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SPECTROMETRIC STUDIES OF FAST REACTIONS

Chemistry Department
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COMPLETED PROJECT SUMMARY

1. TITLE: Spectrometric Studies of Fast Reactions

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3. CONTRACT NO: AF 49 (638)-1257

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Mr. Robert V. Fitzsimmons
Mr. Pradip K. Ghosh
Mr. Kenneth A. Mantei

6. PUBLICATIONS:

Distribution and Relaxation of Vibrationally Excited Oxygen in Flash Photolysis of Ozone, J. Chem. Phys., 40, 451 (1964), Robert V. Fitzsimmons and Edward J. Bair

Study of Vibrationally Excited Oxygen by High Resolution Absorption Spectroscopy Ph.D. Dissertation, Indiana University, Robert V. Fitzsimmons

Hydrogen Atom Induced Decomposition of Hydrazine in Atomic Flame, Ph.D. Dissertation Indiana University, Pradip K. Ghosh

Recombination and Disproportionation of NH_2 Radicals, John D. Salzman and Edward J. Bair, J. Chem. Phys., 41, 3654 (1964)

Kinetic Spectroscopy of Energy Chain Mechanisms in Ozone Decomposition, Ph.D. Dissertation, Indiana University, Vernon D. Baiamonte

Vibrational Energy of Ozone During Photolytic Explosion, Vernon D. Baiamonte, David R. Snelling and Edward J. Bair, J. Chem. Phys., 44, (1966)

Decomposition of Ozone by $O(^1D)$ Atoms, David R. Snelling, Vernon D. Baiamonte and Edward J. Bair, J. Chem. Phys. (Submitted for Publication)

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The project was undertaken in order to develop and demonstrate new spectroscopic procedures for studying both the detailed path and the elementary processes of photolytically initiated explosions, similar in some respects to combustion reactions which also proceed by free radical and energy chain mechanisms. Following the development of a highly reproducible reaction system, different spectroscopic features of the same system are studied by repeating the reaction. Special precautions to ensure that the reacting system is homogeneous tend to isolate the chemical dynamics part of the combustion problem from the fluid dynamics part. With long absorption path and low sample pressure the time resolution of the measurements is reasonably comparable with the time between intermolecular collisions. A fast, high resolution spectrometer designed specifically for this work resolves transient energy features such as the rotational fine structure of free radical absorption with a time resolution of about a microsecond.

The explosive decomposition of ozone was shown to be an energy chain reaction process by relating at least eight different dynamic properties of the same explosion system to features of the time resolved spectrum.

The timing of the time resolved rotational-kinetic temperature increase was measured from the rotational fine structure of oxygen formed by the reaction. Its dependence on the energy of the photolysis flash and on the pressure of added inert diluents shows that the energetics of the reaction cannot be understood in terms of the kinetic energy alone.

The rate of vibrational excitation of ozone, observed as a shift in the ozone spectrum toward longer wavelength and interpreted in terms of a semi-empirical model of the vibrational energy levels, shows that the vibrational temperature of ozone increases faster than the kinetic temperature of the system. While this vibration-

vibration energy transfer appears to be important at most ordinary temperatures, it is faster when the kinetic temperature is higher.

Criteria were developed by which the dynamic quantum yield can be measured in ozone photolysis in order to isolate and distinguish specific secondary processes according to their dependence on temperature, pressure and composition.

In inert gases $O(^1D) + O_3 \rightarrow 2\ O_2\dagger$ is far more rapid than other secondary processes. Its rate and temperature dependence could therefore be examined directly from the ozone decay.

When a large excess of nitrogen is added to the reaction mixture, $O(^1D) + N_2 \rightarrow N_2O^* \rightarrow N_2 + O(^3P)$ becomes the fastest secondary process. Under these conditions the rate of this spin conversion process can be measured directly from the ozone decay.

In nitrogen, as well as in the later stages of the decomposition of pure ozone, vibrationally excited oxygen is formed entirely by the process $O(^3P) + O_3 \rightarrow 2\ O_2\dagger$. The timing of the appearance of the vibrationally excited oxygen distinguishes decomposition of ozone by $O(^1D)$ and $O(^3P)$ and the distribution of the energy of these processes.

The rate of the $O(^3P) + O_3 \rightarrow 2\ O_2\dagger$ reaction derived from ozone decay curves in different gas mixtures at different temperatures indicates that the effective temperature of the reaction is the vibrational temperature of the ozone when that is higher than the kinetic temperature.

In combination, these studies constitute the most detailed examination of an energy chain process that has been made in any laboratory. It opens up a number of new areas for studying energy transfer processes and their interrelationships.

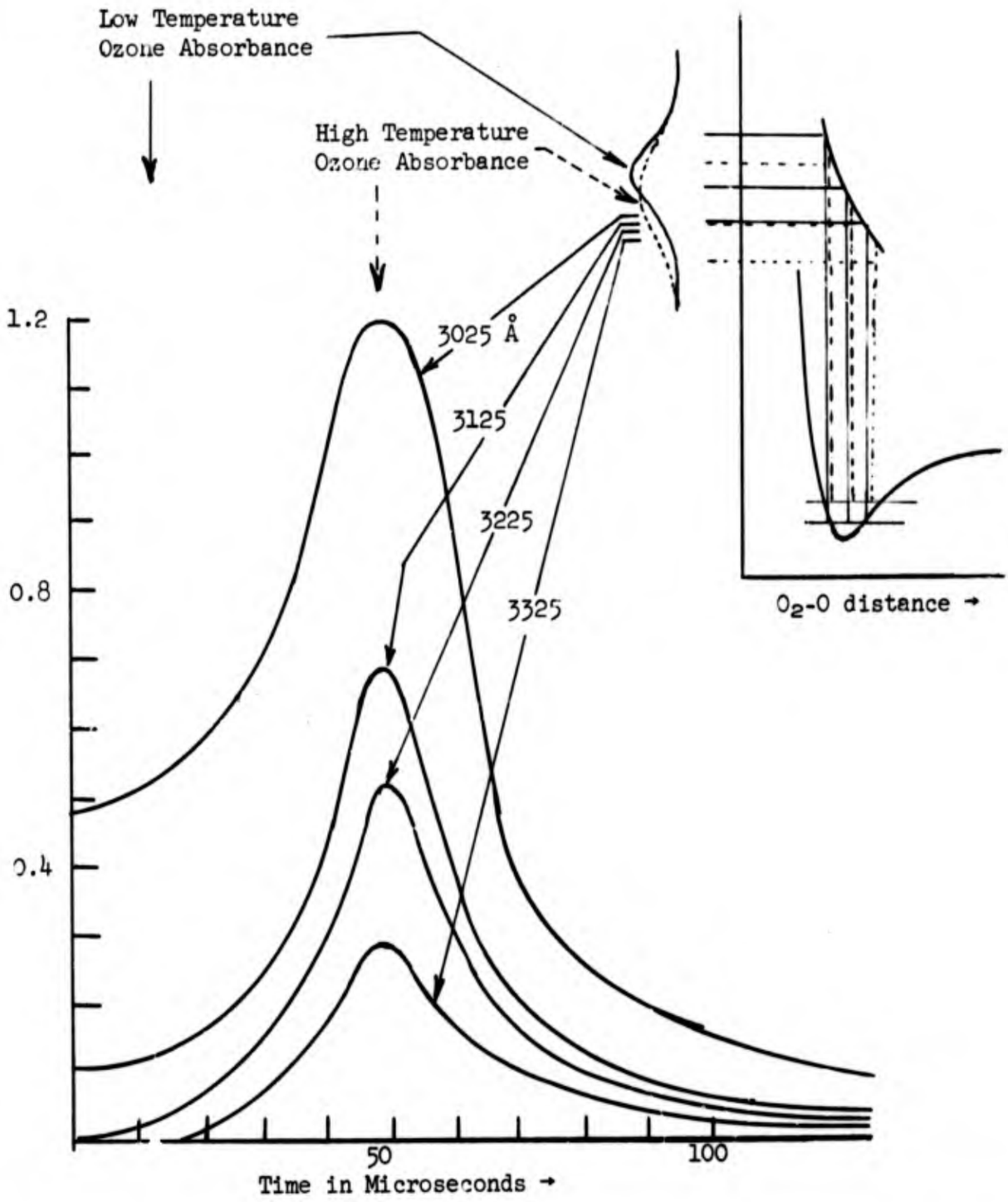
The explosive decomposition of hydrazine, on the other hand, is characterized by free radical chain processes in which the variety of different chemical substances appears more significant than the details of the energetics of their reactions. The nitrogen-hydrogen radical system was studied in this project by photolysis of both ammonia and hydrazine. Spectra arising from at least four different substances are observed.

NH_2, characterized by a system of lines in the 4000-6000 Å region, is formed as the primary photolysis product in both ammonia and hydrazine. In ammonia its disappearance is second order and found to be both recombination and disproportionation.

The NH radical, characterized by lines in the vicinity of 3000 Å, appears at a rate consistent with the disappearance of NH_2 in both ammonia and hydrazine photolysis.

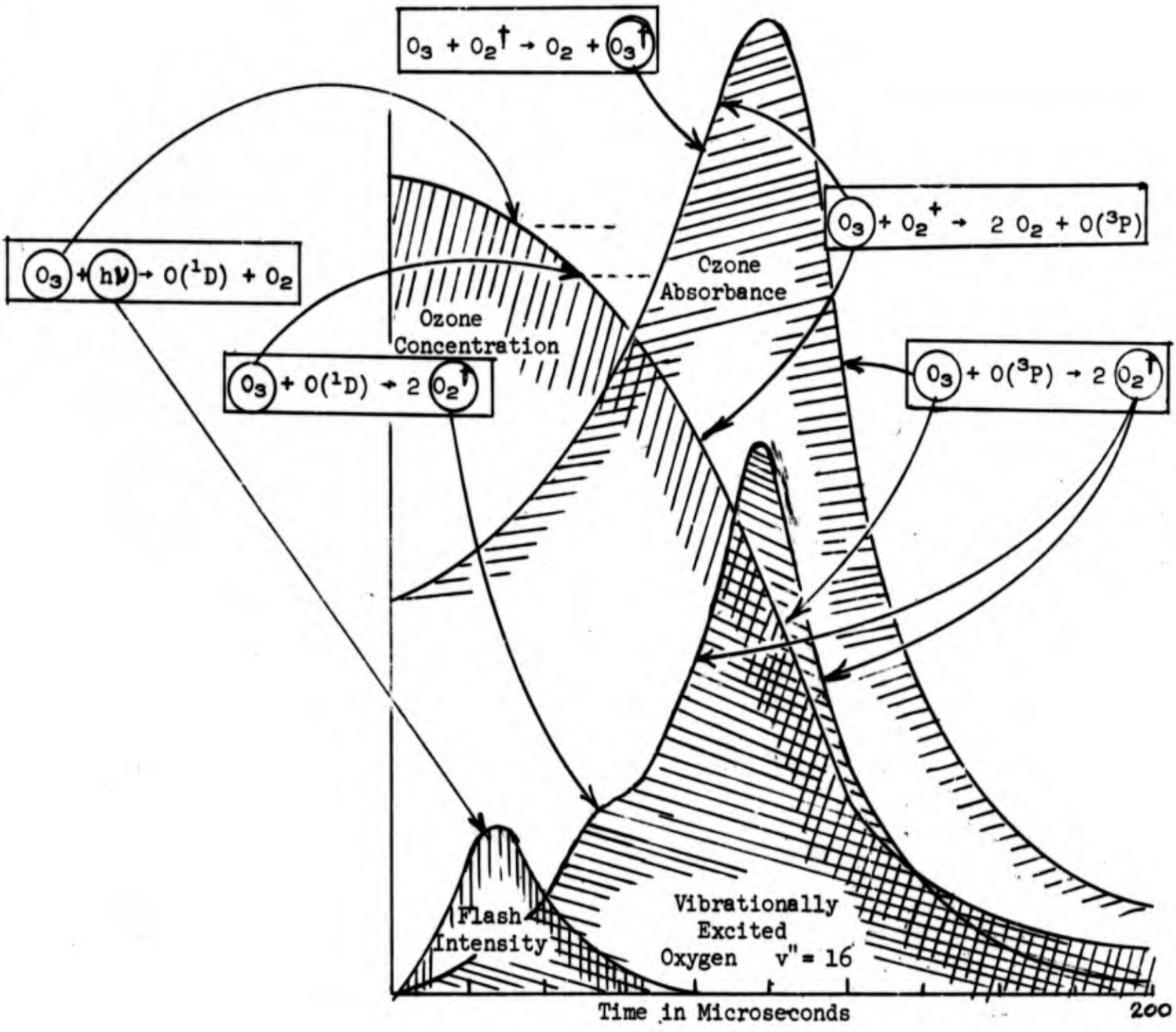
A weak, continuum in the vicinity of 3000 Å is associated with hydrazine.

A transient, diffuse spectrum not previously observed arises in the 6000 Å region concurrently with the disappearance of NH in hydrazine photolysis and is tentatively attributed to the hydrazyl radical, N_2H_3, which has been found in mass spectrometer studies of nitrogen-hydrogen systems but has not previously been seen spectroscopically.

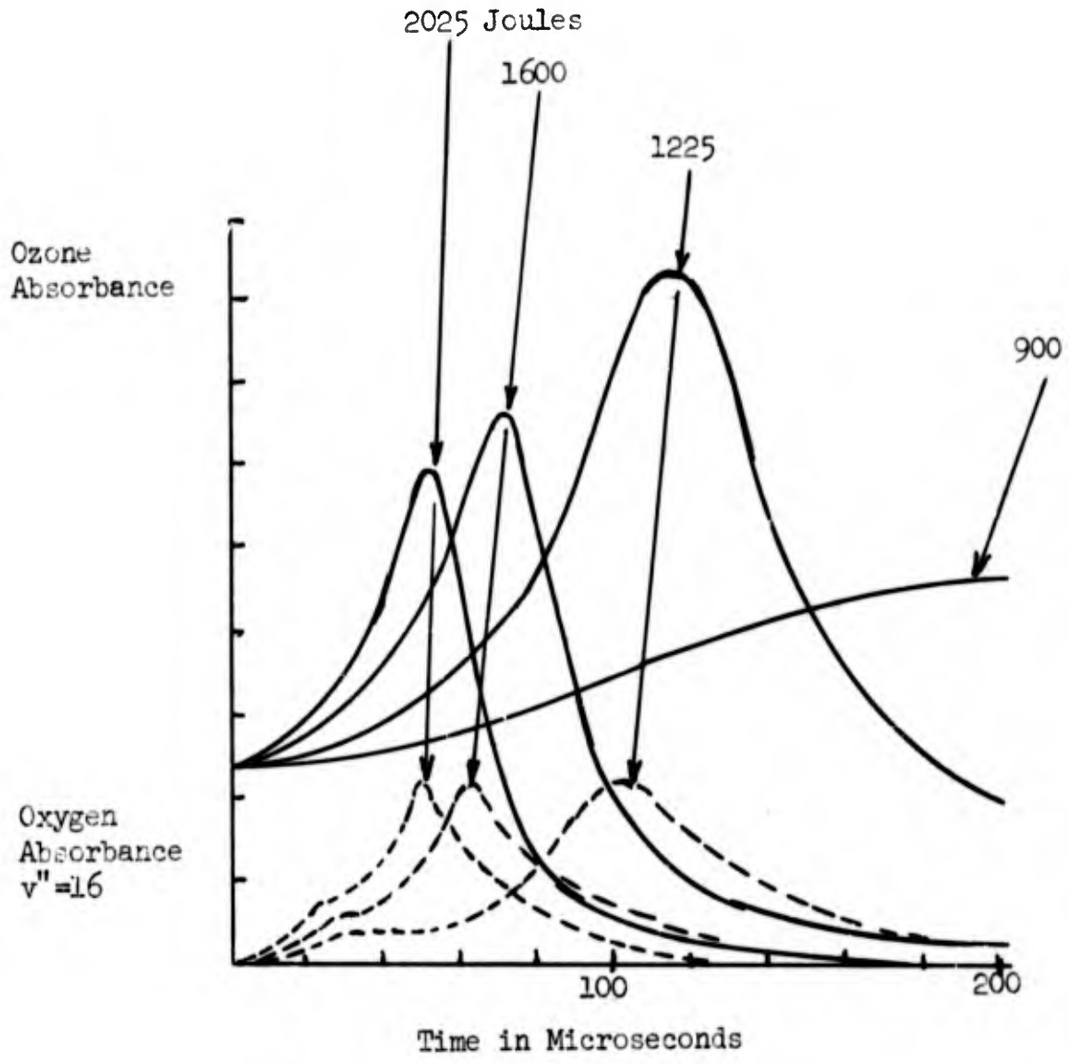


Observed Absorption by Ozone at Four Different Wavelengths During Photolytic Explosion and its relation to the Energy Levels (schematic) and Spectrum

As higher vibrational levels become populated during the early stages of the decomposition the spectrum shifts toward longer wavelengths causing the absorption in this region to increase. Upon further excitation and reaction the ozone is destroyed.

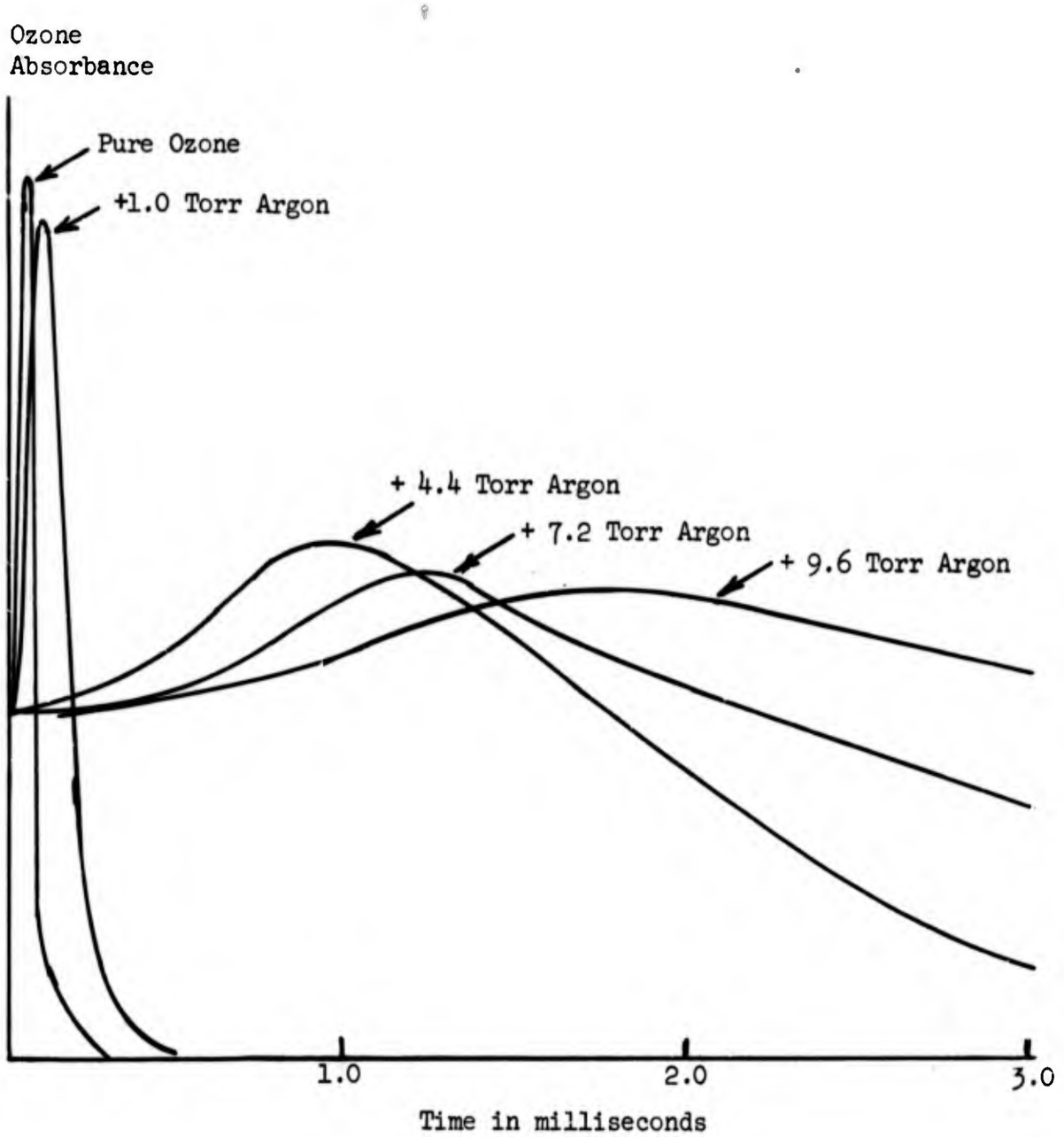


Schematic Relation Between Observed Features of the Time Resolved Spectrum and the Mechanism of Photolytic Explosion of Ozone.



Comparison of the Vibrational Excitation of Ozone and Oxygen During Explosions Initiated by Successively Smaller Amounts of Photolytic Energy

This data obtained during the present project shows the dependence of the rate of reaction on vibrational energy of ozone, vibrational energy of oxygen and kinetic temperature (which increases more slowly when the photolysis energy is smaller).



Effect of Added Inert Gas on the Rate of Vibrational Excitation of Ozone During Photolytic Expolsion

When the rise in kinetic temperature of the system is limited by the addition of inert diluents the vibrational excitation of ozone persists even when the rate is decreased by more than an order of magnitude. The vibrational temperature of ozone is greater than the kinetic temperature in this region.

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13. ABSTRACT

The project was undertaken in order to develop and demonstrate new spectroscopic procedures for studying both the detailed path and the elementary processes of photolytically initiated explosions similar in some respects to combustion reactions which also proceed by free radical and energy chain processes. Following the development of a highly reproducible reaction system, different spectroscopic features of the same system are studied by repeating the reaction. Special precautions to ensure that the system is homgeneous tend to isolate the chemical dynamics part of the combustion problem from the fluid dynamics part. With long absorption path and low sample pressure the time resolution of the measurements is reasonably comparable with the time between intermolecular collisions. A fast, high resolution spectrometer specifically designed for this work resolves transient energy features such as the rotational fine structure of free radical absorption with a time resolution of about a microsecond.

In the photolytic explosion of ozone the time dependence of the ozone concentration, ozone vibrational energy, vibrational energy of the oxygen product in levels up to v"=23 and the rotational-kinetic temperature were corelated.

In the photolytic explosion of Hydrazine the relative time dependence of NH_2 radicals, NH radicals, hydrazine and a new transient spectrum not yet fully identified were compared.

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