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FUNDAMENTAL SPECTROSCOPIC STUDIES OF CARBENES AND  
HYDROCARBON RADICALS

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## PROGRESS REPORT

This past year we (1) made the first spectroscopic identification of the HCCCO and DCCCO radicals; (2) detected new vibrationally excited states of the carbon chain radicals CCH and CCD and the three-membered carbene ring, cyclopropenylidene; (3) determined an accurate structure of the cumulene carbene  $H_2CCC$ ; (4) analyzed the hyperfine structure in the SiC radical; and (5) undertook a systematic search for new sulfur bearing radicals.

*(1) The HCCCO and DCCCO Radicals*

Lander *et al.* (*J. Chem. Phys.*, **94**, 7759 [1990]) found that CCH, a key radical in combustion chemistry, reacts with CO in a three-body addition reaction with the HCCCO radical as the product. We reported the first spectroscopic detection of HCCCO in one paper (Ref. 6) and have extended the millimeter-wave spectroscopy of the HCCCO radical to include a thorough investigation of the rotational spectrum of DCCCO as well in a second (Ref. 7). Our work provides a foundation for future laboratory spectroscopic investigations in the IR and millimeter-wave regions of a potentially important combustion intermediate.

*(2) The Structure of the Cumulene Carbene Propadienylidene,  $H_2CCC$* 

Following our detection of  $H_2CCC$  about one year ago (Ref. 1) we measured the rotational spectra of the  $H_2^{13}CCC$ ,  $H_2C^{13}CC$ ,  $H_2CC^{13}C$ , and  $D_2CCC$  isotopomers and determined the substitution structure. These structures are probably quite close to the equilibrium ( $r_e$ ) structure, because in the structurally similar molecules ketene and formaldehyde the bond lengths and angles in the substitution structures are within 0.002 Å and 0.5° of the  $r_e$  structure. Moreover, it should be possible to derive an excellent  $r_e$  structure for  $H_2CCC$  using vibration-rotation constants calculated *ab initio* by Peter Botschwina (Göttingen). A paper describing this work is about to be submitted to the *Journal of Molecular Spectroscopy* (Ref. 8).

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### (3) *Vibrationally Excited CCH and CCD*

We measured rotational transitions in the  $\nu_3$   $^2\Sigma$ ,  $\nu_1 + \nu_2$   $^2\Pi$ , and  $\nu_2 + \nu_3$   $^2\Pi$  vibronic states of CCH seen previously in the IR and observed, for the first time, the  $2\nu_2$   $^2\Sigma$  and  $2\nu_2$   $^2\Delta$  bending states. The millimeter-wave measurements yield improved rotational and fine structure constants for the  $\nu_3$ ,  $\nu_1 + \nu_2$ , and  $\nu_2 + \nu_3$  states and accurate hyperfine constants which can be compared with the *ab initio* calculations by Sigrid Peyerimhoff and coworkers (*J. Mol. Spectrosc.*, **150**, 56 [1991]; **150**, 70 [1991]). In spite of the extensive IR work on CCH, the  $\nu_1$  band, arising from the C-H stretch, has not been conclusively identified. It is believed that a band at  $3299\text{ cm}^{-1}$  may be due to the C-H stretch (Stephens *et al.*, *J. Mol. Struct.*, **190**, 41 [1988]), however, its counterpart has not been observed in CCD. We observed the rotational spectrum for the upper state of the  $3299\text{ cm}^{-1}$  band and then detected a spectrum in CCD which we believe arises from the same vibrational state. These constants were sent to R. Curl in the hope that they may aid the identification of the  $\nu_1$  mode in the IR. A paper describing our CCH measurements will be submitted to the *Journal of Chemical Physics*.

### (4) *New Vibrationally Excited States of Cyclopropenylidene*

Recently Hirahara *et al.* (*J. Chem. Phys.*, **95**, 3975 [1991]) measured the  $\nu_3$  transition of cyclopropenylidene — the three-membered carbene ring we detected in 1985. Guided by the rotational and centrifugal constants of Hirahara *et al.* we observed strong rotational transitions in the  $\nu_3$  state in an allene discharge, detected rotational transitions in three new vibrational states (two with *A* and one with *B* symmetry), and determined an accurate set of spectroscopic constants for all four vibrational states. We hope to assign these new vibrational states either by comparing inertial defects derived from *ab initio* harmonic force constants with the measured values or by using anharmonic constants which Henry Schaefer has offered to calculate. The millimeter-wave spectroscopic constants should help guide further IR measurements of cyclopropenylidene.

### (5) Hyperfine Structure of the SiC Radical

Following our detection of SiC in its  $X^3\Pi$  ground state we measured the rotational spectra of the  $\text{Si}^{13}\text{C}$  and  $^{29}\text{SiC}$  radicals (Ref. 5). Well-resolved hyperfine splittings in the three fine-structure ladders allowed determination of the magnetic hyperfine constants to 2% or better. Of the seven open shell diatomic SiC molecules observed by high resolution spectroscopy, hyperfine structure of  $^{29}\text{Si}$  has completely analyzed only in SiC. Determination of the spin density in SiC awaits an *ab initio* calculation that reproduces our hyperfine constants and should allow an interesting comparison with isovalent  $a^3\Pi_u$   $\text{C}_2$ .

### (6) Search for New Sulfur Bearing Radicals

Although the HCO, HCCO, and HCCCO radicals are now well characterized spectroscopically, remarkably little is known about the analogous sulfur bearing radicals HCS, HCCS, and HCCCS. We therefore undertook a wide frequency ( $\sim 30$  GHz) survey in a discharge through  $\text{CS}_2$  and  $\text{C}_2\text{H}_2$  and identified many new lines from sulfur bearing molecules. We anticipate that several new sulfur bearing molecules will be identified in the next few months.

## PLANS FOR THE COMING YEAR

Our major effort during the next year will continue to be devoted to searches for new carbenes and radicals with a strong emphasis on three and five membered carbene rings. We plan to measure the structures of these species once the spectra of the normal species are characterized, and, in parallel with our continuing work with discharges, to explore new methods for producing hydrocarbon radicals and carbenes.

### (1) Search for New Carbenes

The search for new carbenes will focus on: (1) vinylidene ( $\text{H}_2\text{CC}$ ) in the  $^3B_2$  state, (2) the five-membered carbene ring cyclopentadienylidene ( $\text{C}_5\text{H}_4$ ), (3) propargylene (HCCCH), (4) cyclopropenylidene carbene ( $\text{H}_2\text{C}_3=\text{C}$ ), and (5) the ring-chain hybrid  $\text{C}_5\text{H}_2$ .

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