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STUDY OF MOLECULAR COLLISION DYNAMICS FOR CHEMICAL LASER SYSTEM--ETC(U)
MAR 82 J C BELLUM, N BURROWS AFOSR-80-0261

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Final Technical Report

for

Grant AFOSR - 80-0261

Study of Molecular Collision Dynamics for Chemical Laser Systems
on research carried out by

Institute for Modern Optics
Department of Physics and Astronomy
University of New Mexico
Albuquerque, NM 87131

Principle Investigator: Professor M.O. Scully

March, 1982

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FINAL REPORT

GRANT AFOSR - 80-0261

1 August 1980 to 31 October 1981.

Grant AFOSR - 80-0261 supported research based on our proposal entitled "Study of Molecular Collision Dynamics for Chemical Laser Systems." The research consisted of theoretical studies at the Institute for Modern Optics in conjunction with experimental work carried out at AFWL.

I. Report on Theoretical Research

The theoretical research for the 15 month period beginning 1 August 1980 is part of an ongoing research program begun prior to 1980 and aimed at developing molecular collision theories particularly suitable for analyzing rate processes which govern the mechanisms of chemical lasers. As outlined in the above mentioned proposal, our theoretical efforts under Grant AFOSR - 80-0261 focused on three basic goals.

First and foremost we continued our investigation of the statistical quasi-classical (SQC) method which we had developed earlier¹⁾ as an approach to calculating the dynamics of molecular collision processes. In the SQC method the Wigner distribution function describes the quantum states of colliding molecules before and after collision, and classical mechanics accounts for the collision dynamics. We studied the limit where the SQC method is exact, as in the case of a free wavepacket or harmonic oscillator.²⁾ We also began developing a perturbative scheme by which increasingly more accurate SQC solutions can be obtained. We applied this scheme to the case of a low-energy Morse oscillator³⁾, and initiated work on a similar analysis of particle-harmonic oscillator

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Chief, Technical Information Division

approximations to molecular collisions. Based on the SQC method we have been able to gain a good intuitive picture of quantum-mechanical motion and tunnelling in terms of trajectories.³⁾

Our next goal concerned treating electronic-vibrational energy transfer processes. Here the problems of dynamics on multiple potential energy surfaces must be confronted. We considered combining the basic SQC method for single-surface dynamics with the trajectory-based decoupling scheme which we developed earlier.⁴⁾ Prospects for approaches such as this look promising.

Our third goal of investigating fully quantum mechanical approaches for describing molecular collision dynamics complements our work on the SQC method. Eventually approximate classical or semi-classical treatments of collisions need to be tested against more accurate quantum-mechanical descriptions. We have considered improved distorted-wave Born approximations for basic atom-diatom molecule chemical reactions, as well as a rigorous quantum mechanical theory for electronic-vibrational-rotational (EVR) energy transfer processes. While such a rigorous quantum mechanical formulation has here-to-fore never been worked out in detail, it is, nevertheless crucial as the starting point for practical quantum mechanical calculations of EVR processes. Such EVR energy transfers play vital roles in many chemical lasers, and electronic energy exchange between excited oxygen ($^1\Delta$) and iodine is a primary example from the iodine chemical laser system. Other competing processes in this laser system, such as the feedback reaction, $I(^2P_{1/2}) + O(^1\Delta) \rightarrow I(^2P_{3/2}) + O(^1\Sigma)$, are also in this basic EVR energy transfer category. Our experience with the exact quantum mechanical theory of EVR processes has put us in a good position to carry out eventual quantum mechanical calculations.

The Wigner distribution function plays a fundamental role in physics in general, and our SQC method is but one of many examples of its usefulness. During the research period of this report seminal ideas were developed for a

major review of the Wigner distribution function, which we are currently writing in collaboration with Professor Wigner.

During this research period we also addressed some specific questions regarding iodine-laser chemistry. Based on extrapolations of data in the literature we found that the rates of quenching of $I^*(^2P_{1/2})$ by typical buffer gases (for example, He and Ne) and by I_2 molecules are very small in the temperature range 300 - 400 K, and in the case of buffer gases remain small down to temperatures in the range 100 - 150 K which obtains under typical supersonic conditions. Quenching rates for I_2 may, however, be appreciable in the lower temperature range. The role of water molecules in quenching $I^*(^2P_{1/2})$ was also found to be minor. We carried out an investigation of the ground state polarizability, α , of atomic iodine⁵⁾ and calculated upper and lower bound estimates of its value. All previous calculations of α yielded values below our lower bound estimate. This work points to the needs for a reassessment of the role of the polarizability of atomic iodine in connection with iodine laser chemistry, and for a more accurate recalculation of α .

The support of Grant AFOSR - 80-0261 helped foster, at the Institute for Modern Optics, a stimulating environment for research related to high-power laser systems. In addition to the work reported above on molecular dynamics pertinent to chemical laser mechanisms, we also investigated an interesting prospect for the use of high-power laser radiation, namely, laser-enhancement of nuclear β decay.⁶⁾

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II. Report on Experimental Research: Chemical Laser Pumping by Explosive Reactions

One of the major technological bottlenecks in current chemical high energy laser systems is the need for thorough mixing of the reagents used to sustain a population inversion by chemiluminescence reactions. Our research goal has been to investigate new chemical reaction systems where the reagents can be premixed and the mixtures ignited by low energy electrical or optical inputs. The resulting chemiluminescence reactions would be self-sustaining by branched chain kinetics and a chemically driven lasing region could be maintained by a continuous (or pulsed) flow of the premixed reagents.

The premixed reagents would, in general, consist of a fuel species and an oxidizer species. To sustain a branched chain reaction scheme the fuel and oxidizer mixture should be highly reactive, possess a low activation energy threshold, and be non-hypergolic. We have concentrated our studies on photosensitive oxidizers such as chlorine dioxide (ClO_2) and hydrazoic acid (HN_3) combined with carbon-containing fuel gases such as acetylene and halogenated hydrocarbons. Mixtures of these gases, and even the oxidizers themselves, can be ignited by single, 10-40 mJ, 20 nsec, focused ultraviolet light pulses from a rare gas-halide excimer laser (KrF for HN_3 or XeF for ClO_2). The nearly pin-point ignition region serves as the nucleus or starting point for a chemically driven shock front which then rapidly propagates down the bore of the reaction cell resulting in intense emission throughout the visible spectrum. The emission was observed well downstream from the UV laser ignition region in an observation side-arm using an Optical Multichannel Analyzer (OMA) system. Thus, the detonation reactions were observed in a region where the reaction was self-sustaining by branched chain kinetics and no significant excitation by the initial UV laser pulse occurred.

As one would expect from past spectroscopic studies of flames and detonations,¹ the detonation of acetylene and ClO_2 mixtures yields intense $\text{C}_2(d^3\Pi \rightarrow a^3\Pi)$ Swan band emission in the blue-green. Mixtures of HN_3 and acetylene yield, in addition to the C_2 Swan bands, strong $\text{CN}(B^2\Sigma \rightarrow X^2\Sigma)$ Violet band and $\text{CN}(A^2\Pi \rightarrow X^2\Sigma)$ Red band emission. The spectra from these detonations were then temporally resolved by gating the OMA detector to determine the time intervals following ignition when C_2 and CN emission was a maximum. The detonations were then probed at these times (typically of 100 μsec duration) for gain using 5 nsec pulses from a nitrogen pumped dye laser. Although visible wavelength lasers operating on the CN Red bands resulting from the photodissociation of CN containing molecules have been demonstrated,² our detonation reactions displayed only strong attenuation of the probe laser pulses. The initial gas mixtures were transparent to probe laser pulses, but throughout the 2 msec duration of the detonation essentially total attenuation was observed at probe wavelengths from 380 to 700 nm. After the detonation had subsided the medium was again transparent. This strong, essentially continuous absorption by the detonation medium is probably due to the formation of polymeric species¹ of the form $\text{C}_x\text{N}_y\text{H}_z$ ($x, y > z$). These species are transient in nature, since proper oxidizer/hydrocarbon mixture ratios did not yield visible soot formation or accumulation in the reaction cell even after several dozen detonations. This transient nature is further confirmed by the aforementioned probe laser attenuation which occurs only during the detonation.

For the CN Violet bands this strong absorption is also consistent with the observation of radiation trapping by high concentrations of $\text{CN}(X^2\Sigma)$ ground state molecules. Radiation trapping manifests itself in the form of strong, time-dependent variations in the relative intensities of the $\text{CN}(B \rightarrow X)$ $\Delta v=0$ and $\Delta v=-1$ bands during the course of the detonations. Time resolved spectra from detonations of a typical reaction mixture are displayed in Figure 1.

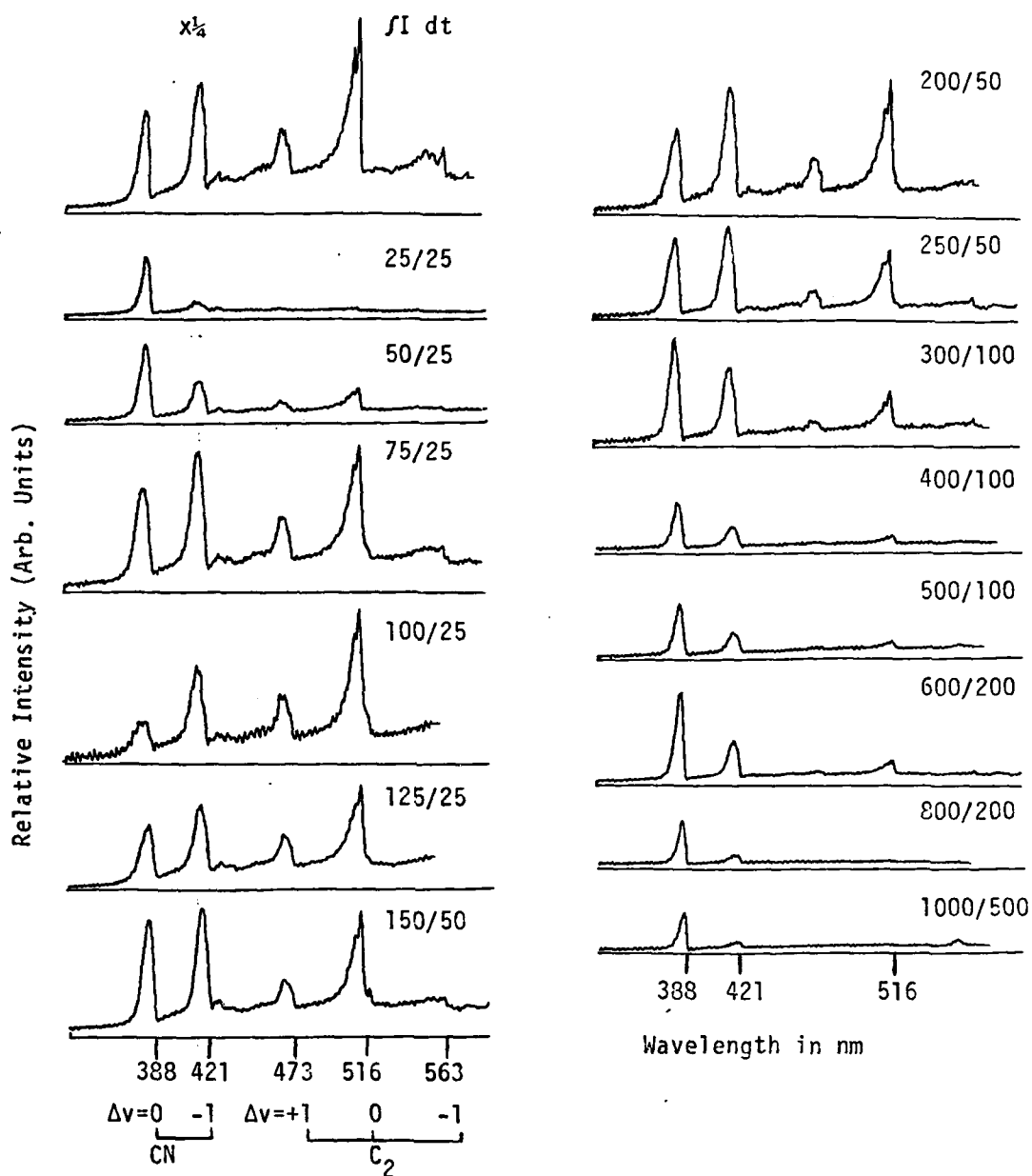
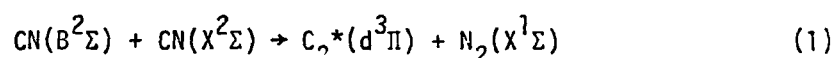


Figure 1. Time evolution of emission intensity from the detonation of mixtures of 40 Torr HN_3 + 40 Torr C_2H_2 + 120 Torr N_2O + 120 Torr Helium. The same relative intensity scale applies to all spectra and the spectrum labeled $\int I dt$ was accumulated over the total time duration of the detonation. The time delay/ observation time interval (both in μsec) is given to the right of each spectrum. The CN $\Delta v=0, -1$ Violet band heads are at 388.3 and 421.6 nm, respectively, while the C_2 $\Delta v=-1, 0, +1$ Swan band heads are at 563.6, 516.5, and 473.7 nm, respectively.

These variations are most dramatic when the C_2 Swan band emission intensity is a maximum and, in fact, the variations occur only for times when C_2 emission is observed. In addition, at those times when C_2 emission peaks, CN emission on the $\Delta v=0$ and $\Delta v=-1$ bands is observed to decrease in intensity (Figure 2). Hence, in our HN_3 plus acetylene detonations a major portion of the C_2 Swan band emission is due to the reaction



with radiation trapping of $CN(B \rightarrow X)$ emission serving as a time extended source of $CN(B^2\Sigma)$. The $CN(B^2\Sigma)$ excitation energy of approximately 3.3 eV is sufficient to overcome the activation energy of 43 kcal/mole given by Greene³ for the reaction $2CN(X^2\Sigma) \rightarrow C_2(a^3\Pi) + N_2(X^1\Sigma)$, who also measured a rate of $2.6 \times 10^{-9} \exp(-43 \text{ kcal/RT})$ for this reaction in the shock tube decomposition of BrCN. The exact mechanisms for C_2 Swan band excitation in a wide variety of sources is still the subject of debate¹, but our work, which extends that of Greene, demonstrates that the CN radical is a major C_2 precursor in combustion systems where nitrogen is present in the fuel or oxidizer. In combustion processes involving oxygen (such as our ClO_2 plus acetylene mixtures), a different C_2 excitation mechanism is operative.

The exact mechanism of CN formation and excitation is unknown and we can propose no consistent single mechanism for CN formation in our detonation experiments. Once CN radicals are formed, however, they can be electronically excited by a modification of the reaction scheme originally proposed by Bayes⁴, with free CN radicals catalyzing the recombination of azide (N_3) radicals.

The reaction sequence



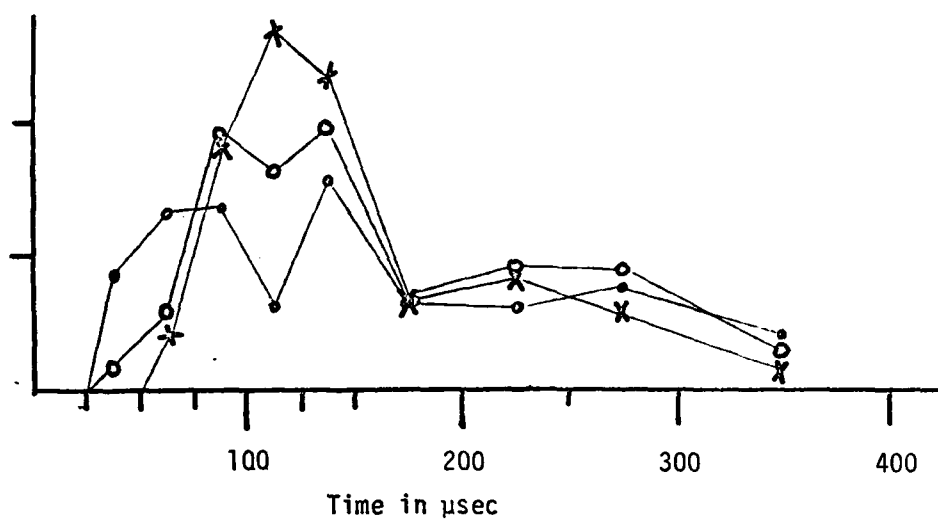
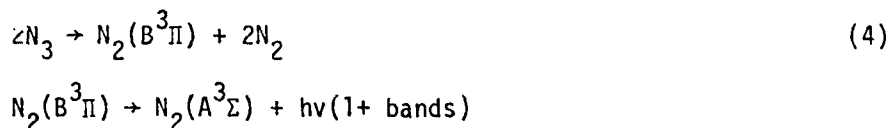


Figure 2. Time profiles of peak C_2 and CN emission obtained from time resolved spectral sequence in Figure 1. The time axis increments correspond to the observation time intervals in Figure 1. (x) denotes $C_2(d \rightarrow a)$ at 516.5 nm, (o) CN(B $\rightarrow$ X) at 421.6 nm, and (•) CN(B $\rightarrow$ X) at 388.3 nm. The dips in CN(B $\rightarrow$ X) emission intensity for the 388.3 and 421.6 nm bands that occur when $C_2(d \rightarrow a)$ reaches a maximum are attributed to reaction (1).

has a net exothermicity of 8.6 eV for an N-N₂ bond energy⁵ of 0.6 eV. If this energy is partitioned equally among the CN radical and the three N₂ molecules, the N₂ will be vibrationally excited and CN(A²) could be excited to a v' of 3 to 4. The CN(A X) emission intensities in our detonation spectra are peaked at v'=3 (Figure 3), indicating that the reaction exothermicity is almost equally partitioned. The gas phase decomposition of azide radicals produced by the thermal decomposition of sodium azide (NaN₃) has been observed⁶ to yield nitrogen first positive band emission due to the reaction



Although N₃ radicals are a major chain propagation species in the photolytic⁵ decomposition of HN₃, we did not observe N₂(B→A) or N₂(A³Σ→X¹Σ) emission (the Vegard-Kaplan bands) in our detonations of pure HN₃ or HN₃ plus acetylene mixtures. The possibility exists, however, that laser initiated detonations at shorter wavelengths such as 193 nm (ArF excimer) or 157 nm (F₂ laser) will alter the decomposition kinetics sufficiently to permit N₂(B³Π) and, therefore, N₂(A³Σ) excitation by reaction (4). At 157 nm essentially all the F₂ photons (10 mJ from commercial excimer lasers) will be absorbed by HN₃ compared with only 1% absorption which we currently achieve at 248 nm (KrF). The primary photodissociation fragment (NH(c¹Π)) is much more highly excited than the corresponding primary fragment⁵ (NH(a¹Δ)) for 248 nm excitation, which should alter the HN₃ decomposition kinetics significantly. Chemical generation of N₂(A³Σ) would be an attractive chemical laser pumping scheme since these molecules possess 6.2 eV of excitation energy while being reasonably metastable (radiative lifetime of one second). Thus, they could serve as a chemically pumped energy transfer source analogous to O₂(¹Δ) in the oxygen-iodine laser. An ideal N₂(A³Σ) energy transfer partner possessing a nearly gas kinetic

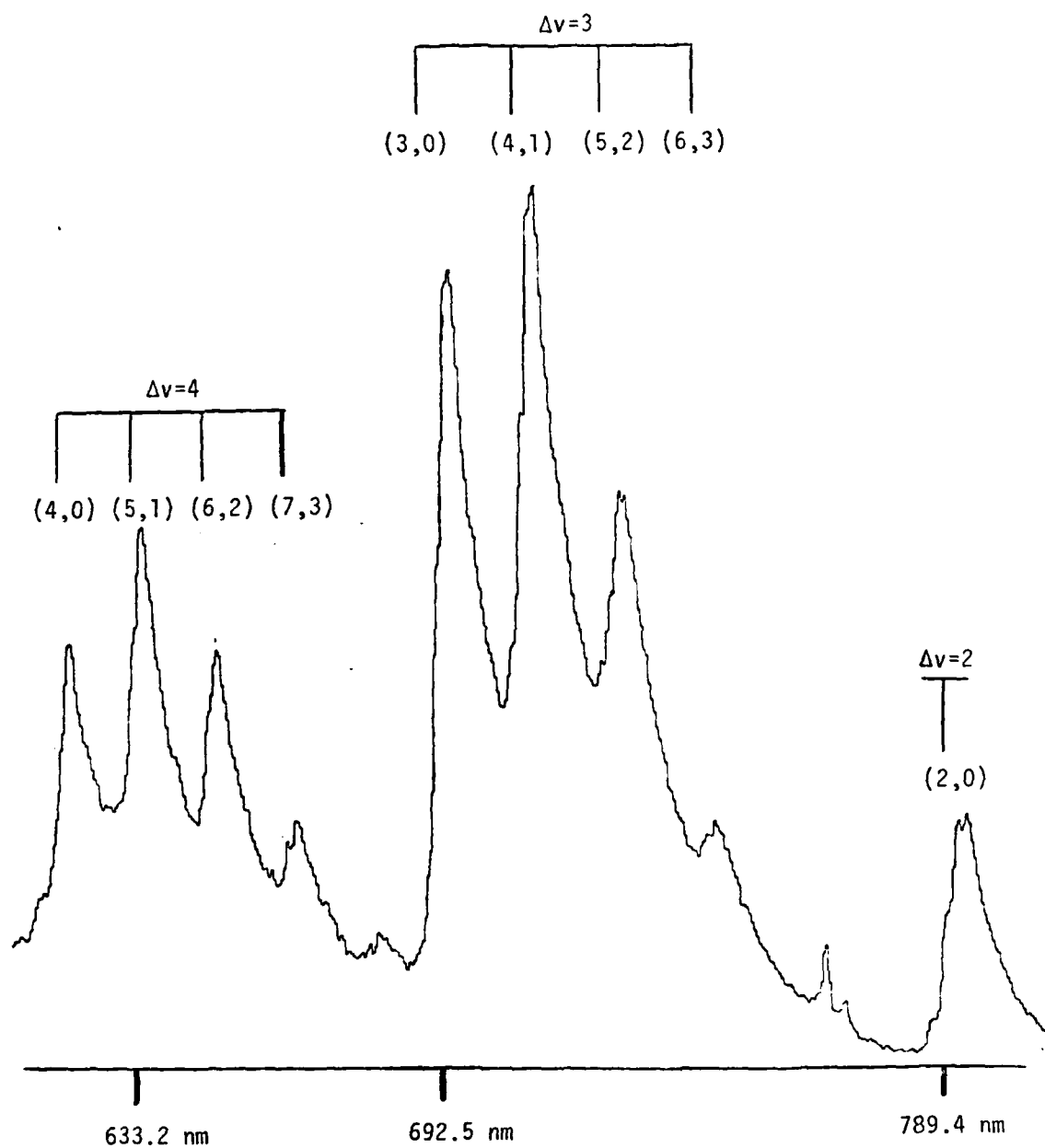
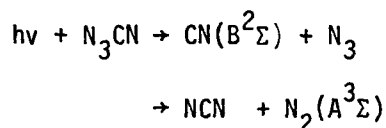
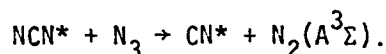
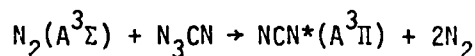


Figure 3. Spectrum of CN Red band ($A^2\Pi \rightarrow X^2\Sigma$) emission integrated over the duration of a detonation of a mixture of 60 Torr HN_3 + 20 Torr C_2H_2 + 120 Torr of Helium. Unlike the case for the CN Violet bands in Figure 1, no time-dependent variation in the various CN Red band intensities was observed.

rate⁷ would be nitric oxide (NO), which would yield NO⁺-band emission in the ultraviolet near 250 nm for the $\text{NO}(A^2\Sigma(v'=0) \rightarrow X^2\Pi(v''=2))$ transition. An additional $\text{N}_2(A^3\Sigma)$ source is the photolytic decomposition^{5,8} of cyanogen azide (N_3CN). At 157 nm the primary photolysis channels for N_3CN are



followed by



Thus, the photolysis of N_3CN or mixtures of N_3CN and HN_3 may be expected to yield $\text{N}_2(A^3\Sigma)$.

While we have not succeeded in making an explosively pumped visible wavelength laser using hydrocarbon fuels, the premixed reagent concept remains an enticing chemical laser concept due to its inherent technical simplicity. The use of higher exothermicity fuels such as PH_3 or BH_3 with ClO_2 or HN_3 to generate PO^* or BO^* is one area that warrants examination. Phosphorous or boron containing fuels are highly reactive, but these elements also tend to polymerize and the possibility of polymer formation, as in the carbon fuel case, cannot be ruled out. A photolytically initiated $\text{N}_2(A^3\Sigma)$ to NO transfer pumping scheme is also attractive and would be circumvent the polymer formation problem.

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