

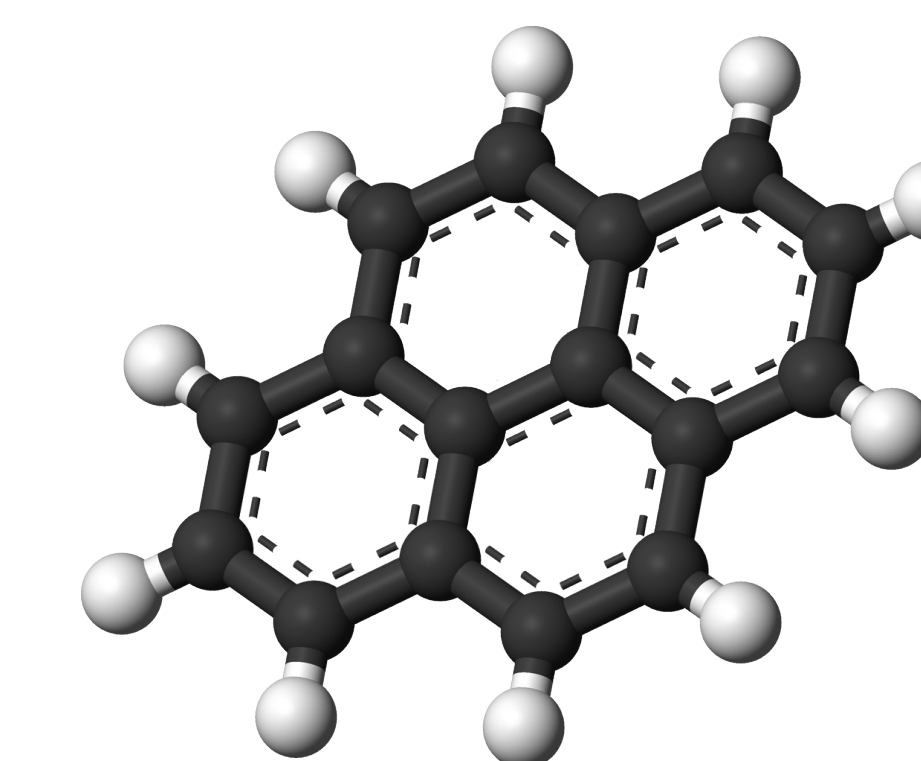
Rotationally-Resolved Infrared Spectroscopy of the Polycyclic Aromatic Hydrocarbon Pyrene ($C_{16}H_{10}$)

Jacob T. Stewart*, Brian E. Brumfield*,†, and Benjamin J. McCall**

*Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801

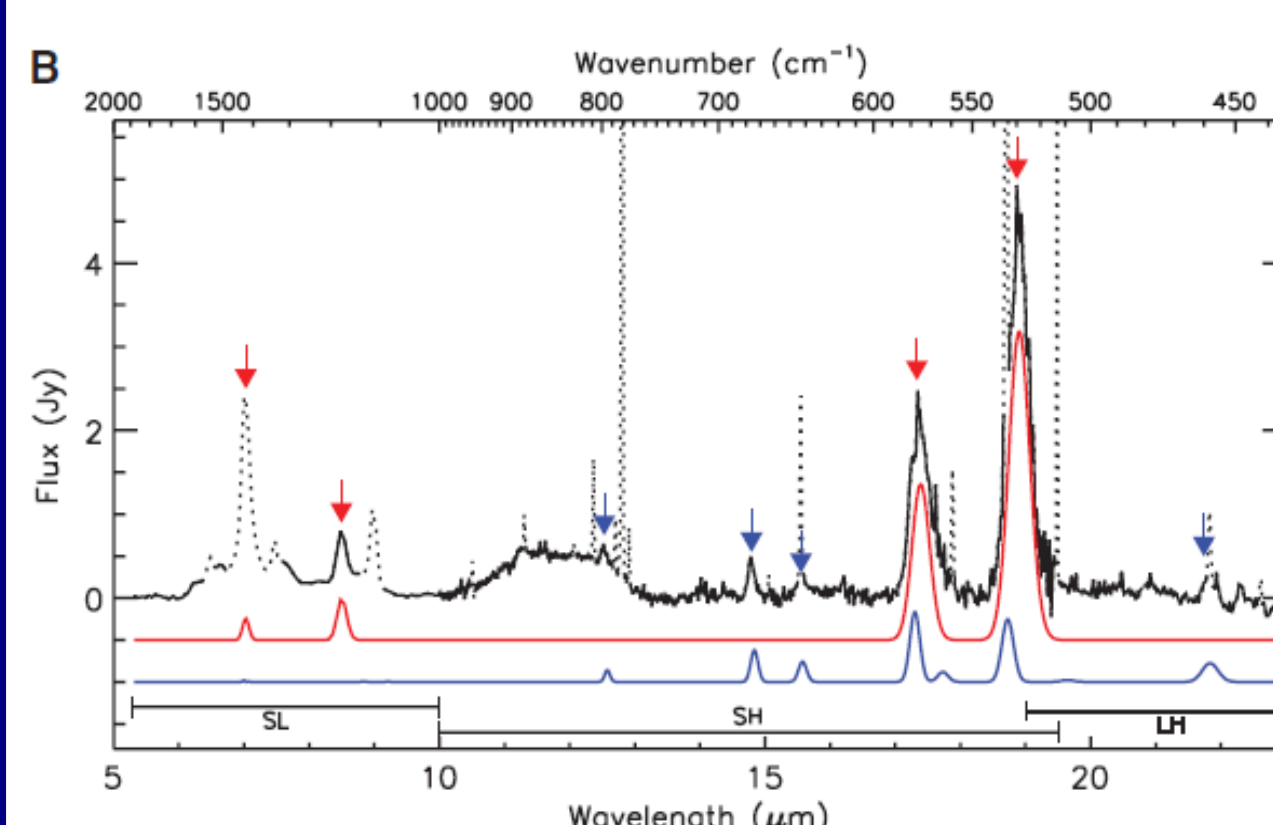
**Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801

†Present address: Department of Electrical Engineering, Princeton University, Princeton, NJ 08544



Motivation

Large, symmetric molecules (linear carbon chains, polycyclic aromatic hydrocarbons (PAHs), and fullerenes) are important to interstellar chemistry. We are particularly interested in C_{60} , which has been detected by infrared emission spectroscopy in various environments

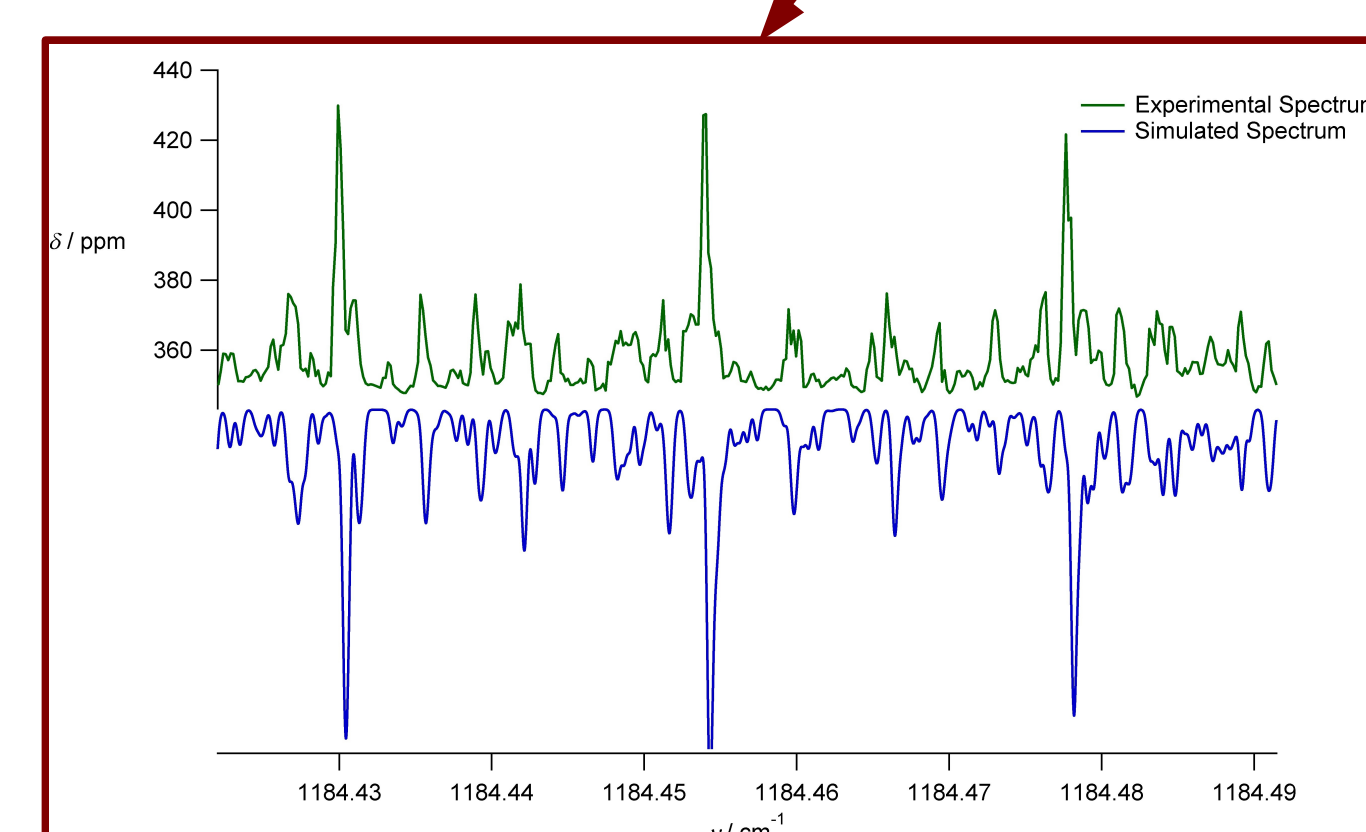
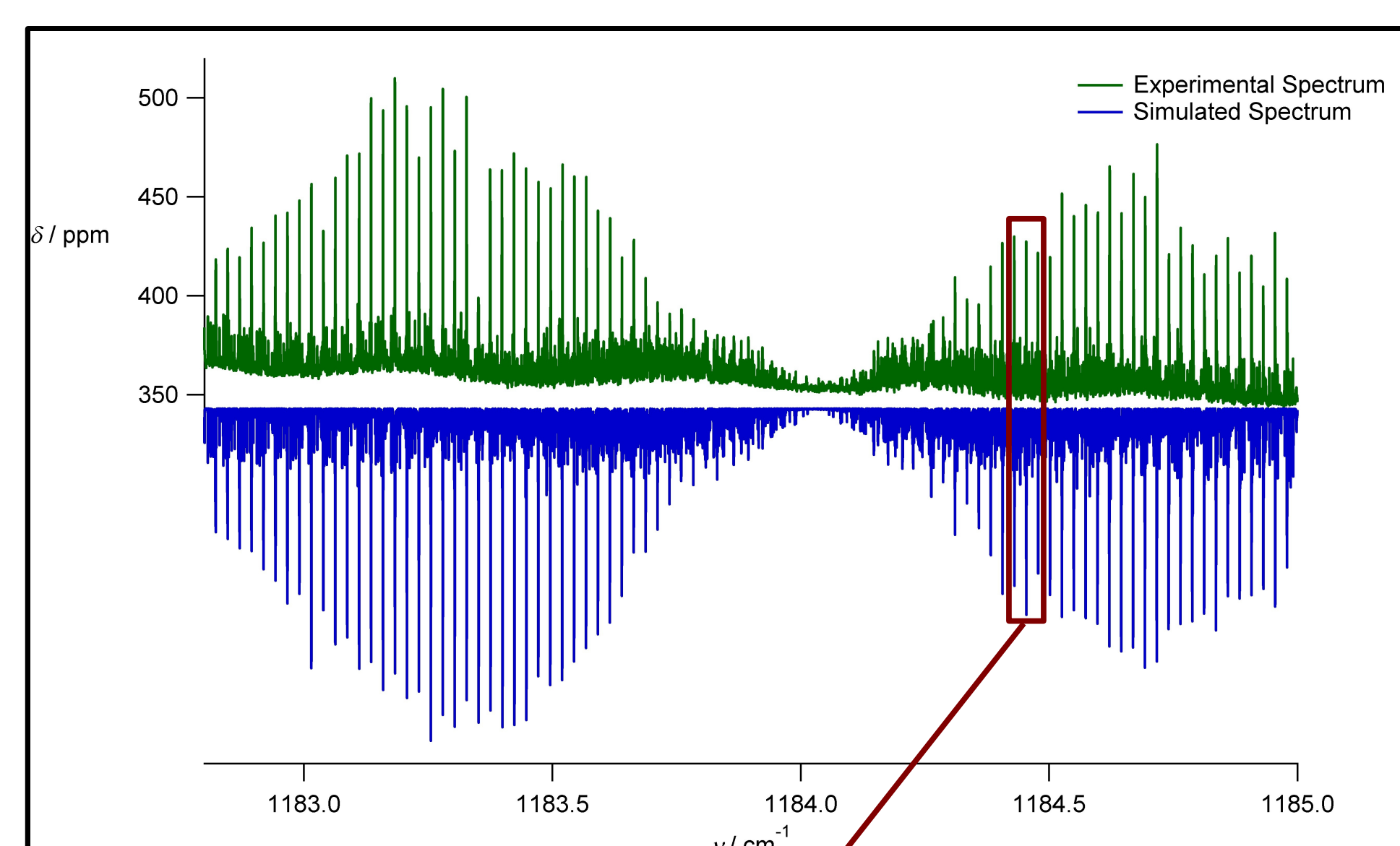


Infrared emission from C_{60} (red arrows) and C_{70} (blue arrows) in planetary nebula Tc1[1]

We want to obtain a high-resolution gas phase absorption spectrum of C_{60} near $8.5 \mu m$ to aid astronomical searches for C_{60} absorption, which will help us better understand the chemistry of interstellar C_{60} .

As an intermediate step, we have acquired a rotationally-resolved gas phase spectrum of the PAH pyrene. We have used this molecule to assess cooling of large molecules by supersonic expansion.

Rotationally-Resolved Spectra



The simulation was generated with a rotational temperature of 25 K and a linewidth of 0.0004 cm^{-1} (12 MHz) using the constants from our fit. δ represents the measured fractional loss per pass in parts per million.

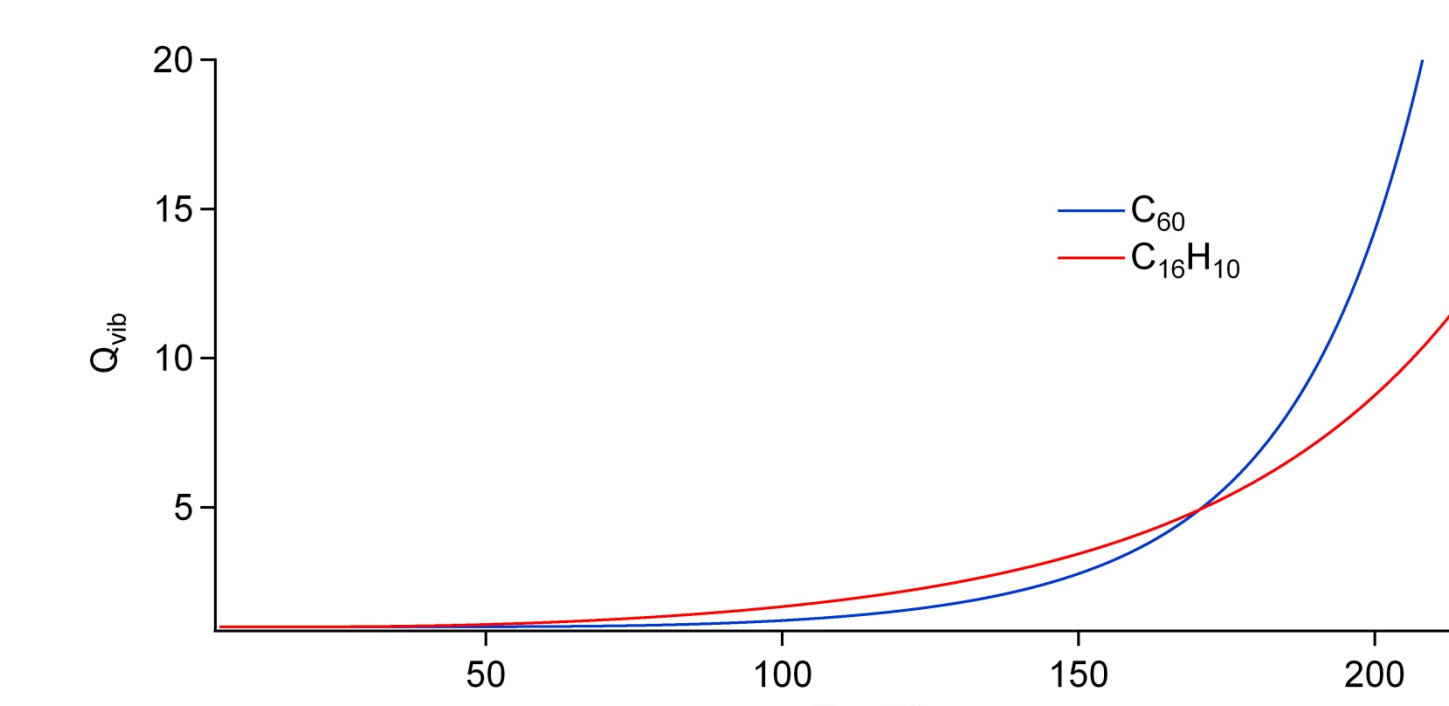
- We have acquired the rotationally-resolved spectrum from 1182.8 to 1185 cm^{-1} .
- We used PGOPHER[2] to assign and fit ~ 700 lines in the spectrum to an effective asymmetric top Hamiltonian
- The root mean square deviation of the fit is 0.00049 cm^{-1} (15 MHz)
- The deviation only increases to 0.00053 cm^{-1} (16 MHz) if no distortion terms are included, indicating that pyrene acts as a nearly ideal rigid rotor

	Ground State	Excited State
ν_0		1184.035714(21)
A	0.0337104(11)	0.0337032(11)
B	0.01855616(40)	0.01855630(39)
C	0.01197389(31)	0.01197210(31)
D_K	$-3.19(18) \times 10^{-8}$	$-3.84(20) \times 10^{-8}$

Rotational constants and band center obtained from our fit, in cm^{-1}

Estimating Cooling

Cooling the vibrational degrees of freedom will be key to obtaining a high-resolution spectrum of C_{60} , so we used pyrene to test vibrational cooling of large molecules in a supersonic expansion. We used the measured band strength to calculate a maximum possible absorption signal and then compared it with our actual absorption signal to estimate the vibrational temperature to be 25-90 K.



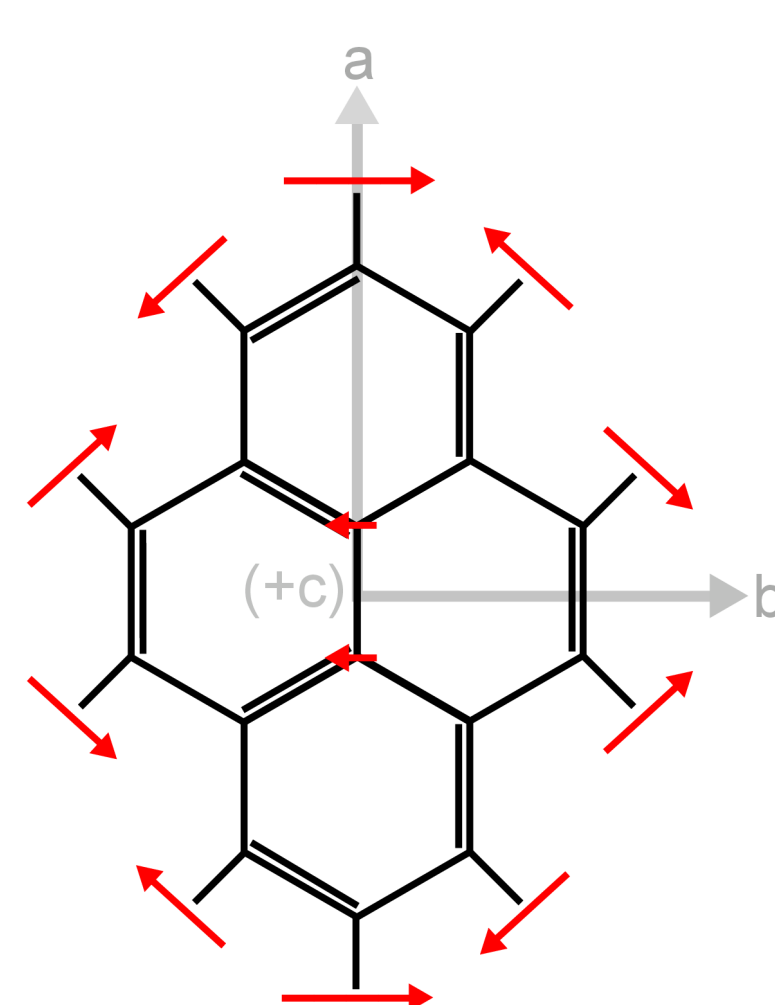
This plot shows the vibrational partition function for pyrene and C_{60} as a function of vibrational temperature. As the partition function increases, there are fewer molecules in the ground vibrational state, making absorption spectroscopy more difficult.

Characteristics of Pyrene

Pyrene is a planar asymmetric top of D_{2h} point group symmetry. We observed a C-H bending mode near 1184 cm^{-1} . Pyrene is the largest molecule to be observed with rotational resolution by absorption spectroscopy.

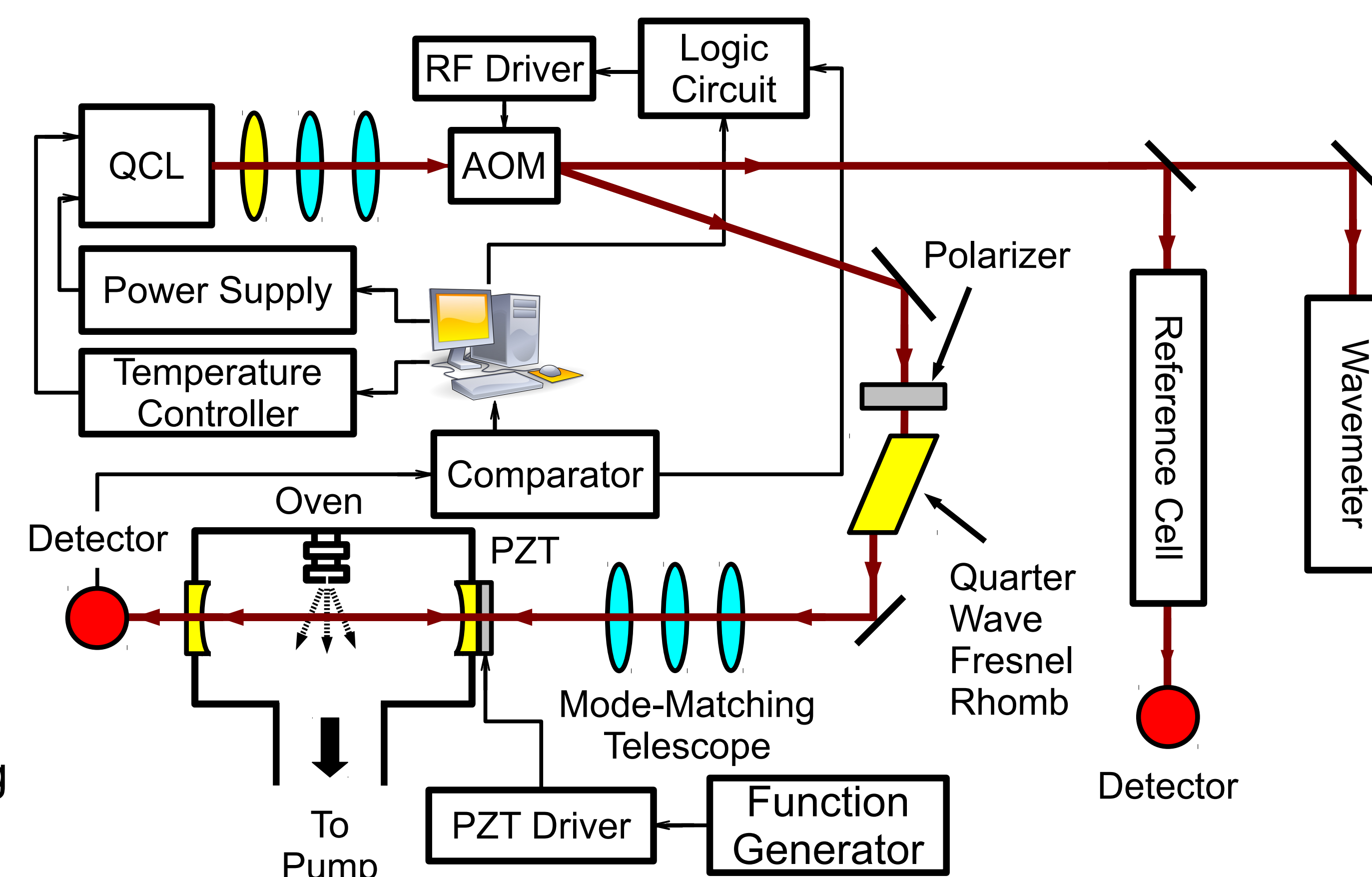
The red arrows indicate the motion of the nuclei for the particular C-H bending mode we observed.

The principal axes (a,b,c) are labeled in the figure.



Experimental Setup[3]

- We use a cw quantum cascade laser (QCL) as our mid-IR light source (provided by Claire Gmachl's group at Princeton)
- We use cavity ringdown spectroscopy, a sensitive absorption technique, to obtain our infrared spectra
- To generate gas phase samples of pyrene, we heated it in a high temperature oven to $\sim 160^\circ\text{C}$
- To cool pyrene (or C_{60}) after generating it in the gas phase we seed it in an argon supersonic slit expansion



Future Work

- Continue to larger PAHs, such as coronene ($C_{24}H_{12}$)
- Develop an external cavity quantum cascade laser system to extend our frequency coverage in the mid-IR
- Explore other means to produce gas phase C_{60} at a lower temperature

References and Acknowledgments

- [1] Cami et al. *Science* **329**, 1180 (2010).
- [2] Western, <http://pgopher.chm.bris.ac.uk>
- [3] Brumfield et al. *Rev. Sci. Instrum.* **81**, 063102 (2010).