

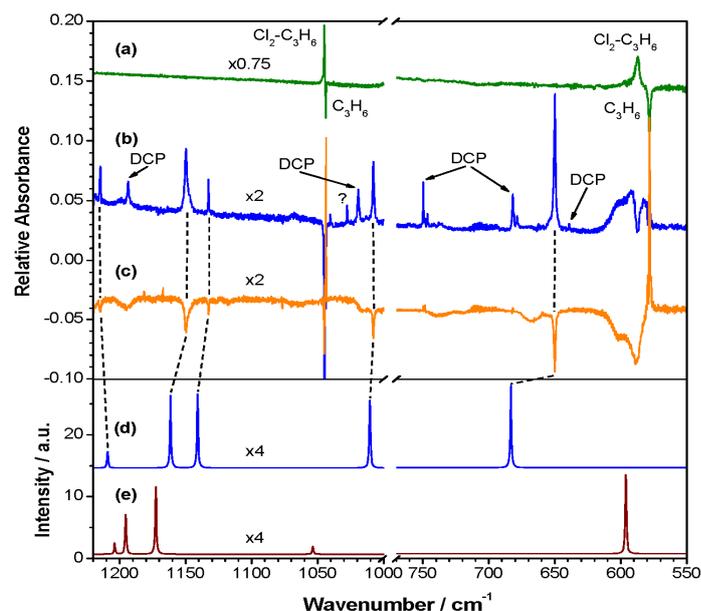
## 3A10 Studying Infrared Absorption of Reaction Intermediates Using Step-scan FTIR and *p*-H<sub>2</sub> Matrix Isolation Techniques

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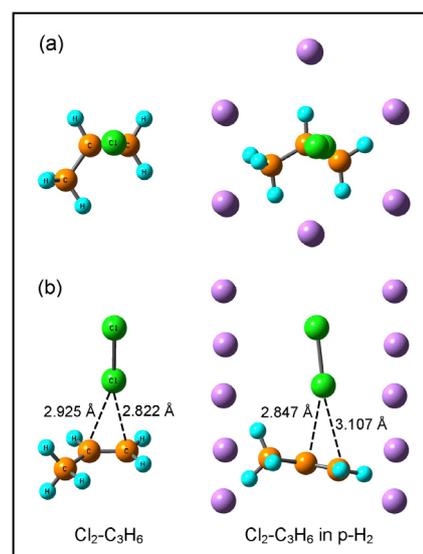
Among several techniques employed in our laboratory for studying transient species in chemical reactions two will be discussed. We developed the time-resolved Fourier-transform infrared (TR-FTIR) absorption spectroscopy to investigate IR absorption of gaseous transient species. A flow reactor with a multipassing UV photolysis beam and a multipassing IR probe beam is coupled to a step-scan FTIR spectrometer with both dc- and ac-detection to record temporal profiles of the infrared absorption of reaction intermediates. IR absorption spectra of several reactive species such as CH<sub>3</sub>OO [1], CH<sub>3</sub>SO<sub>2</sub> [2], ClCOOH [3], and CH<sub>3</sub>C(O)OO [4] were recorded. Spectral assignments were made based on reaction mechanisms and comparison of observed vibrational wavenumbers and rotational contours with those predicted quantum-chemically. The identifications of two conformers of CH<sub>3</sub>C(O)OO and the determination of the relative energy of these conformers will be discussed. In the reaction of CH<sub>3</sub>CO + O<sub>2</sub>, absorption bands with origins at 1851 ± 1, 1372 ± 2, 1169 ± 6 and 1102 ± 3 cm<sup>-1</sup> are attributed to *t*-CH<sub>3</sub>C(O)OO, and those at 1862 ± 3, 1142 ± 4 and 1078 ± 6 cm<sup>-1</sup> are assigned to *c*-CH<sub>3</sub>C(O)OO. A weak band near 1960 cm<sup>-1</sup> is assigned to α-lactone, *cyc*-CH<sub>2</sub>C(=O)O, a coproduct of OH. The observed relative intensities indicate that *t*-CH<sub>3</sub>C(O)OO is more stable than *c*-CH<sub>3</sub>C(O)OO by 3.0 ± 0.6 kJ mol<sup>-1</sup>. Based on these observations, the branching ratio for the OH + α-lactone channel of the CH<sub>3</sub>CO + O<sub>2</sub> reaction is estimated to be 0.04 ± 0.01. A simple kinetic model is employed to account for the decay of CH<sub>3</sub>C(O)OO. Preliminary results on CH<sub>3</sub>OSO and CH<sub>3</sub>SO will also be presented.

*Para*-hydrogen (*p*-H<sub>2</sub>) has recently emerged as a new matrix host. Because of the 'softness' associated with the extensive delocalization of the H<sub>2</sub> moieties, new characteristics of molecules isolated in this quantum solid are explored. We demonstrated that the internal rotation of methanol persists in solid *p*-H<sub>2</sub> by observation of splittings of the *E/A* torsional doublets in internal-rotation-coupled vibrational modes [5]. We also provided direct spectral evidence that CH<sub>3</sub>F isolated in *p*-H<sub>2</sub> rotates about only its symmetry axis, and not about the other two axes by observation of two weak absorption lines from the *E* (*K* = 1) level and one intense feature from the *A* (*K* = 0) level for degenerate modes ν<sub>4</sub>-ν<sub>6</sub> of CH<sub>3</sub>F [6]. We demonstrated another feature of solid *p*-H<sub>2</sub>, the absence of cage effect, by reaction of Cl, produced from *in situ* photodissociation of Cl<sub>2</sub>, with CS<sub>2</sub>. Absorption lines of ClSCS, not ClCS<sub>2</sub> or Cl<sub>2</sub>CS<sub>2</sub>, were observed at 1479.5 and 1480.8 cm<sup>-1</sup> [7]. This feature opens up a new method to prepare free radicals by barrierless reactions of atom and molecules. In the reaction

of Cl with propene, lines at 1382.2, 1214.7, 1149.6, 1132.7, 1007.6, and 649.9  $\text{cm}^{-1}$  are assigned to 2-chloropropyl radicals (Fig. 1). Only 2-chloropropyl radicals, not 1-chloropropyl radicals, were observed in this reaction, in sharp contrast to what is generally accepted in the gas-phase and solution chemistry. This demonstrates a preferential attack in the addition reaction of Cl with propene in solid  $p\text{-H}_2$  (Fig. 2). Possible reason for this selectivity will be discussed. We can also produce free radicals via in situ photolysis which is difficult in noble-gas matrices. Production of  $\text{CH}_3\text{S}$  from photolysis of  $\text{CH}_3\text{SSCH}_3$ ,  $\text{CH}_3\text{SCH}_3$ , and  $\text{CH}_3\text{SH}$  and the first identification of the IR spectrum of  $\text{CH}_3\text{S}$  will also be discussed.



**Fig. 1.** Experimental difference spectra (a–c) and simulated harmonic IR spectra for the 2-chloropropyl (d) and 1-chloropropyl (e) radicals in the regions 550–770 and 1000–1220  $\text{cm}^{-1}$ . (a) Recorded at 3.2 K upon annealing of a  $\text{C}_3\text{H}_6/\text{Cl}_2/p\text{-H}_2$  (1:1.3:2000) matrix to 4.3 K for 1 hour after deposition for 5 hours. (b) Recorded at 3.2 K upon irradiation of a  $\text{C}_3\text{H}_6/\text{Cl}_2/p\text{-H}_2$  (1:1:2000) matrix at 365 nm for 5 hours after deposition for 10 hours. Annealing was not done prior to 365 nm photolysis. (c) Recorded at 3.2 K upon irradiation of the matrix described in (b) at 254 nm for 4 h. Annealing to 4.5 K for 50 minutes was done prior to 254 nm photolysis. (d) and (e) Simulated spectra based on the unscaled harmonic frequencies of 2-chloropropyl and 1-chloropropyl radicals, respectively, computed at the B3LYP/aug-cc-pVDZ level of theory, with a simulated half-width of 0.5  $\text{cm}^{-1}$  and a resolution of 0.25  $\text{cm}^{-1}$ .



**Fig. 2.** Minimum energy structures of the  $\text{Cl}_2\text{-C}_3\text{H}_6$  complex in the gas phase (left panels) and within a model hexagonal close-packed lattice of  $p\text{-H}_2$  (right panels) calculated with B3LYP/aug-cc-pVDZ. Panel (a) is a view looking down the Cl–Cl bond axis and panel (b) is a side view  $\sim 90^\circ$  from that displayed in (a). In the  $p\text{-H}_2$  model structure, the  $p\text{-H}_2$  molecules are being represented by single pink spheres and some *para*-hydrogen molecules have been removed to reveal the structure of  $\text{Cl}_2\text{-C}_3\text{H}_6$ .

## References

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