Unimolecular and Bimolecular Reactions Studied with the Chirped-Pulse Millimeter-Wave (CPmmW) Spectroscopy

Robert W. Field, Department of Chemistry, Massachusetts Institute of Technology

I. A classical unimolecular reaction was revisited using CPmmW spectroscopy. Vibrational population distribution of photolysis products as well as their relative abundances are measured with CPmmW. The dominant role of the four-center elimination mechanism in photolysis of vinyl cyanide has been demonstrated.

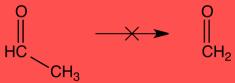
HCN vib. g.s. 00^{0} 30 Photolysis of **HCN** bend HNC vib. a.s. $00^{\circ}0$ 20 HCN bend $04^{0}0$ **HCN** stretch HCN bend $08^{\circ}0.7$ CPmmW signal, μV Photolysis of HCN vib. a.s. $00^{\circ}0$ HNC vib. g.s. HCN bend 00^{0} 20 02°0 HCN bend CN bend **HCN** stretch 08°0? 10 87.5 88.0 88.5 89.0 89.5 90.0 90.5 91.0 Transition frequency, GHz

II. Hydrogen atoms can be an effective catalyst for breaking up large organic molecules and converting biomass to biofuel. We have demonstrated the H-atoms-mediated thermal decomposition of acetaldehyde by CPmmW spectroscopy of pyrolysis reaction products.

Stop

Go!

Acetaldehyde does not decompose unimolecularly to formaldehyde even at high temperatures



Methyl nitrite decomposes at T = 1000 K, and can be used as a convenient source of H-atoms

$$H_3C$$
 $\stackrel{O}{\searrow}\stackrel{S}{\searrow}$ $\stackrel{O}{N}$ $\stackrel{\Delta}{\longrightarrow}$ $\stackrel{O}{\underset{CH_2}{\parallel}}$ $+$ $\stackrel{\bullet}{H}$ $+$ $\stackrel{\bullet}{NO}$

If methyl nitrite is added, acetaldehyde breaks apart following the H-atoms attack