

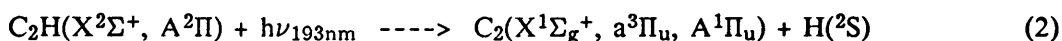
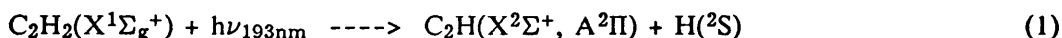
LABORATORY STUDIES OF PHOTODISSOCIATION PROCESSES RELEVANT TO THE FORMATION OF COMETARY RADICALS

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The strength of the $C_2(d^3\Pi_g \rightarrow a^3\Pi_u)$ Swan band emission in the spectra of cometary comae identifies this species as a prominent constituent of the coma gas, although its photochemical origin remains yet uncertain. It was previously suggested^[1] that the formation of cometary C_2 proceeds via the secondary photolysis of the C_2H radical, which is itself generated by dissociation of the stable acetylene molecule. The detection of C_2H in the interstellar medium^[2] and the recent analysis of the radial variation in $C_2(\Delta V=0)$ surface brightness of Comet Halley^[3] support the postulate that C_2 is a third-generation molecule. Although these astrophysical observations provide evidence for the proposed two-step dissociation process, laboratory verification of the mechanism is currently incomplete.

Measurement of the C_2 and C_2H translational energy distributions produced from the multiphoton dissociation (MPD) of acetylene at 193nm^[4] identifies the primary processes to be:



Time-resolved FTIR emission studies of the nascent C_2H radical formed in reaction (1)^[5] verify that this species is produced both vibrationally and electronically excited. A survey of the internal energy distributions of the C_2 fragments produced from the MPD of acetylene using a high intensity ArF laser is currently in progress in this laboratory. Previous results using the techniques of laser-induced fluorescence (LIF) and time-resolved emission^[6] allowed estimation of nascent radical concentrations, with $[C_2(A^1\Pi_u)] \gg [C_2(C^1\Pi_g)]$, $[C_2(a^3\Pi_u)] > [C_2(d^3\Pi_g)]$, and $[C_2(a^3\Pi_u)] \simeq [C_2(A^1\Pi_u)]$.

Recent experiments have focused on the measurement of rotational energy distributions for the $C_2(A^1\Pi_u, a^3\Pi_u)$ fragments. Figure 1 illustrates the distribution of rotational energies for the nascent $C_2(A^1\Pi_u)$ fragment produced during the MPD of various C_2H precursors. The distributions can each be fit using low and high temperature components, which implies the dissociation of C_2H occurs through a statistical process such as predissociation or internal conversion to the ground state continuum. The rotational energy distribution of nascent $C_2(a^3\Pi_u)$ from the MPD of acetylene is shown in Figure 2. Although the fit to a single temperature is fair, there is some indication of a low temperature component in the region of low rotational energies. Since the measurement of this distribution requires the use of low gas

pressures and short pump/probe delay times, interference from $C_2(d^3\Pi_g \rightarrow a^3\Pi_u)$ emission limits the achievable signal to noise ratio. We are currently trying to improve our $C_2(a^3\Pi_u)$ detection capability by performing this experiment in a molecular beam, thus allowing for discrimination between initial emission and LIF.

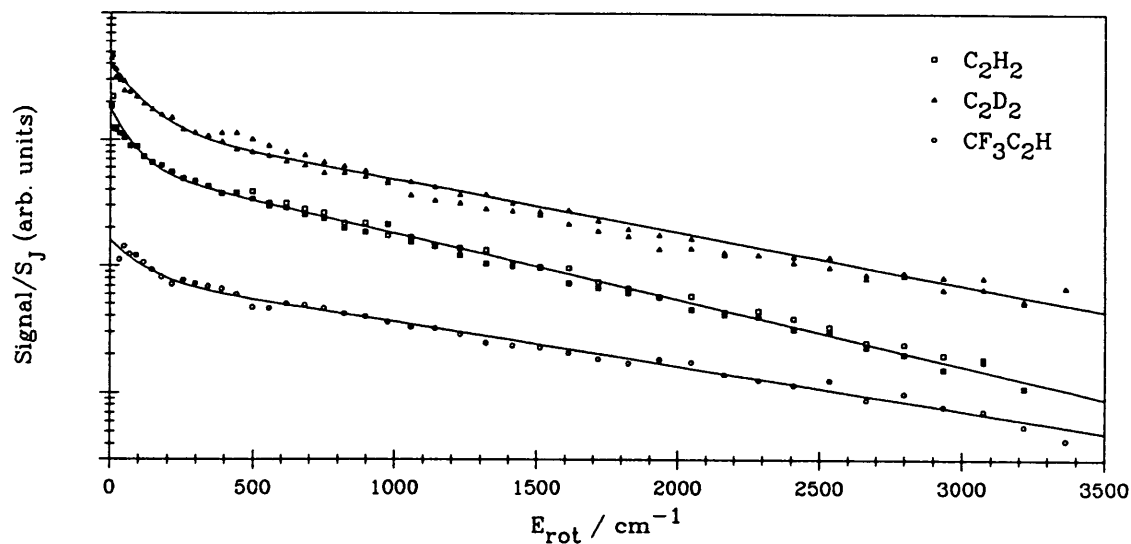


Figure 1. Rotational energy distributions for nascent $C_2(A^1\Pi_u, v''=0)$ formed in the photolysis of various C_2H precursors. The solid curves are fit to the temperature pairs of 100K+1200K, 150K+1500K, and 150K+1800K for C_2H_2 , C_2D_2 , and CF_3C_2H , respectively.

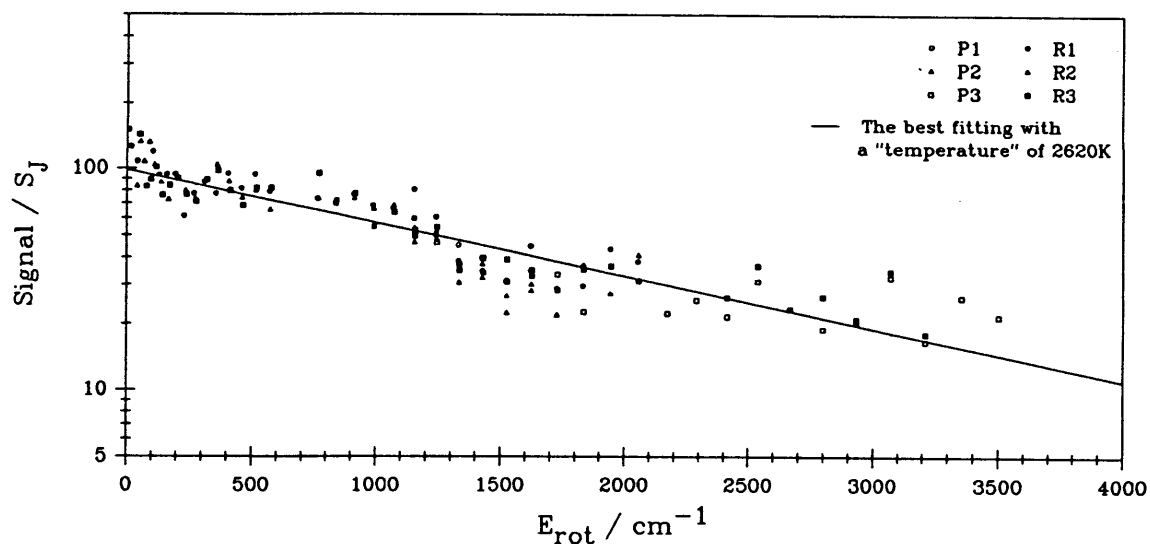


Figure 2. Rotational energy distribution for nascent $C_2(a^3\Pi_u, v''=0)$ formed in the photolysis of C_2H_2 .

A portion of the two-photon laser excitation spectrum of $C_2(X^1\Sigma_g^+)$ is shown in Figure 3. Since the signal was only observable after the inclusion of a buffer gas, it appears that $C_2(X^1\Sigma_g^+)$ is not formed appreciably during the initial dissociation process but rather as a result of radiative and collisional quenching of the $A^1\Pi_u$ and $a^3\Pi_u$ primary fragments.

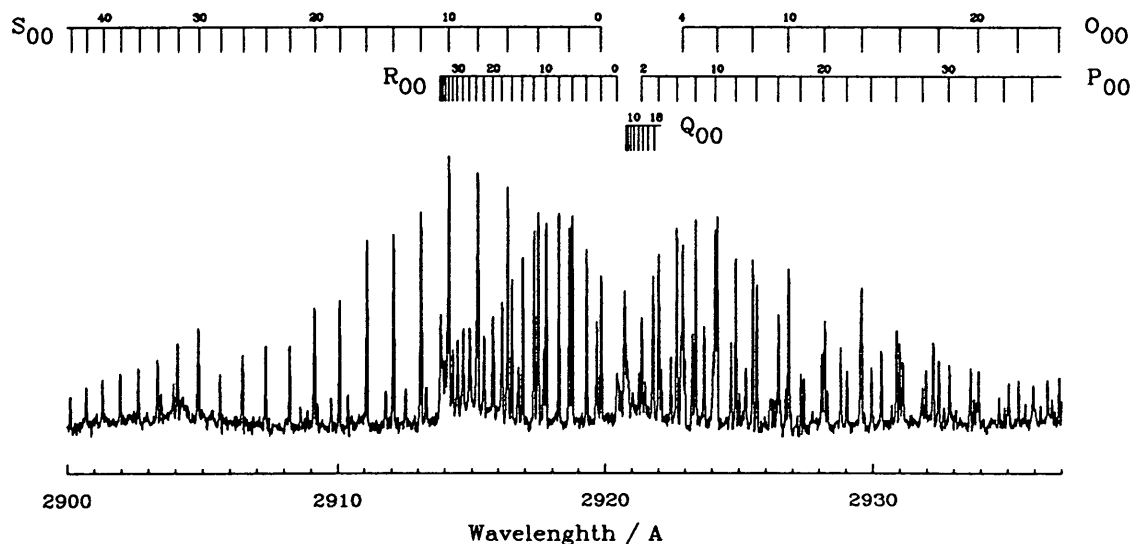


Figure 3. Two-photon laser excitation spectrum of $C_2(X^1\Sigma_g^+)$ produced in the MPD of C_2H_2 at 193nm, observed at a delay of $2\mu s$ (100mtorr C_2H_2 , 10torr Ar).

Another class of experiments being performed considers the mechanism and dynamics of CH and C_3 formation during the photodissociation of allene with a focused ArF laser. The laser excitation spectra of $CH(X^2\Pi)$ and $C_3(X^1\Sigma_g^+)$ given in Figures 4 and 5 verify the production of these cometary radicals, but give little insight into whether they are formed by primary or secondary dissociation processes. Again, the extraction of this information may be possible through the use of a molecular beam, since the possibility of forming a product by collisional processes is minimized.

Although the experiments performed to date provide considerable evidence in support of reaction (2), there is an important distinction to be made when comparing the laboratory conditions to those typically found in comets. Since the C_2H radicals generated in the laboratory experiments are formed vibrationally and/or electronically excited, the theoretical calculations of Shih et al.^[7] predict 193nm vertical excitation of the bent(115°) $C_2H(1^2A' \rightarrow 2^2A'')$ transition. Alternatively, any rotationally/vibrationally excited C_2H present in cometary comae will quickly undergo radiative relaxation in the infrared to their lowest rotational and vibrational state. The vertical excitation energy for the linear(180°) $C_2H(X^2\Sigma^+ \rightarrow ^2\Pi)$ transition then increases to $\approx 8.1eV$ ^[7], well into the vacuum UV region. Experiments are currently under

way in our laboratory to confirm the cometary formation of C_2 via the VUV dissociation of cold C_2H .

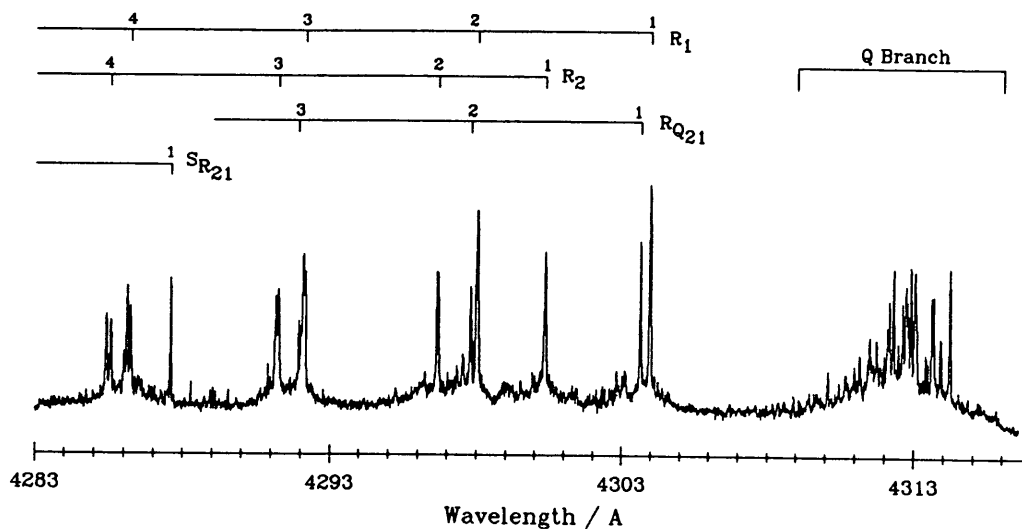


Figure 4. Laser excitation spectrum of $CH(X^2\Pi, v''=0)$ formed in the photolysis of allene, observed at a delay of $5\mu s$ (50mtorr C_3H_4 , 10torr Ar).

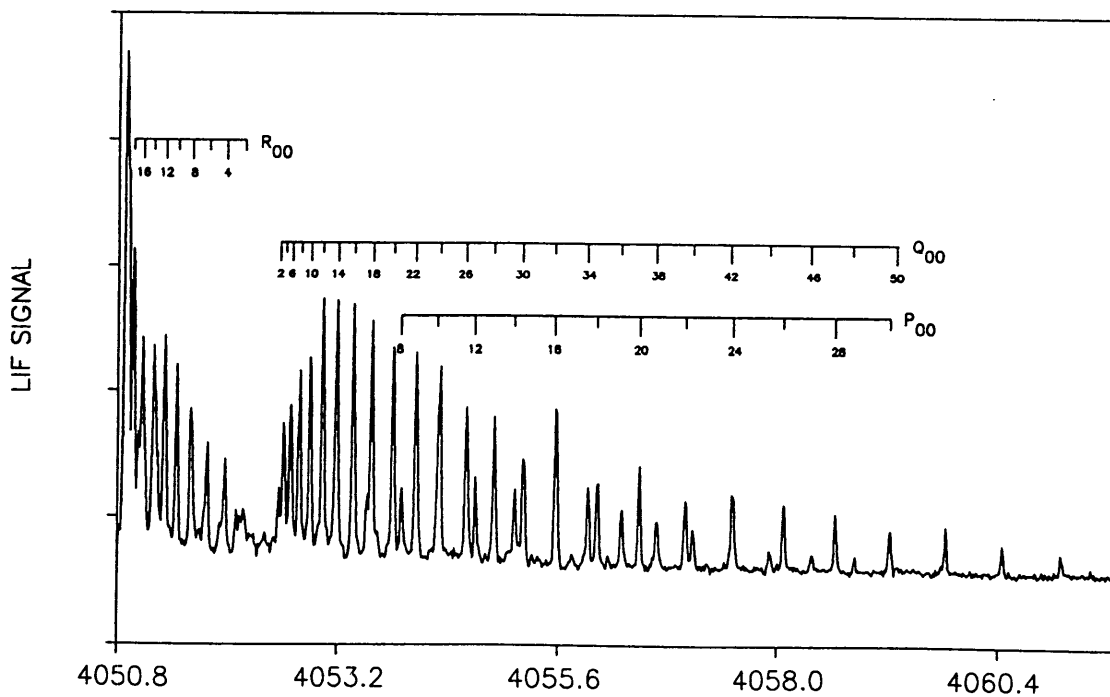


Figure 5. Laser excitation spectrum of $C_3(X^1\Sigma_g^+, 000)$ formed in the photolysis of allene, observed at a delay of $5\mu s$ (100mtorr C_3H_4 , 10torr Ar).

ACKNOWLEDGEMENTS

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