

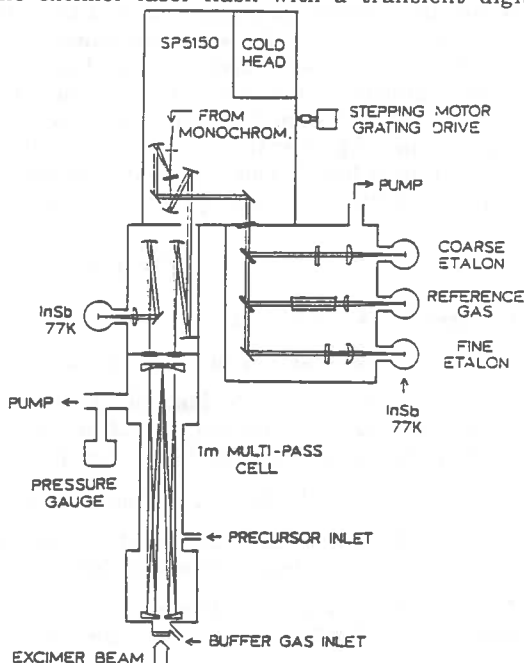
DIODE LASER KINETIC SPECTROSCOPY

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Diode laser kinetic spectroscopy has been used to obtain the high resolution spectrum of the CH stretching fundamental of the formyl radical (HCO). The analysis of this band was performed combining the diode data with the difference frequency laser spectroscopy data of C. B. Moore's group at Berkeley on this band.

The diode laser system and its method of operation for normal absorption spectroscopy has been described previously¹. The diode laser kinetic spectroscopy experimental arrangement is shown in Fig. 1. HCO was produced in the multipass White cell by XeCl (308nm) flash photolysis of acetaldehyde. The excimer laser was introduced just below the "D" mirrors of the White cell and intercepted by a beam block above the notched mirror. Thus the infrared interference from the excimer was small. Within the confines of this geometry the infrared diode probe beam and the excimer photolysis beam were as collinear as possible. The transient absorption signal is detected by acquiring the output of the signal detector immediately before and after the excimer laser flash with a transient digitizer (Biomation 805).

Fig. 1 Experimental set-up. The optical arrangement allows data to be collected from the experiment as well as the three diagnostic channels in a single scan.



Typical operating conditions were total pressure=7.5Torr, acetaldehyde pressure=2.5Torr, acetaldehyde flow rate=60scc/min, excimer repetition rate=20Hz, and excimer pulse energy=75mJ. The HCO frequencies were calibrated against N_2O in the reference cell. Generally the accuracy of the resulting line positions was limited by the accuracy of the calibration lines which is typically $\pm 0.001\text{cm}^{-1}$.

The rotational assignment was made by comparing the intensity of the second to first member of the two obvious a-type Q-branches observed thereby determining their K quantum numbers. The rotational, spin-rotational, and centrifugal distortion constants of the two vibrational states involved in the CH stretch were determined² by least squares fitting of ~ 750 diode laser and difference frequency absorptions. The resulting ν_1 band origin was $2434.47790(24)\text{cm}^{-1}$. This agrees satisfactorily with the matrix isolation CH stretching frequency³ of 2483cm^{-1} and the stretching frequency estimated from laser fluorescence⁴ of $2432\pm 20\text{cm}^{-1}$.

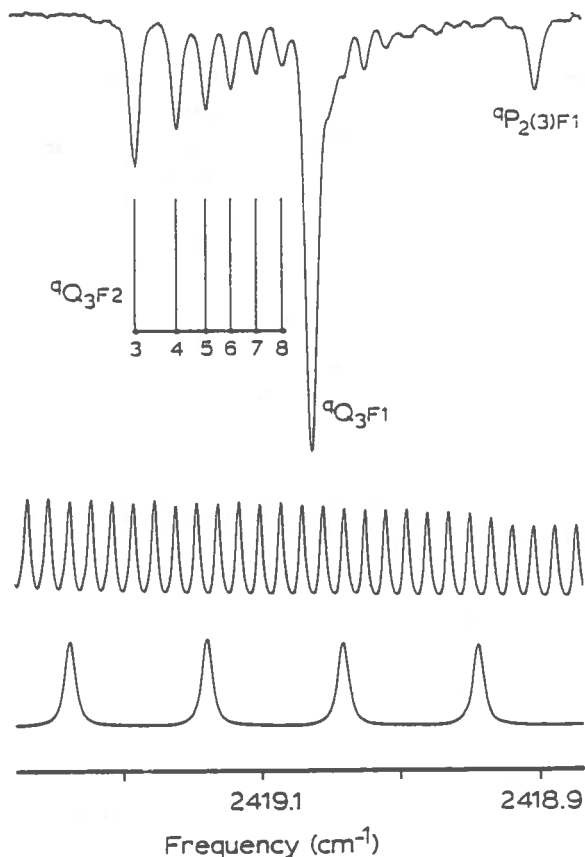


Fig. 2. K=3 parallel Q-branches of the CH stretching fundamental of HCO. 50 transient digitizer points each of 500nsec duration are averaged before and after each excimer shot and subtracted. The laser is stepped 20MHz in scanning with 30 shots averaged per step. Also shown are the 500MHz and 3GHz etalon fringes used in calibration.

The kinetic spectroscopy technique also enables time resolved study of a transient species. The time dependence is used to measure rate constants, and the signal amplitudes are used to measure product yields. Methods have been developed for frequency locking the diode laser to a PZT tunable cavity, which can then be tuned to the peak of an absorption line and the time dependence studied. HCO is relatively long lived as can be seen by the transient digitizer trace of its decay shown in Fig. 3. In our system, the principal decay mechanism is the recombination of two HCO molecules as can be seen by the roughly second order decay curve. The system was tested by measuring HCO decay rates in the presence of varying pressures of O₂. The resulting rate constant for the reaction $\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$ agrees with the published measurement⁵ within experimental uncertainty.

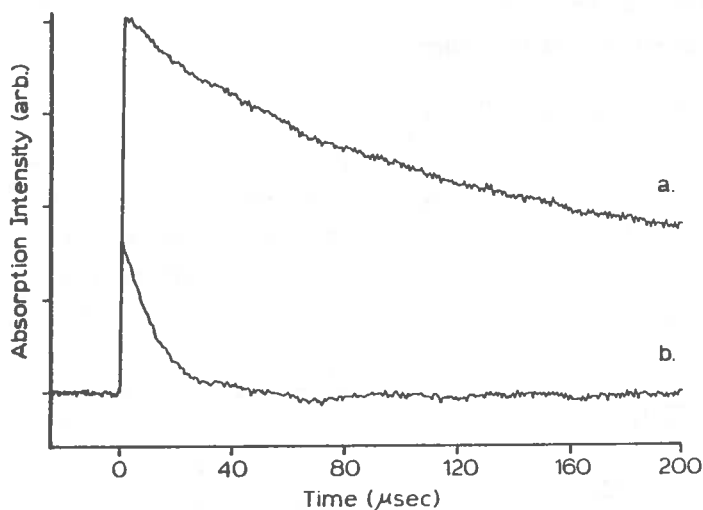


Fig. 3. Time decay of the signal from the HCO. 3000 traces were averaged.
a. no oxygen added.
b. 500mTorr oxygen added.

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1. C. B. Dane, R. Bruggemann, R. F. Curl, J. V. V. Kasper, and F. K. Tittel, *Appl. Opt.* **26**, 95 (1987).
2. C. B. Dane, D. R. Lander, R. F. Curl, F. K. Tittel, Y. Guo, M. I. F. Ochsner, and C. B. Moore, accepted for publication in *J. Chem. Phys.*
3. D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **51**, 277 (1969).
4. B. M. Stone, M. Noble, and E. K. C. Lee, *Chem. Phys. Lett.* **118**, 83 (1895).
5. R. S. Timonen, E. Ratajczak, and D. Gutman, *J. Phys. Chem.* (in press).