KINETIC SPECTROSCOPY USING A COLOR CENTER LASER

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Infrared kinetic spectroscopy has been used to study the ethynyl radical, C_2H. In this work, three new C_2H absorption bands in the infrared have been discovered and the reaction rate constants of C_2H with O_2, H_2, and NO have been measured.

The kinetic spectroscopy experimental arrangement has been described in detail elsewhere[1]. Briefly, the C_2H radicals are produced by the photolysis of C_2H_2 or CF_3C_2H in a 1 meter cell. The photolysis is accomplished by a 10 nsec laser pulse from the 193 nm ArF line of an excimer laser while the the resulting species are probed with a scanning color center laser spectrometer[2] operating between 2.3 and 3.3 μm. The 3 MHz line width of the color center laser along with the ability to make continuous high resolution scans of up to 10 cm^{-1} provide the ability to observe easily the rotational structure of C_2H.

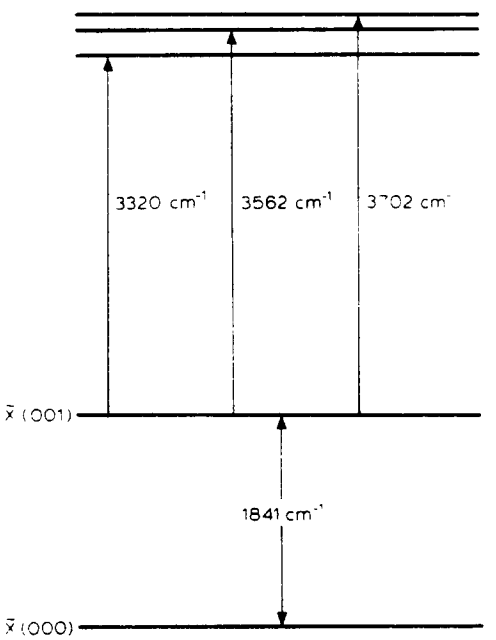

Fig. 1. The three new bands observed by excimer laser flash photolysis. The transition at 1841 cm^{-1} has been observed previously by Kanamori and Hirota.

Recently, three new bands of C_2H have been observed upon the photolysis of C_2H_2 in our cell[3]. The spectrum was recorded by subtracting data immediately before the excimer laser flash from data taken immediately after the flash. By setting these two channels 200 nsecs apart, the noise is greatly reduced. The three

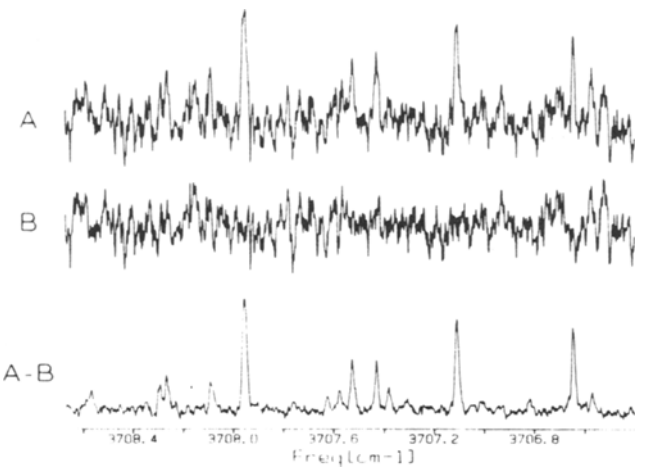

Fig. 2. (A) Data taken immediately after the excimer laser flash. (B) Data taken immediately before the flash. (A-B) The two channels are subtracted to reduce noise.

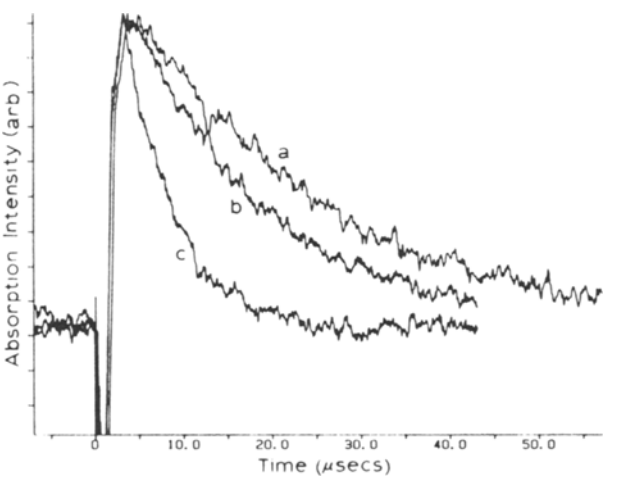

Fig. 3. Decay in C_2H absorption at several O_2 pressures. (a) No O_2 (b) 18.8 mTorr O_2 (c) 111 mTorr O_2. The spike at time = 0 is due to electrical interference from the excimer laser.

transitions lie at 3320, 3562, and 3702 cm^{-1} and are all of $^2\Sigma$ - $^2\Sigma$ symmetry. These transitions all share a common lower state, the $X^2\Sigma^+(001)$ state observed by Kanamori and Hirota[4].

For the rate constant measurements, C_2H was produced by the photolysis of CF_3C_2H. The decay in the C_2H absorption due to reaction of C_2H with O_2, H_2, or NO was monitored by using liquid nitrogen cooled InSb infrared detectors with fast preamplifiers giving a system time contant of less than 1 μsec. The transient digitizer signal was fitted to an exponential decay. The decay constants obtained were corrected for reaction of C_2H with the precursor and the resulting constants plotted versus the reactant pressure to yield the reaction rate. The rates measured for C_2H with O_2, H_2, and NO were 4.2×10^{-11}, 4.8×10^{-13}, and 3.5×10^{-11} cm^3 $molecule^{-1}$ sec^{-1} respectively.

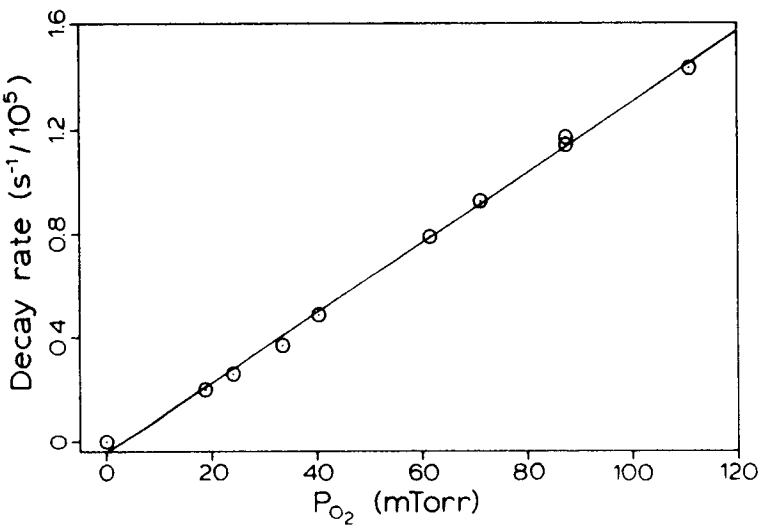

Fig. 4. Decay constants for various pressures of O_2.

1. J. L. Hall, D. Zeitz, J. W. Stephens, J. V. V. Kasper, G. P. Glass, R. F. Curl, and F. K. Tittel, J. Phys. Chem. 90, 2501 (1986)
2. J. V. V. Kasper, C. R. Pollock, R. F. Curl, Jr., and F. K. Tittel, Appl. Opt. 21, 236 (1982)
3. W.-B. Yan, J. L. Hall, J. W. Stephens, M. L. Richnow, and R. F. Curl, J. Chem. Phys., in press.
4. H. Kanamori and E. Hirota, to be published.

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