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DETERMINATION OF V = 0 RATE CONSTANTS FOR THE REACTION: D + F2,(U)
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Determination of v = 0 Rate Constants for the Reaction: D + F_2

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I. Introduction

Various chemiluminescence techniques (Measured Relaxation ~~(ref. 1)~~, Arrested Relaxation ~~(ref.~~ 2), and Chemiluminescence Mapping (ref. 3) provide a powerful tool for obtaining detailed rate constants and energy disposal information for exoergic chemical reactions. These techniques rely on observing emission of vibrationally excited products so that steady state populations of these excited states can be deconvoluted into the microscopic rate constants of the formation reaction. The inherent weakness of these techniques is that the rate constants into the ground vibrational state can not be obtained. Nonetheless, ground state vibrational populations are often reported; the upper level populations are extrapolated to v = 0 by an information theory approach (~~ref. 4)~~. Obvious deviations can result if the reaction dynamics are not well behaved.

In theory the v = 0 populations can be obtained by two independent experimental techniques, laser fluorescence and chemical laser studies. The former technique relies on laser excitation to an excited electronic state followed by the monitoring of the fluorescence as a function of the wavelength of the laser. The chemical laser techniques are based on the observation of population differences between radiatively coupled states; if gain exists between coupled states then lasing will occur. The laser fluorescence technique is not appropriate for DF population analysis due to the high energy required to reach the first excited electronic state. Hence a chemical laser technique was selected for this project.

Both the free running (FR) and grating tuned (GT) chemical laser techniques are available. The GTCL technique (ref. 5) is an extension to higher resolution of the FR cavity pioneered by Berry (ref. 6). This method allows effective experimental probing of ground vibrational product populations and is sensitive to difference in populations. Gaseous reactants are placed within a grating tuned optical cavity and reaction is initiated by a photolytic flash. The time for the onset of the laser emission (τ) is recorded for each transition (particular transitions are tuned by adjustment of the grating angle). Vibrational populations are then determined by comparison with calculated gain for the same transitions. For the $v = 0$ population the 1-0 laser emission lines would be recorded.

II. GTCL Apparatus and Parameterization

This section describes: (A) the apparatus and test reactions used for this project, and (B) the modeling necessary to abstract the populations from the observed set of laser timing pulses.

A. Apparatus and Test Reactions

The basic design described by Bittenson (ref. 5) was improved so that a shorter flash pulse could be attained leading to a higher gain (more sensitive) system. In order to interpret these experiments a rotational equilibrium with a known temperature must be present; this is obtained by using a high pressure buffer gas (50 to 500 torr argon) and a slow flash repetition rate. The buffer gas provides a mechanism for translational and rotational equilibrium (without vibrational relaxation during the observation time) while the slow flash rate provides sufficient time for the apparatus to equilibrate to room temperature. Additionally the flash output duration should be minimized so that appreciable reaction does not take place before the flash is complete; a well defined zero time is needed.

A schematic of the apparatus is shown in Figure 1. The cavity was formed by gold coated reflectors at each end; a curved mirror (1M radius of curvature) at one end and a flat mirror or plane diffraction grating at the other. The lasing media was enclosed by a Suprasil or Vycor glass tube (65 cm by 12.5 mm O.D.) with Brewster's angle NaCl windows located at each end. The flash lamp (45 cm long) was coaxial to the laser tube. Tungsten rods were mounted on each end to be used for the discharge electrodes; one was attached to the spark gap and the other to ground via a copper foil which surrounded the laser tube (this kept the inductance low). The flash tube was filled with xenon to a pressure (approximately 10 torr) to optimize the flash energy and profile for a given discharge voltage. The energy (maximum of 900 joules) was supplied by a 2.4 microfarad capacitor charged up to 30 kv. A Tachisto nitrogen filled spark gap was fired by a pulser. For safety and convenience reasons, the high voltage power supply and pulser had remote controls located 20 feet from the laser cavity.

The mode of operation could be changed from FR to GT by replacing the plane flat mirror with a plane diffraction grating (2 gratings were available one blazed at 2.5 microns with 600 grooves/mm and the other blazed at 4.0 microns with 300 lines/mm). The useful spectral range for these gratings was 2.0 to 5.5 microns so that both HF and DF fundamental emission could be tuned. The grating was mounted on a polar rotator and could be adjusted to within ± 15 sec. The mounted diffraction grating was calibrated with a HeNe alignment laser. For alignment, the grating was further adjusted to direct the zero order radiation along the optical path back to its source. The polar rotator was adjusted to send higher order reflections along the optical path; if necessary the grating was adjusted in its mount so that the reflected ray coincided with the incoming beam. This was continued until the order corresponding to the wavelength region expected for the chemical laser emission was set. A plot of wavelength vs diffraction angle (β) based on the equation

$$n\lambda = 2a \sin \beta$$

where n is the order and a is the groove spacing, was used for wavelength determination.

The laser cavity (Brewster's angle windows/detector) was also aligned with the HeNe laser. The grating was set to return an appropriate order of the HeNe radiation; some of the radiation was reflected by the NaCl windows. Interference fringes (between radiation reflected off the windows from different multipass rays) were observed when the cavity was correctly tuned; mirrors were adjusted until this requirement was met.

A conventional vacuum system with teflon stopcocks and oil diffusion pump was used for gas handling and storage; the cavity was directly connected to the gas handling system. Chemicals [Xe, CF_3I, CCl_4, DI, and F_2] were purchased from Matheson Gas (99.995%), PCR, Aldrich (99%), Merck & Co., Inc. (98% min. D), and Air Products (98% purity), respectively. Pressures were measured with a capacitance manometer.

The laser pulse was detected by an InSb detector; the resulting signal voltage was amplified and used as input to a dual trace 20 MHz oscilloscope. The flash profile and intensity were monitored with a photodiode; this signal was also fed into the oscilloscope and was used to trigger the sweep. Under certain circumstances both inputs were combined and fed into a single trace. The oscilloscope screen was recorded on Polaroid type 47 film. A typical flash profile is shown in Figure 2. The time to reach maximum intensity is < 2 microseconds which compares favorably with the 4 to 6 microseconds time on Bittenson's (ref. 5) apparatus; likewise the FWHM of 2 microseconds on the new system is to be compared with 6 microseconds.

To check the functionality of the apparatus three reactions were performed. Two torr of CF_3I was photolyzed and I* laser emission was observed with a delay of 4 microseconds. A 1:1 mixture of HI and CCl_4 was flashed in the GT mode; 3P8 emission was observed. A DI/CCl_4 mixture when photolyzed produced a laser spike with a delay of 4 microseconds. This experiment indicated that the system was functional in the HCl spectral region (this is also the DF region) as a GTCL. Another mixture comprised of CF_3I, HI and argon (1:1:50) at 50 torr when flashed produced an HF laser spike (2P4 in GTCL mode) indicating that the system was producing H atoms. In this example the HF is produced from excited CF_3H formed by the combination of H atoms and CF_3 radicals. Hence all diagnostics indicate a functional GTCL for the DI/F_2 system.

B. Computer Modeling of System

Computer modeling the chemical laser system provides a method in obtaining vibrational level populations from the appearance times of the laser spikes.

The FRCL is of great complexity; we used this mode only in determining if gain was present. The complexity of a FRCL is related to the rapid cascading producing a multiple laser pulse pattern. The GTCL technique, by allowing oscillation on only one transition, can be analyzed with a somewhat simplified approach. Bittenson (ref. 5) has performed various computer simulations. The important processes include microscopic formation rates, spontaneous emission, stimulated absorption and emission and collisional energy transfer. Using a two level system he showed that the appearance of lasing is directly related to the population ratio between the lasing states; large inversion ratios produce shorter appearance times. Once the threshold point for lasing has been achieved maximum intensities are comparable over a large range of population ratios. At the onset of lasing, radiation intensity rapidly increases; experimentally the oscilloscope trace of the laser pulse will appear as a sharp spike with a well defined initiation time (τ). This spike is followed by relaxation oscillations as the population ratio undergoes rapid changes.

It can be shown (ref. 5) that by defining a relative gain, $\alpha^{rel}_{vj,v'j'}$, for a particular vj → v'j' transition as

$$\alpha^{rel}_{vj,v'j'} = \sigma_{vj,v'j'} h_{vj,v'j'}$$

where $\sigma_{vj,v'j'}$ is the stimulated emission cross section for the vj to v'j' transition

$$h_{vj,v'j'} = [C_{vj}\frac{N_v}{N_{v'}} - C_{v'j'}][1+\frac{N_v}{N_{v'}}]^{-1}$$

and

$$C_{vj} = \frac{e^{(E_{vo}-E_{vj})/KT}}{\Sigma g_j e^{(E_{vo}-E_{vj})/KT}} .$$

E_{vj} is the energy of the vj level, k is the Boltzmann constant and g_j is the rotational degeneracy so that (κ a constant)

$$\kappa = \alpha^{rel}_{vj,v'j'} f(\tau)$$

$$f(\tau) = \int_0^{\tau}\int_0^{T} g(t)\,dt\,dT$$

while g(t) is the rate of formation at time t, and τ is the appearance time of the laser pulse. So that for the appropriate values of $N_v/N_{v'}$, a linear plot of $\alpha^{rel}_{vj,v'j'}$ vs $f^{-1}(\tau)$ will be observed. In practice laser pulse times for P and R transitions are recorded and for each observation $\alpha^{rel}_{vj,v'j'}$ is calculated for various population ratios and plotted versus $f^{-1}(\tau)$. The best linear plot of the scattered data defines the correct population ratio. If rotational equilibrium is not reached then a linear plot will not be obtained.

Another method of obtaining population ratios is to evaluate relative gain as a function of populations. Plots of log α^{rel} vs $N_v/N_{v'}$ are produced for different transitions as shown in Figure 3. From these plots upper and lower population ratio limits can be estimated by whether a level lases or not.

III. Results and Discussion of the DI/F_2 System

To obtain the v = 0 populations for the reaction $D + F_2 \rightarrow DF + F$ a mixture of F_2 and DI was used; D atoms were produced by the flash photolysis of DI. Both F_2 and DI have absorptions in the region of the flash which can lead to photodissociation; however the absorption coefficients are such that only 2% and 0.1% of the light is absorbed per cm of path length for DI and F_2, respectively. Thus complications from the F_2 photodissociation to produce DF from the F + DI reaction can be ignored. The long wavelength cutoff Vycor flash tube cavity was used for these experiments.

Initially mixtures of DI and F_2 were prepared in the vacuum line and then expanded into the cavity to give a total pressure of 1 to 2 torr. No lasing was observed with the grating in place so the FR mode was then used; again no lasing was observed. When the mixture was prepared a faint "click" would sometimes be heard; it was assumed that this click was the result of a catalyzed (surface?) reaction between DI and F_2. In a similar manner the mixture was prepared in the cavity by adding DI to F_2, as it was thought that any pre-reaction would then be minimized. Entrance valves were solenoid operated so that the time between vessel loading and photolysis would be minimized due to the smaller exposed surface area. These experiments also did not display any lasing characteristics.

In order to further reduce the time for pre-reaction a flow system was used; again no lasing spikes were observed. Before this project was initiated preliminary experiments indicated that when HI and F_2 flowed through a copper vessel with NaCl window HF formation was not observed; HF concentration was monitored by IR absorption. In the present experiments extended seasoning of the Vycor cavity did not change the negative results. It appears that the Vycor cavity promotes reaction of either DI or F_2 so that the population of DF from the pumped reaction is insufficient to provide enough gain for laser action.

Other groups (ref. 7) have reported problems associated with the stability of H_2/F_2 mixtures in glass vessels; consequentially some have used vessels fabricated with magnesium (ref. 8) or added large amounts of oxygen (ref. 9) to the reactant mixture. These possibilities can not be used in the present experiments. The coaxial cavity must be transparent for the flash to initiate reaction so that the magnesium vessel is not appropriate. Likewise, oxygen may absorb some of the flash energy and promote unwanted reactions; if OD were formed complication in spectral analysis would arise due to the similarity with the DF emission.

Two alternate approaches will be considered when this project is continued. If a coaxial type flash tube is used then the F_2 concentrations will be monitored by following the absorption of F_2 (ref. 10) in the cell of a mixture containing F_2 and D_2. Similarly the pre-reaction of DI will be monitored by following the DI absorption in a mixture of DI and D_2. A mixture of DI and F_2 will also be monitored for pre-reaction of DF by observing the IR absorption of the DF. It is hoped that an appropriate surface could be found so that the mixture will be stabilized; additionally a fast flow system could be used.

Alternatively the reaction could be pumped by a rare gas halide (ArF) laser so that high gain would be possible due to the high instantaneous D atom concentration. For this system the ArF laser beam would be nearly parallel to the chemical laser cavity (fabricated out of magnesium with NaCl windows.

In a similar fashion a CO_2 laser could be used to form D atoms in a CD_4/F_2 mixture. Calculations indicate that these systems would provide sufficient D atoms for lasing.

It should be noted for these systems that not only does the pre-reaction prevent lasing due to the diminished initial concentration of reactants but it also substantially decreases the N_1/N_0 population ratio. Thus the absence of lasing from $v = 1$ may be due to an insufficient absolute population in $v = 0$ or be due to either the nascent population distribution or the $v = 0$ population built up by pre-reaction.

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Figure I. Schematic of Apparatus

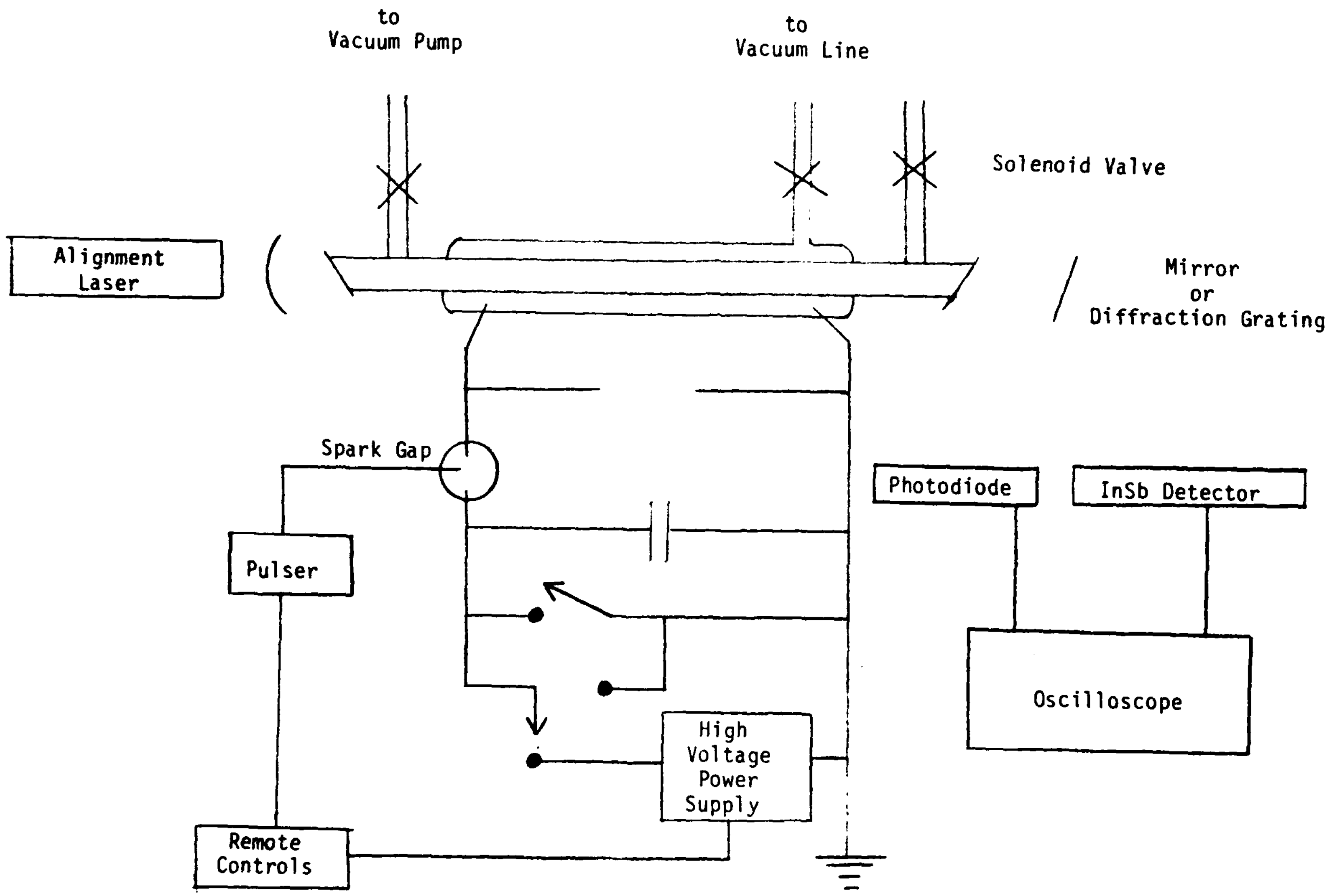

Figure II. Flash Lamp Output Profile

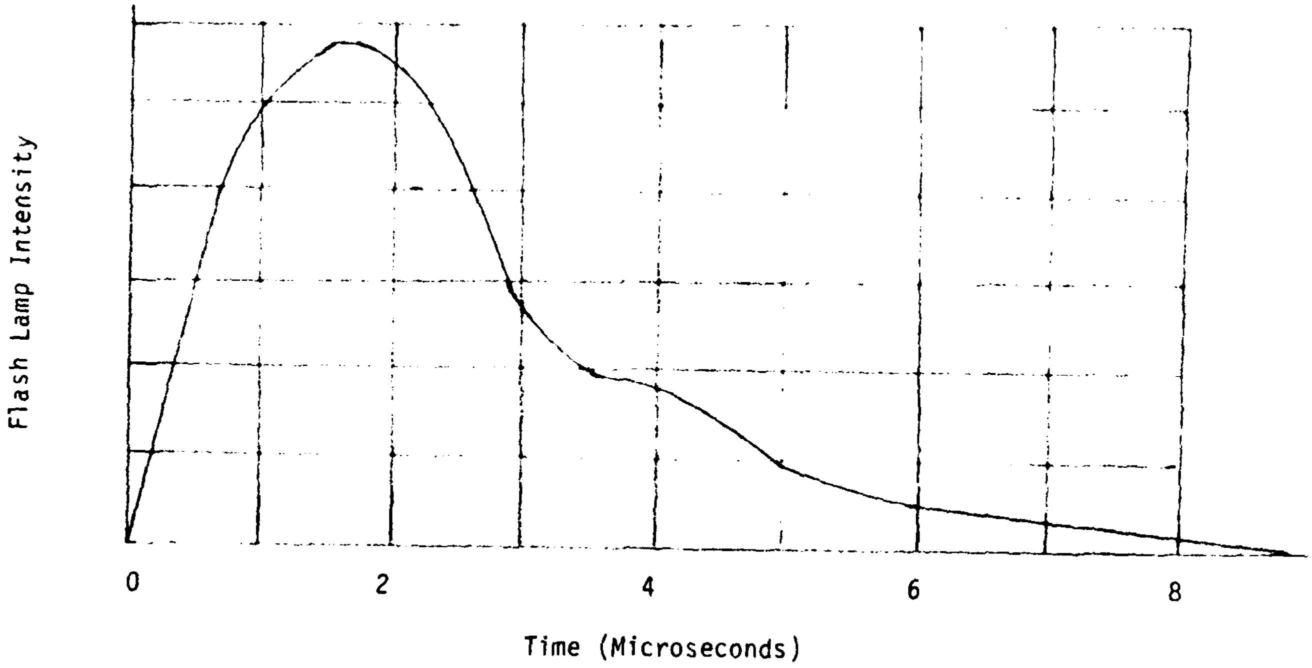

Figure II. Typical Calculate Gam Plots