THE STUDY OF COMBUSTION AND FLAME PROCESSES INITIATED BY IR LASER-INDUCED ABSORPTION

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The overall long term objective of this project is to obtain an indepth understanding of combustion and flame processes. The areas of investigation are non-relaxed and relaxed Boltzmann photochemistry; state-selective reactions of energetically prepared fragments with selected substrates; state-to-state study of energy migration and dispersion; and the detailed mechanism of IR multiple-photon absorption (MPA) and unimolecular dissociation. The unique aspect of these studies is that the simulated flame and combustion processes are initiated by multiple-photon absorption from high power infrared (IR) laser sources. Subsequent examination of the system is performed by dye laser induced fluorescence (LIF), multiphoton spectroscopy, and visible and infrared emission.

One of the questions critical in the understanding of combustion and flame reactions is the kinetic role of free radicals such as C_3, CH, C_2, and OH.[1,2] The detailed behavior of these species is in general, not known, due largely to the fact that they have not been prepared under controlled experimental conditions. These molecules are expected to be rather reactive in general and therefore, a knowledge of their kinetic behavior is crucial to the understanding of these systems.

One of our major efforts at present is the study of the reaction dynamics of the C_3 radical in the presence of O_2, NO, and various hydrocarbons. The C_3 radical has been observed to be a constituent of carbon vapor as well as hydrocarbon flames, yet little is known about its reaction dynamics. Study of elementary state-selective reactions and state-to-state vibronic relaxation of $C_3(\tilde{X}^1\Sigma_g^+$ and $\tilde{A}^1\Pi_u)$ are discussed below.

A. "C_3 Production, Vibrational Relaxation and Chemical Kinetics Following IR Photolysis of Allene", Chem. Phys. Lett., 71, 72 (1980.

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We recently completed and published[3] a study of the state-selective reactions of C_3 with NO and O_2. The C_3 radical was generated in a *clean* manner by the IR multiple-photon dissociation (MPD) of allene ($H_2C=C=CH_2$). Using the LIF technique, we were able to obtain the decay rates of $C_3(\tilde{X}^1\Sigma_g^+$ 0,0,0) in the presence of allene, O_2, and NO. The elementary state-selective bimolecular rate constants were 4.3×10^{-13}, 2.1×10^{-13}, and 1.5×10^{-14} $cm^3/$ molecule-sec for allene, NO, and O_2, respectively. These are the first reported rate constants of ground state C_3 with major combustion components and are 10^3 to 10^4 slower than the gas kinetic collision rate. The implication is that C_3-radical reactions might be more important as decay processes for C_3 in these systems, than C_3-stable molecule reactions.

In addition to the "state" of the C_3 reactant we also determined the "state" of the product C_2 using LIF. Assuming the elementary reaction

$$C_3(\tilde{X}^1\Sigma_g^+\ 0,0,0) + O_2 \rightarrow C_2(\tilde{a}^3\Pi_u) + CO_2, \qquad \Delta H = -88.0\ Kcal \qquad (1)$$
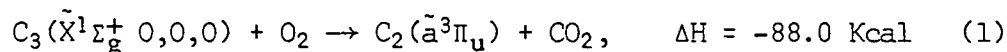
we observed vibrational excitation in $C_2(\tilde{a}\,^3\Pi_u)$ up to v"=4. To characterize the distribution, we fit the data to the Boltzmann equation and obtained an effective vibrational temperature of ~2900°K.

Work is presently in progress to characterize the reaction dynamics of the $C_2(\tilde{a})$ product using LIF and we plan to similarly study CO_2 in the near future using two photon spectroscopy.

B. "State-to-State Vibronic Relaxation Dynamics of $C_3(\tilde{X}^1\Sigma_g^+)$ and $C_3(\tilde{A}^1\Pi_u)$". (Manuscript in preparation.)

As a result of the relatively slow reaction rates of $C_3(X)^1$ (discussed above), we recently performed the study of vibronic relaxation processes within the $C_3(\tilde{X})$ state, which proceed on a faster time scale. The IRMPD of allene generated $C_3(\tilde{X})$ with a population distribution that could be characterized by

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a vibrational temperature. We then mapped the temporal profile of selected excited vibrational levels in order to obtain elementary relaxation rate constants. We used a simplified kinetic model which included four vibrational levels (Figure 1) and considered the coupling between these levels as a function of added collision partner. Vibrational relaxation rate coefficients were obtained for Ar, He, Ne, N_2, O_2, and C_2H_2 in addition to the reaction rate constant for $C_3(^1\Sigma_g^+,0,0,0)$ with C_2H_2. These data are shown in Table 1.

In anticipation of state-to-state kinetic studies of excited $C_3(\tilde{A}^1\Pi_u)$ vibronic states, the relaxation dynamics among these states were also performed. In order to accurately characterize the vibronic state-to-state dynamics, emission spectra were obtained for successive excitation to the $\tilde{A}^1\Pi_u$ $000(\Pi_u)$, 010 (Σ_g^-), $010(\Delta_g)$, $020(\Pi_u^-)$, $030(\Sigma_g^-)$, $040(\Pi_g^-)$, and $100(\Pi_u)$ vibronic levels. These spectra were taken at 10 mtorr of allene pressurized to 5.0 torr of Ar and are shown in Figure 2. The spectra are progressively more complicated as excitation occurs higher into the $\omega_2^!$ manifold (with the exception of the 100 spectrum), indicating incomplete relaxation down this manifold. The emission spectrum from the excitation of 100 is most consistent with practically *non-relaxed* emission and assignable to the three major peaks $(100 \rightarrow 000)$, $(100 \rightarrow 100)$, and $100 \rightarrow 200)$. The relevant vibronic levels of the $\tilde{A}^1\Pi_u$ state of C_3 having u and g symmetries (diagrammed left and right, respectively) are shown in Figure 3.

We were able to confirm the previously reported [4] radiative lifetimes for the $(0,0,0)$ level of 204 ± 10 nsec and a deactivation rate constant for Ar of 4.33×10^{-11} cm^3 molecule^{-1} sec^{-1}. A Stern-Volmer plot of each of the strong emissions in Figure 2G gave a deactivation constant of 3.16×10^{-11} cm^3 molecule^{-1} sec^{-1} and identical radiative lifetimes of 183 nsec. The identical lifetimes support the assumption of practically non-relaxed emission from (100), since all three emissions observed in Figure 2G would originate from the same level, $100(\Pi_u)$.
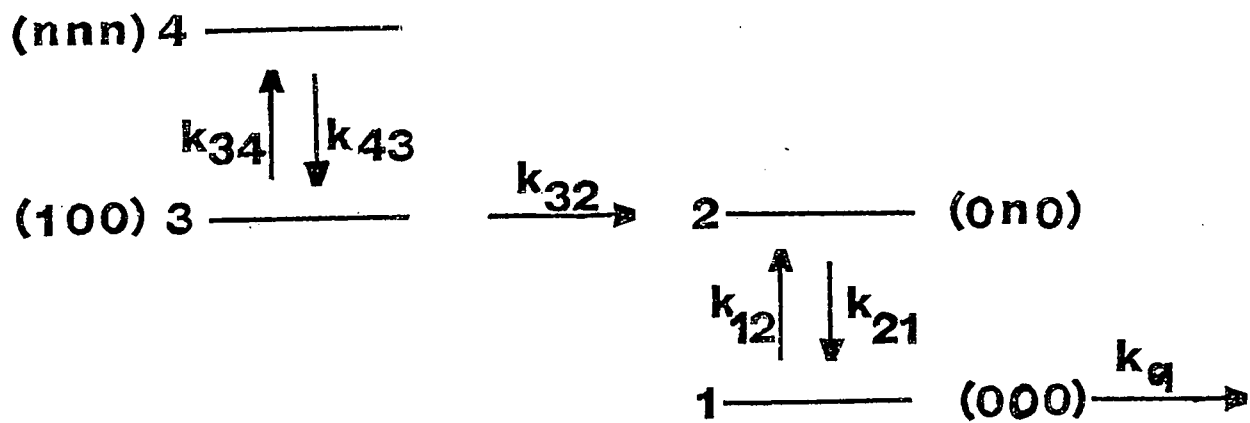
Figure 1. Levels and rate processes included in the kinetic model.

TABLE 1. Experimentally observed rates of rise and fall.

$C_3(^1\Sigma_g^+, 100 \text{ or } 110)$:

Species	Rate of Rise	Rate of Fall
Ar	$1.56 \pm .40 \times 10^4$ torr^{-1}sec^{-1}	$1.14 \pm .05 \times 10^4$ torr^{-1} sec^{-1}
He	$1.86 \pm .66 \times 10^4$	$1.09 \pm .21 \times 10^4$
Ne	$3.06 \pm .47 \times 10^4$	$0.82 \pm .05 \times 10^4$
N_2	$4.17 \pm .82 \times 10^4$	$1.33 \pm .07 \times 10^4$
O_2	$3.87 \pm .52 \times 10^4$	$1.20 \pm .04 \times 10^4$
C_2H_2	$11.0 \pm .50 \times 10^4$	$4.64 \pm .10 \times 10^4$
C_3H_4	-- -- -- --	$5.04 \pm .40 \times 10^6$

$C_3(^1\Sigma_g^+, 000)$:

Ar	$1.23 \pm .37 \times 10^4$	-- -- --
C_2H_2	$44.5 \pm 7.4 \times 10^4$	-- -- --

Figure 2. Emission spectra of 10 mtorr of allene pressurized with 5 torr Ar over the spectral 450 to 350 nm, for the successively pumped $\tilde{A}^1\Pi_u$ vibronic states A) 000(Π_u), B) 010(Σ_g^-), C) 010(Δ_g), D) 020(Π_u^-), E) 030(Σ_g^-), F) 040(Π_g^-), G) 100(Π_u).

26600

26200

25800

25400

25000

24600

040 — — — — — — — — — Π_u^+
040 — — — — — — — — — Φ_u^+

030 — — — — — — — — — Σ_g^+
030 — — — — — — — — — Δ_g^+

100 ——————————— Π_u

050 — — — — — — — — Δ_g^-
050 ——————————— Σ_g^-

040 — — — — — — Π_u
040 — — — — — — Φ_u^-
020 ——————————
040 ——————————— Π_u^- Π_u

030 — — — — — — — — Γ_g
030 ——————————— Δ_g^-
030 ——————————— Σ_g^-
010 ——————————— Σ_g^+

020 — — — — — — — — — Φ_u
020 ——————————— Π_u^-

010 ——————————— Δ_g^-
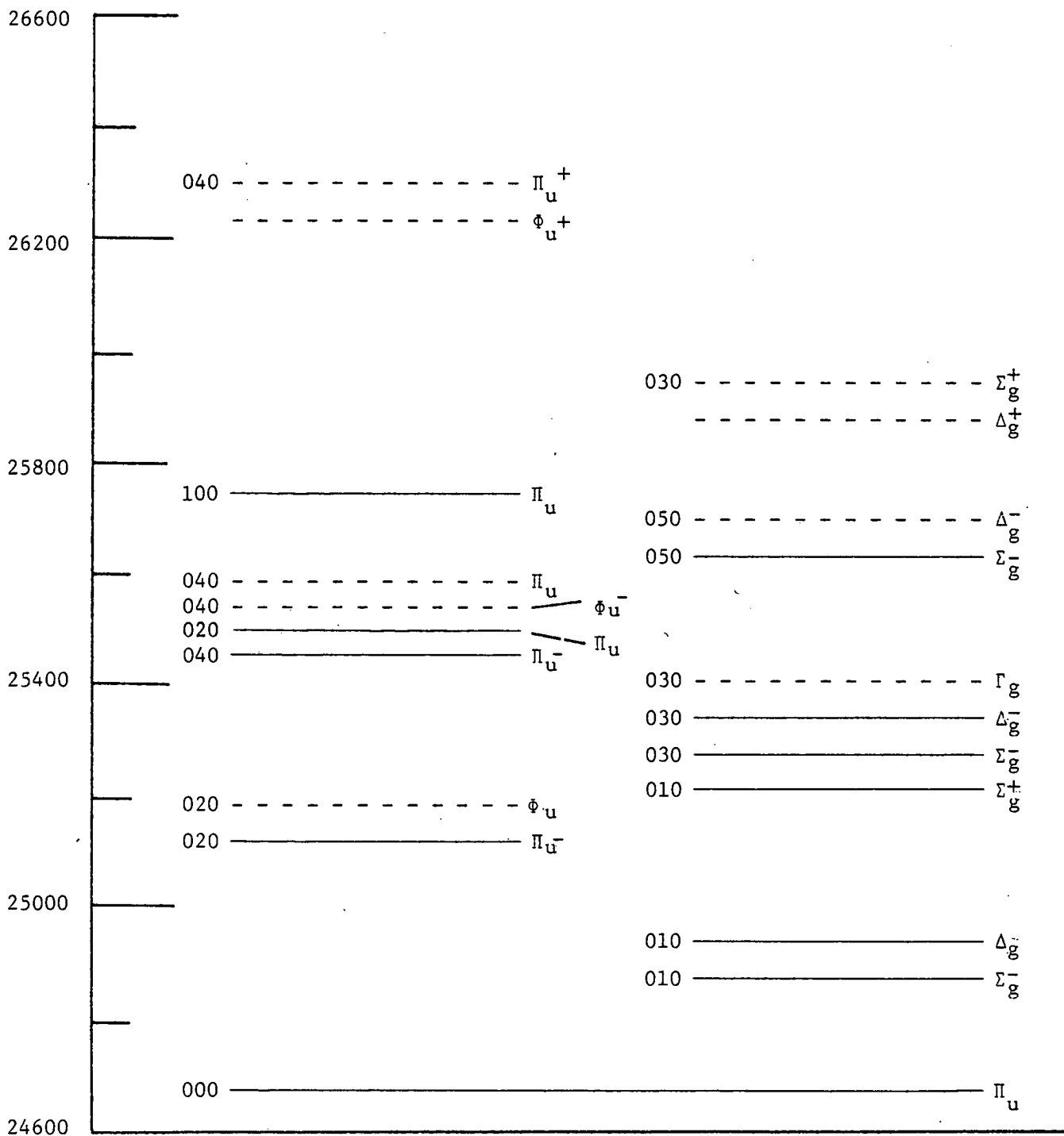010 ——————————— Σ_g^-

000 ——————————————— Π_u
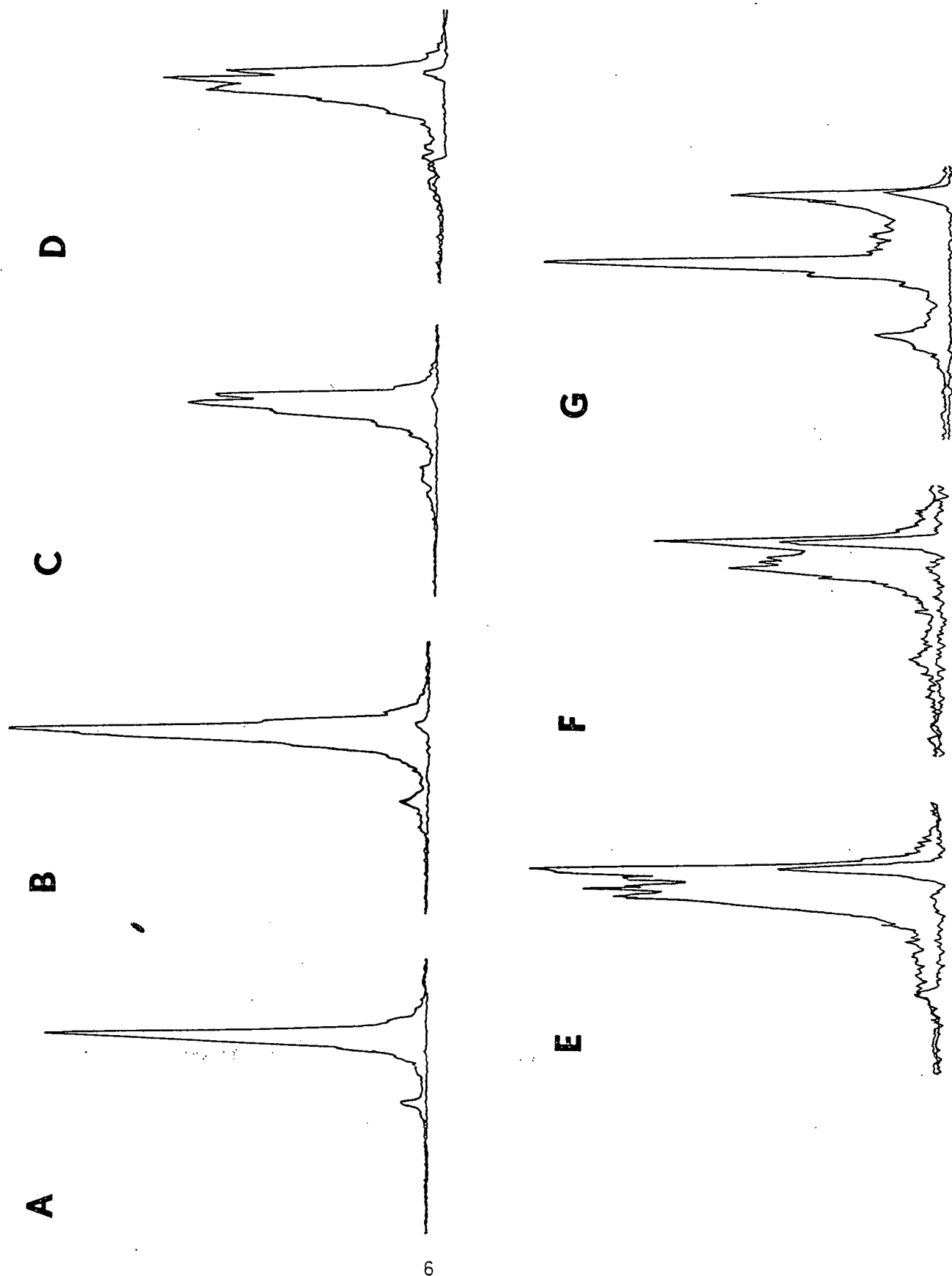
FIGURE 3: OBSERVED VIBRONIC LEVELS OF $\tilde{A}^1\Pi_u$ C_3 WITH u AND g SYMMETRY PLOTTED AT THE LEFT AND RIGHT, RESPECTIVELY. LEVELS ESTABLISHED ONLY BY BAND HEADS ARE INDICATED BY BROKEN LINES.

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Extention of these state-selective experiments to the CH radical is in progress. Although CH has been observed in many hydrocarbon flames, the kinetics and mechanisms of its reactions are still not well understood.[5,6] The progress made to date on the reaction of CH and O_2 is described below. In spite of the normal difficulties we have encountered in this study, we anticipate the completion of a manuscript by September 1, 1980.

C. State-Selective Reaction Between $CH(X^2\Pi$, v=0,1) and O_2

Our attempts thus far have been heavily weighted on the reactants' side of this combustion reaction. Initial experiments were directed toward finding a difference, if it existed, between the absolute reaction rates of CH(v"=0) and CH(v"=1) with O_2 and eventually NO and other oxidants. Unfortunately (or fortunately), the naive notion of how these diatomics react did not prove to be successful when applied to the present method of CH production, *i.e.* IRMPD of small hydrocarbons such as CH_3OH, CH_3F, CH_3NH_2, and others. As it turned out, determination of the pseudo-first order reaction rate constants for CH from temporal spectra obtained by LIF studies was not a trivial matter.

A complete description of the dynamics of CH radical over the course of the experiment proved to be an interesting task. We have found that CH production by IRMPD differs temporally from precursor to precursor and because of the timescale over which these processes occur, resolution of reaction data becomes quite complicated.

At least five precursors have been studied thus far. These are (in order of CH "production efficiency"):

$$AC_2O > MeCN > MeOH > MeF > MeNH_2,$$

where AC_2O is acetic anhydride and Me is the methyl group. The importance of

production efficiency is as follows. MeNH$_2$ data are described by a simple dynamic model where CH rise is described by a single exponential and decay by a second exponential. The problem here is insufficient amounts of CH for study of the CH(v=1) excited state. This excited state can easily be observed when MeOH is the precursor, but modelling indicates a two exponential decay, where the origin of the second exponential is unknown. In searching for a precursor with reasonable CH production, but simple first order dynamics, we found AC$_2$O to yield a two exponential rise and a single exponential decay. This leads us to the conclusion that the second decay constant appearing from the use of precursors like MeOH is actually just a very slow, secondary CH production step, as yet, cannot be deconvoluted from our data.

Absolute reaction rate of CH(v=0) with O$_2$ has been reported [7] and is in agreement with the faster of the two constants obtained from the study using the MeOH precursor. The rate of CH(v=1) reaction with O$_2$ can now be obtained, but the more interesting question of describing the overall CH dynamics, dependent on precursor, still remains. There apparently exists a limited range where even these more complicated models apply. Experiments have been done with varying pressures of both precursor and total buffer gas (Ar) pressure from 10 mtorr of precursor and 5 mtorr total pressure (1/500 dilution) up to 1 mtorr of precursor in 40 torr total Ar (1/40,000). Our three exponential models (or 2 exponential models) only can describe the data from 1/2,000 to 1/5,000. Diffusion has also been noted to occur in total pressures even greater than 30 torr which is an additional problem to deal with in modelling.

Another major area of interest is energy transfer and relaxation processes in medium-sized polyatomic hydrocarbons. We recently reported [7] the detailed state-to-state energy transfer and dispersion dynamics of propynal

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over the pressure range of 5 to 500 mtorr. This study suggested very important dynamical information, which probably applies to most medium-sized polyatomics such as propynal, HC≡C-CHO. When a polyatomic (such as propynal) is IR laser pumped in a mode specific manner, a hole is burned in the rotational distribution. At collisional pressures, this hole is filled by relaxation, allowing more molecules to be laser-pumped. At collisionless pressures, this hole is very slowly filled via intramolecular relaxation, setting a limit on the number of molecules pumped, and hence the detectability of pumped molecules in the system. At collisional pressures, the near resonant energy transfer in the IR pumped manifold occurs faster than the gas kinetic rate. Energy transfer to other vibrational modes was about 10 times slower than gas kinetic, with ~10 μsec relaxation times. Reestablishment of the equilibrium prior to the IR laser pump, occurs with ~1 msec relaxation time. The former appears to be the establishment of a quasi-equilibrium among the vibrational modes (with a corresponding higher temperature) and the latter vibration to rotation/translation (V→R/T). The relaxation by V→R/T preferably occures via the lowest frequency vibrational mode(s). These basic features are of fundamental importance in terms of constructing a working model for possibly IR laser directing combustion processes.

Further studies to date on the propynal system have yeilded a better understanding of its infrared-induced energy transfer characteristics, through both computer modelling and spectroscopy. Detailed wavelength resolved spectroscopy has revealed the CO_2 laser induced rotational hole burning as postulated in our most recent propynal study.[5] Whereas, the computer modelling is helping to define, in more detail, the contribution that each vibrational mode makes in the energy transfer scheme, as well as how diffusion influences the observed rate constants.

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By increasing the energy flux of the IR pumping source, we have observed population increases red of those reported in the above reference; however, more conclusive studies are underway to verify these observations. Extensive testing of our stimulated Raman Scattering cell has recently been completed, and we are now prepared to begin studies where we pump vibrational modes higher than those allowed by the CO_2 laser (~ 1000 cm^{-1}).

These energy dispersion and relaxation studies are presently being extended to biacetyl, CH_3OC-$COCH_3$.

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