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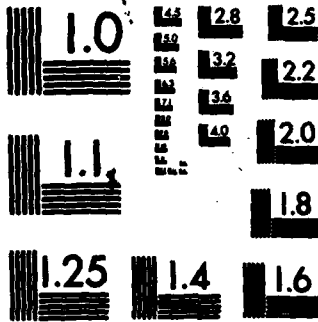
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FINAL REPORT

SEQUENTIAL EXCITATION PREPARATION OF MOLECULAR ENERGY LEVELS WITH SPECIAL STRUCTURAL AND CHEMICAL PROPERTIES

AFOSR-80-0254

DEPARTMENT OF CHEMISTRY  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY  
CAMBRIDGE, MASSACHUSETTS 02139

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  <b>Three types of experiments are discussed: Stimulated Emission Pumping (SEP) on H<sub>2</sub>CO, Modulated Gain Spectroscopy (MGS) on Na<sub>2</sub>, and sub-Doppler spectroscopy of the Ca+O<sub>2</sub> flame. The SEP experiments have reached the intensive data-generation stage. With 10,000 cm<sup>-1</sup> of vibrational excitation, H<sub>2</sub>CO is shown to behave as a normal mode oscillator in low rotational levels, exhibits extensive Coriolis mode mixing in J ≈ 10, K<sub>a</sub> ≈ 4 -</b>		

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rotational levels. A laser-locking scheme has improved the sensitivity of MGS by a factor of  $10^3$ . A new but puzzling assignment has been made of the  $\text{Ca} + \text{O}_3$  flame orange band system.

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## I. Research Progress

### A. Pulsed Laser Experiments

Our Stimulated Emission Pumping and SEP-Stark experiments on the  $\text{H}_2\text{CO}$  molecule have started to yield huge quantities of spectral data. Nonrotating  $\text{H}_2\text{CO}$ , at vibrational energies up to  $10,000 \text{ cm}^{-1}$ , appears to be behaving like a small molecule. The energies, rotational constants, and electric dipole moments of levels involving combinations of C-O stretch ( $\nu_2$ ) and out-of-plane bend ( $\nu_4$ ) seem to fit simple Dunham-type expansions. Two nearly degenerate pairs of vibrational levels have been located and the Fermi-interactions between them are so small ( $<1 \text{ cm}^{-1}$ ) that accidental mode-mixing at high energy seems likely to be a rare event. Coriolis- and c-axis interactions begin to appear at high  $J$ ,  $K_a$  values.

These mode-mixing and K-mixing interactions are negligible when either  $J$  or  $K_a$  is small, but, by  $J \approx 10$ ,  $K_a \approx 4$ , seem to couple all vibrational levels in the neighborhood of the  $2_4^4$  level accessible by SEP.

The most important results of our  $\text{H}_2\text{CO}$  SEP experiments are:

1. demonstration that non-rotating  $\text{H}_2\text{CO}$  is vibrationally well-organized. The normal-mode quantum numbers are good labels of the predominant vibrationally averaged structure. Near degenerate levels are capable of very different internal vibrational energy distributions (i.e. relative excitations of C-O vs. C-H stretch). This suggests that bond-specific chemistry might be observable in SEP-prepared  $\text{H}_2\text{CO}$  provided that the collisional cross-section for vibrational redistribution is smaller than that for chemical reaction.

2. suggestion that rotation, especially that about the C-O axis is an extremely effective mode-mixing mechanism. At high  $J$ ,  $K_a$ , molecules forget their vibrational identity. All vibrational eigenstates begin to have similar internal vibrational energy distributions (because all nearly isoenergetic rotationless basis functions become intermixed by Coriolis interactions). Thus rotational heating will provide a severe limit to the observability and utility of bond-specific photochemistry.

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MATTHEW J. KERPER  
Chief, Technical Information Division

## I. Research Progress, Cont'd.

We plan to continue the  $\text{H}_2\text{CO}$  SEP experiments until we reach the maximum vibrational energy accessible by SEP. One particularly important spectroscopic question is whether the C-O stretch or out-of-plane bending vibration is more subject to Coriolis mixing with "background" levels. The two most important chemical questions that we hope to answer are: does tunnelling through the  $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$  or  $\text{H}_2\text{CO} \rightarrow \text{HCOH}$  barrier become observable at SEP-accessible levels of the  $\tilde{X}^1A_1$  state; are the total population removal rates from single vibration-rotation levels so large as to prohibit the observation of structure  $\leftrightarrow$  reactivity correlations. We also expect to initiate exploratory experiments on propynal, which is the smallest two-chromophore molecule known to have a bound excited electronic state and resolved rotational structure, the two prerequisites for SEP.

### B. Modulated Gain Spectroscopy

Our  $\text{Na}_2$   $A^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$  optically pumped laser is now excited by a cw dye laser and operating in a servo-controlled configuration that has resulted in a  $10^3$ -fold signal-to-noise improvement in modulated gain spectra. The sensitivity of the MGS scheme is now so great that we are observing many previously unobservable collisional and multiple resonance effects. The most interesting of these is laser oscillation from collisionally populated upper levels which appears only when the probe laser removes population from the lower level of the collisionally coupled transition.

Preliminary experiments with the new MGS scheme are nearly complete. We expect to resume systematically recording the spectra of the highest vibrational levels of the  $A^1\Sigma_u^+$  and  $B^1\Pi_u$  states of  $\text{Na}_2$ .

### C. Calcium Oxidation Reactions

The  $\text{Ca} + \text{N}_2\text{O}$  and  $\text{Ca} + \text{O}_3$  flames reactions result in completely dissimilar fluorescence excitation spectra in the 600nm region. There is not a single strong feature that appears in the spectra of both  $\text{N}_2\text{O}$  and  $\text{O}_3$  flames. Our initial interpretation of the  $\text{O}_3$  flames spectrum as originating from a  $b^3\Sigma^+$  state now appears to be incorrect.

The spectra of the  $N_2O$  and  $O_3$  flames are so congested and complex that sub-Doppler techniques are required to resolve individual rotational lines. Several years ago, detailed rotational analysis showed that only the  $v = 0$  and  $1$  levels of the  $a^3\Pi$  and  $A'^1\Pi$  states were responsible for the 600nm bands of the  $N_2O$  flame. Largely because only one other low-lying electronic state exists for CaO, we predicted that the carrier of the  $O_3$  flame bands would be the not yet observed  $b^3\Sigma^+$  state. On the basis of sub-Doppler excitation and resolved fluorescence spectra of the Ca+ $O_3$  flame, we now suspect that the  $O_3$  flame bands arise from a single excited vibrational level of the  $a^3\Pi$  state.

We expect to complete the analysis of the Ca+ $O_3$  flame bands (probably  $c^3\Sigma^+ + a^3\Pi$ ) and to search for an explanation of the unusual vibrational and electronic selectivity of the  $N_2O$  and  $O_3$  calcium oxidation reactions.

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