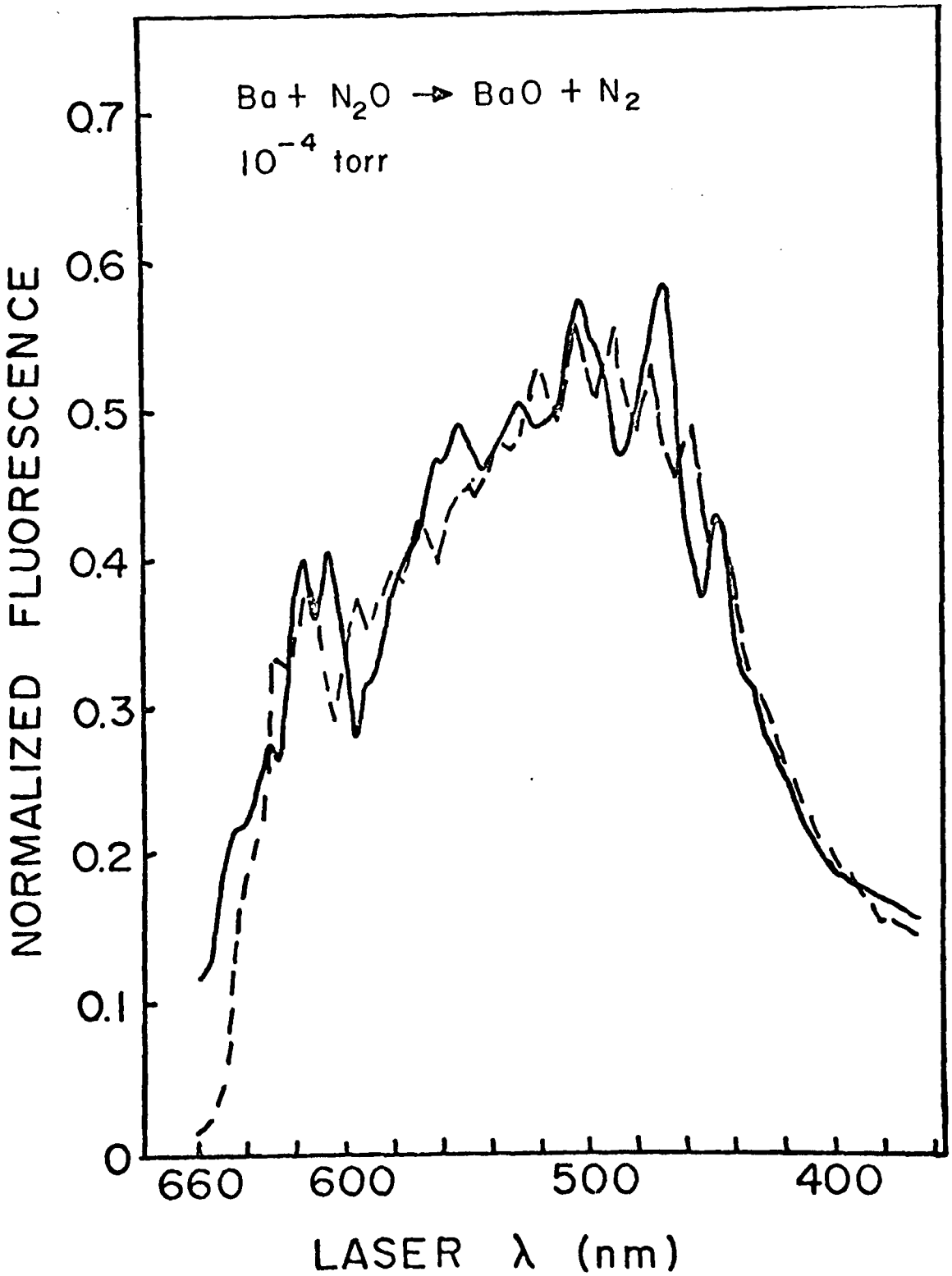
which indicates highly efficient energy transfer processes in energetic BaO states, but these effects could not be correlated with known BaO $C'\Sigma^+$ state perturbations and produced no observable satellite emission lines. The BaO $C^1\Sigma^+$ state (v=0) lifetime measured was 10.5 $\pm$ 1 nsec and was independent within error of the rotational level excited.

In separate experiments at higher pressures, fluorescence from the C state was spectrally resolved using a sensitivity calibrated detection system to measure the electronic emission branching ratios to various lower lying states. These measurements, coupled with Franck-Condon factor calculations and previously measured radiative lifetimes of the $A^1\Sigma^+$ and $A'^1\pi$ state, allowed the calculation of the following electronic transition moments: $\mu^2(C-X) = 9.9\ D^2$, $\mu^2(C-A) = 16.8\ D^2$, $\mu^2(C-A') = 9.8\ D^2$, $\mu^2(C-b) = 3.10\ D^2$, $\mu^2(A-X) = 3.2\ D^2$, and $\mu^2(A'-X) = 0.14\ D^2$. In addition, indirect arguments allowed an estimate of $\mu^2(B-X) = 4\ D^2$.

With relative electronic transition moments, we have now been able to interpret our laser fluorescence intensities and have studied both the Ba + NO_2 and Ba + N_2O reactions under molecular beam and flow conditions.[4] Since these results are only published in preliminary form,[6] a brief statement of the relevant facts is necessary. Under single collision molecular beam conditions we see predominantly ground state BaO products (90% X $^1\Sigma^+$ for Ba + N_2O, 99% X $^1\Sigma^+$ for Ba + NO_2). The vibrational state production, however is vastly different. The Ba + N_2O reaction produces an inverted vibrational distribution which peaks at v = 30 and extends only to $\pm$10 vibrational levels (see Figure 1). This represents a release of approximately 50% of the reaction exothermicity to

Figure 1. Excitation spectrum of BaO, normalized to constant laser intensity. All intensity between 400 and 600 nm corresponds to rotationally hot band spectrum of $C'\Sigma^+$ (v=5-20) ← $X'\Sigma^+$ (v=10-40). Dashed line represents computer simulation of the spectrum assuming a $X'\Sigma^+$ vibrational distribution peaked at v=30 with a width of ± 10 vibrational levels.

Figure 1


Ba + N2O → BaO + N2
10^-4 torr
NORMALIZED FLUORESCENCE
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
660
600
500
400
LASER λ (nm)

product vibration. The spectra appear rotationally unresolved with no band head formation, indicating very rotationally hot molecules. Even very high product vibrational levels showed hot rotational populations. No rotational contours were available to fit to any type of distribution, but we estimate a rotational temperature near $2000^{\circ} \pm 1000^{\circ}$. This would represent a mean rotational energy of ~25% of the exothermicity. All excited electronic states account for less than 10% of the product formation, but the individual contributions of $A^1\Sigma^+$, $A'^1\pi$, and $b^3\pi$ could not be assessed.

For the Ba + NO_2 reaction under molecular beam conditions, the results are strikingly different (see Figure 2). Partly because the reaction exothermicity is less, the product vibrational levels are considerably less energetic. In this reaction, 99% $\pm$5% of the molecules are produced in the ground electronic state but the vibrational distribution continues to rise below v = 6 and probably peaks near v = 0. This gives an average product vibrational energy which is only 20% of the reaction exothermicity. These ground electronic state molecules are, however, highly rotationally excited, indicating a significant fraction of the energy is released as product rotation.

The excited electronic states produced in the Ba + NO_2 reaction, however, are rotationally and vibrationally cold. Figure 3 shows the excitation spectrum in the area of the $C^1\Sigma^+ - A\ ^1\pi$ and $C'\Sigma^+ - b\ ^3\pi$ $\Delta v = 0$ systems. The spectra are rotationally relaxed and show strong band head structure.

These results show clearly the nascent formation of the $b\ ^3\pi$

Figure 2. Excitation spectrum of BaO, normalized to constant laser intensity. All intensity at 600 nm and shorter wavelengths corresponds to $C^1\Sigma^+ \leftarrow X^1\Sigma^+$ bands. Intensity is peaked towards $X^1\Sigma^+$ ($v < 10$) transitions.

Figure 2

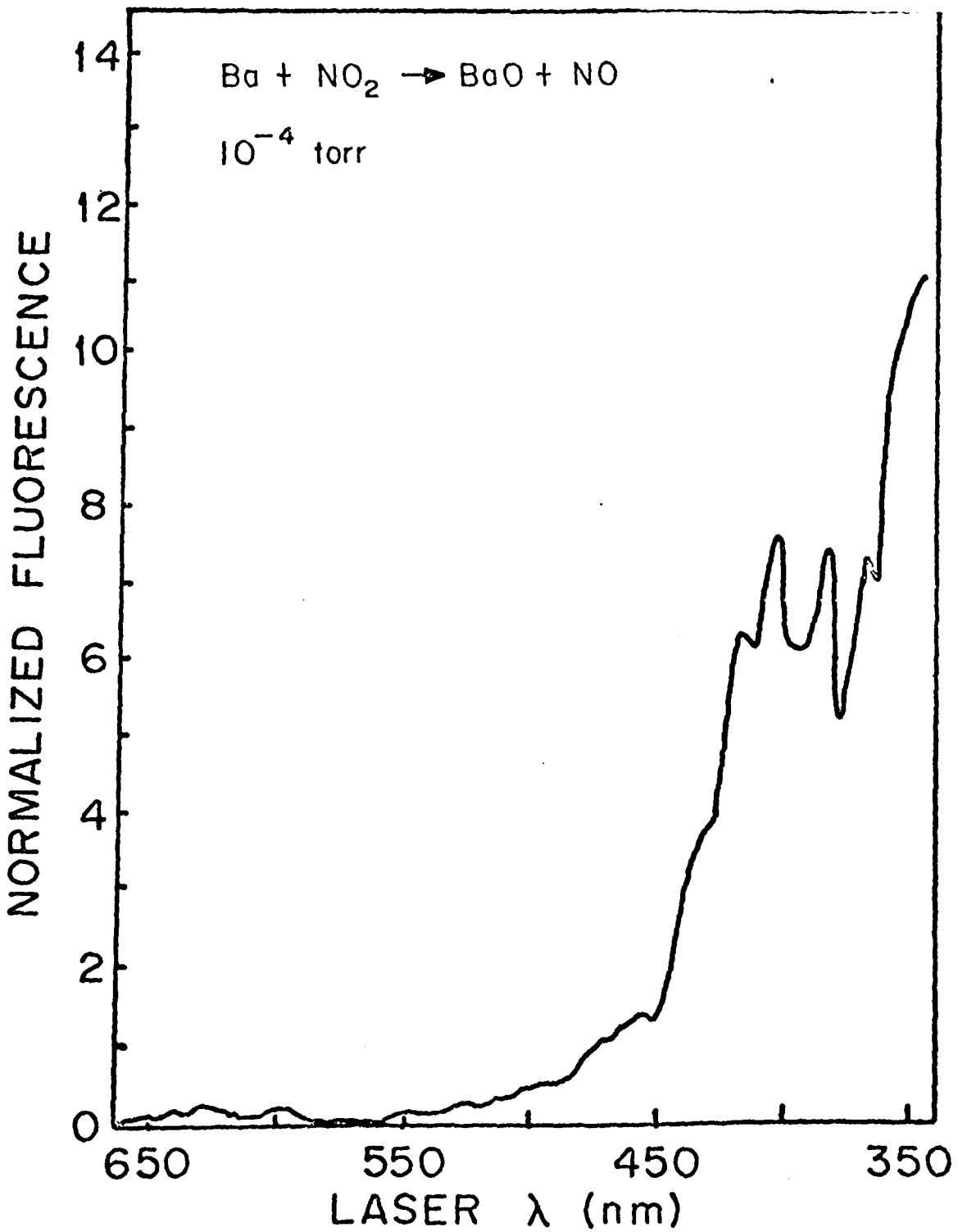
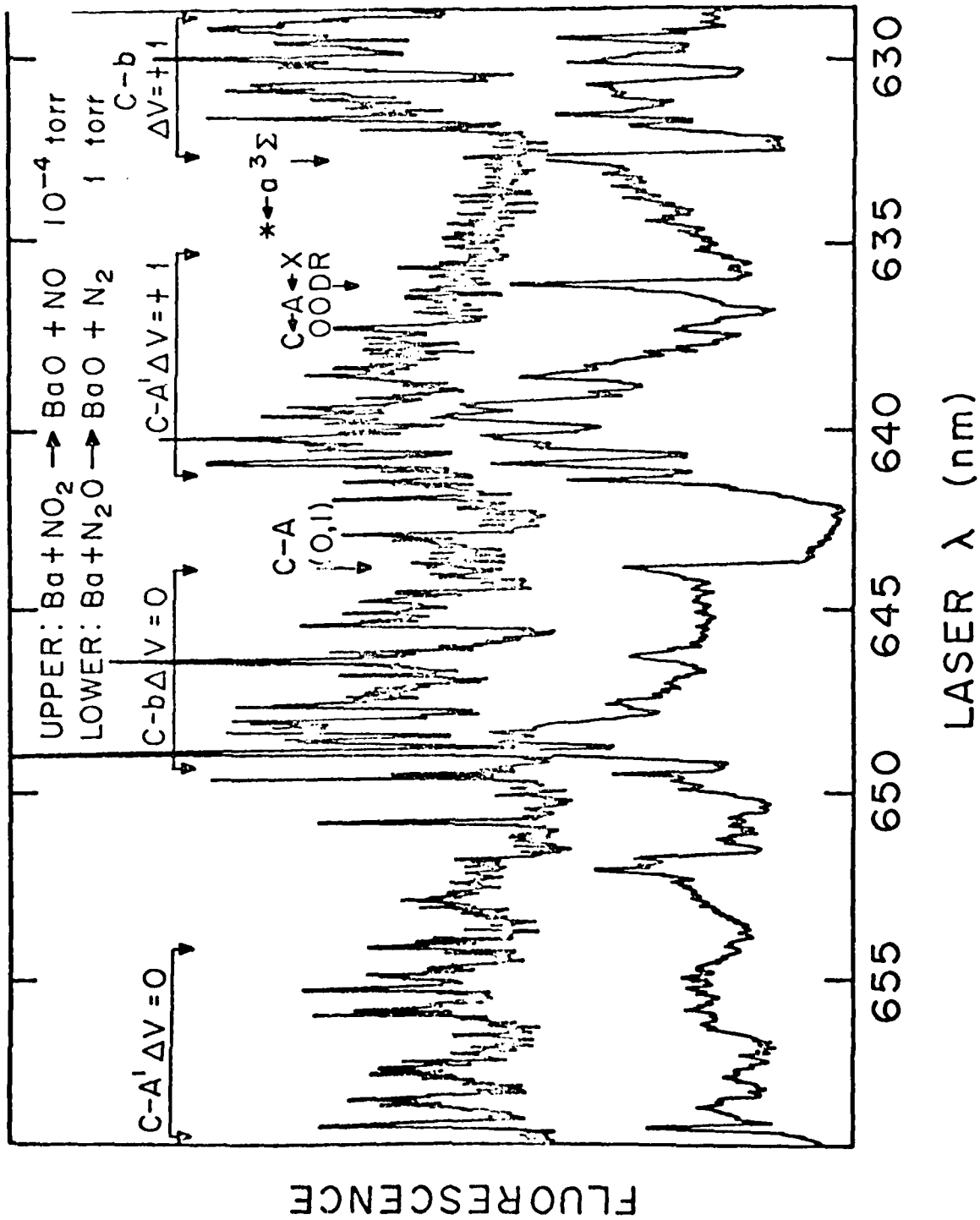

Ba + NO2 → BaO + NO
10^-4 torr
NORMALIZED FLUORESCENCE
0
2
4
6
8
10
12
14
650
550
450
350
LASER λ (nm)

Figure 3. Medium resolution (1 cm^{-1}) excitation spectra of BaO under two different conditions. High correlation between the spectra exist except at noteworthy locations: * ← $a^3\Sigma$ at 633 nm and accidental optical-optical double resonance on low J lines of the $C^1\Sigma^+ \leftarrow A^1\Sigma^+ \leftarrow X^1\Sigma^+$ (v=6) indicating low production of low J states in the beam reaction.

Figure 3


UPPER: Ba + NO2 → BaO + NO 10^-4 torr
LOWER: Ba + N2O → BaO + N2 1 torr
C-b ΔV=+1
C-A' ΔV=+1
C-b ΔV=0
C-A' ΔV=0
C-A (0,1)
C→A→X OODR
*→a 3Σ
630
635
640
645
650
655
LASER λ (nm)
FLUORESCENCE

state in a reaction for which triplet state products are spin forbidden. We can only monitor, however, the $^3\pi_1$ sublevel due to its spin orbit mixing with the $^1\pi$ state, and it is probable that this reaction channel is open primarily due to the singlet character of the $^3\pi_1$ sublevel.

In the flow condition (100 μ of Ar) reaction of Ba + N_2O three strong bands have been seen which we have now assigned to the a $^3\Sigma$ state of BaO recently seen by Gottsho et al. (see Figure 3).[9] This clearly shows the pooling of population through energy transfer into the lowest metastable state of BaO. It is interesting to note that these bands do not appear in the Ba + NO_2 beam condition experiments (Figure 3) confirming the hypothesis that spin forbidden products appear only to the extent that the molecular eigenstates are mixtures of spin basis functions. These bands do begin to appear, however, if the pressure in the beam scattering chamber is raised to 5×10^{-4} torr. This indicates a very rapid relaxation process.

As a natural outcome of our dynamic investigations we have also generated several noteworthy spectroscopic contributions to the level structure of BaO. High vibrational levels of the $C^1\Sigma^+$ state have been analyzed, lifetimes and absolute transition moments have been measured and direct observation of the a $^3\Sigma^+$ state has been accomplished.[5]

Two additional areas of interest have arisen from our studies to date. We have completed some preliminary experiments in which we have excited optical-optical double resonance in BaO using the $A'^1\pi$ state as an intermediate state.[5] The reason for this choice

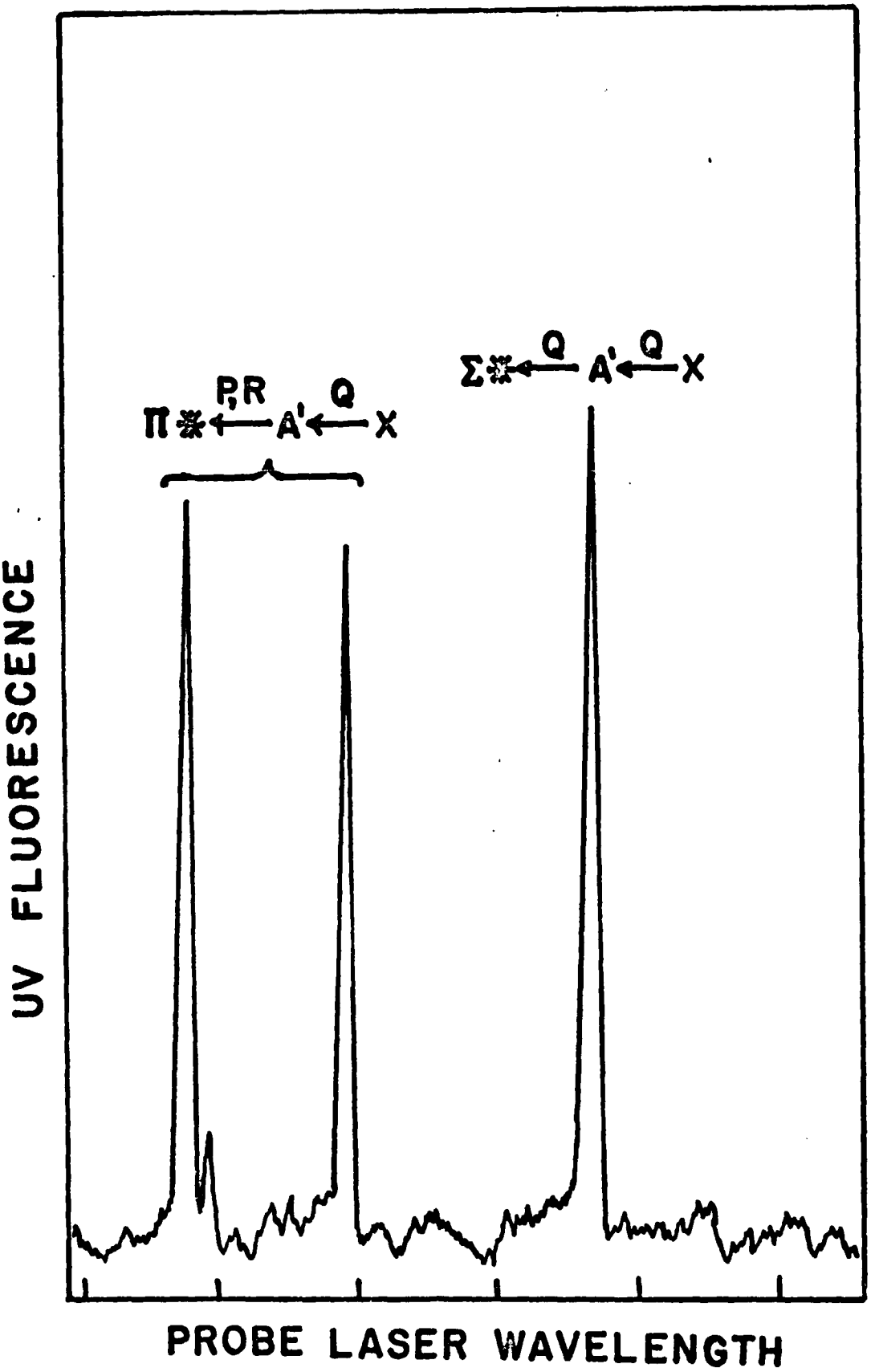
of intermediate states is two fold. Early and more recent double resonance experiments on BaO utilized the strong $A^1\Sigma^+$ - $X^1\Sigma^+$ transition as the first resonance.[8,9] Both studies were able to reach states of only $^1\Sigma^+$ character. By going to the $A'^1\pi$ state, new electronic states of BaO can be accessed (i.e. π or Δ states) with the eventual hope of resolving emission to the proposed lower $^1\Delta$ state presumed to be near the other low lying electronic states. The weak $A'^1\pi$ - $X^1\Sigma$ transitions can be isolated by narrow band pressure tuning of a nitrogen pumped dye laser with intracavity etalon, while observing lifetime delayed excitation spectra.[10]

Once an isolated P, Q, or R branch line is obtained, a second dye laser, synchronized to the first, can be scanned while observing ultraviolet fluorescence. The resulting double resonance signal reveals the electronic symmetry of the excited state through calculable two-photon line intensities, which vary sensitively with the laser polarization and symmetry of the upper state. Figure 4 shows one such striking result in which a Q branch line is pumped on the first transition. An upper state of Σ symmetry appears as a single line (Q branch) since P and R branches are, in this case, not allowed due to the population in the π state of only one Λ component of the Q branch line. For an upper π state, however, P, Q, and R branches are allowed with the Q branch being very weak at high J values.

The second reason for using the $A'^1\pi$ state as an intermediate state is that its long radiative lifetime allows enough time for many collisions to occur before significant radiative decay. Thus

Figure 4. UV fluorescence detected optical-optical double resonance in BaO using the $A'^1\pi$ state as an intermediate state. The first transition is fixed on a Q branch line of the $A'^1\pi \leftarrow X'\Sigma$ system, which selects an e parity level. Subsequent double resonance to an upper Σ state can only access an f parity level through a $\Delta J=0$ Q branch line. An upper π state, however, is identified by prominent pared R branches, since all J levels are doubly degenerate (neglecting Λ doubling or perturbations) with both parity levels available. The Q branch line of the $\pi \leftarrow \pi$ transition is very weak at moderate and high values of J.

Figure 4



if the second laser is delayed from the first, collisional transfer of energy out of the initially pumped rotational level and into nearby rotational levels of the same or of different electronic states can occur. This process can be followed easily as a function of delay time between the two lasers. Figure 5 shows a low resolution spectrum of the (10,9) band of the $C'\Sigma^+ - A'^1\pi$ system following pulsed exciation from the ground state to the $A'^1\pi$ state. Different delay times easily show the collisional relaxation effect.

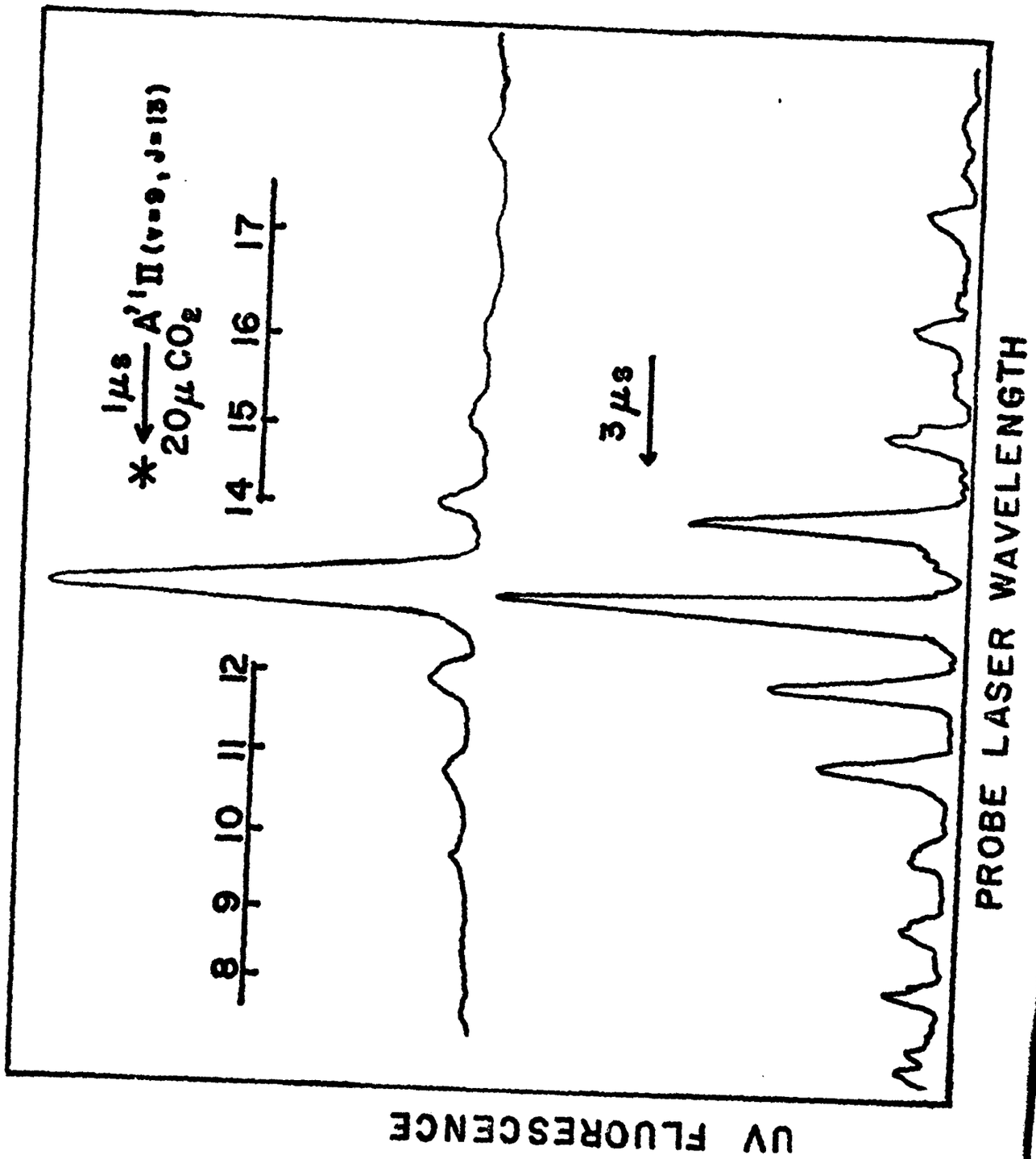
Since in a reasonably small spectral range we have access to all of the first four excited electronic states of BaO, all of the following types of energy transfer can be studied:

$M + A'^1\pi^e (V,J) \rightarrow$	$A'^1\pi^e (V,J')$	pure rotational relaxations
	$A'^1\pi^f (V,J)$	parity relaxation
	$A'^1\pi^e (V',J')$	rotation-vibration relaxation
	$A^1\Sigma^+ (V',J)$	electronic relaxation between perturbing level
	$A^1\Sigma^+ (V',J')$	electronic relaxation between non-perturbing levels
	$b\ ^3\pi (V',J')$	electronic relaxation between spin-orbit mixed levels
	$a\ ^3\Sigma$	spin non-conserving relaxation between unmixed levels

We have completed the study of the first two members of this list, with a manuscript now in preparation.[7] Our basic findings

Figure 5. Time delayed optical-optical double resonance spectrum showing prominent single parent rotational line (J=13) and weak satellite lines ($8 < J < 18$) at two different delay times between laser pulses. The two spectra are not normalized to constant total population. All signal dies away with the characteristic $A'^{1}\pi$ radiative lifetime of 10μsec.

Figure 5


1μs
20μ CO2
A'1Π (v=0, J=13)
14 15 16 17
3μs
8 9 10 11 12
PROBE LASER WAVELENGTH
UV FLUORESCENCE

are that rotational relaxation in BaO $A'^1\pi$ are faster than gas kinetic, and very similar to those of the BaO $A^1\Sigma^+$ state.[11] Parity relaxation, however, is significantly slower. This is important in the kinetic modeling of these systems because only one parity level of the $A'^1\pi$ state is perturbed by the $A^1\Sigma^+$ state. The result of this will be that population of the perturbed π state parity level will transfer efficiently into the radiating $A^1\Sigma^+$ state, while the other parity level will tend to relax within itself more quickly and decrease the chemiluminescent production.

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5. Yen Chu Hsu and J. Gary Pruett "Pulsed Optical-Optical Double Resonance in BaO Using the $A'^1\pi$ Intermediate State" in preparation.
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PUBLICATIONS:

PUBLICATIONS RESULTING FROM CONTRACT

1. Yen Chu Hsu, Bruce Hegemann, and J. Gary Pruett, "Lifetimes and transition moments among excited electronic states of BaO", J. Chem. Phys., 72, 6437 (1980).

2. R. W. Field, R. A. Gottscho, J. Gary Pruett, and J. J. Reuther, "Barium Oxide, the Questions Unanswered" Proceedings of the YAMADA Conference on Free Radicals (1979).

3. Yen Chu Hsu and J. Gary Pruett, "Nascent Metastable Products in the Reactions Ba + NO_2 and Ba + N_2O" J. Chem. Phys. (accepted for publication).

4. Yen Chu Hsu and J. Gary Pruett, "Pulsed optical-optical double resonance in BaO using the weak $A'^1\pi \leftarrow X^1\Sigma^+$ transition as an intermediate" (manuscript in preparation, to be submitted J. Mol. Spect.).

5. Yen Chu Hsu and J. Gary Pruett "Rotational and parity relaxation in the $A'^1\pi$ state of BaO" (manuscript in preparation, to be submitted to J. Chem. Phys.).

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