

Progress towards a rotationally-resolved spectrum of C₆₀

by Nicole C. Koeppen, Bradley M. Gibson, and Benjamin J. McCall

Buckminsterfullerene (C₆₀) was first discovered back in 1985 by Kroto et al.^[1] while they were simulating carbon star chemistry in the laboratory and noticed that carbon clusters comprised of 60 carbon atoms dominated other even number clusters. The presence of these molecules in the outflows of stars was confirmed in 2010, when it was detected in the planetary nebula Tc1^[2]. Also during this time C₆₀ was detected in the interstellar medium (ISM) through infrared (IR) emission transitions from reflection nebulae. Although its presence in these environments was confirmed, the exact amount of C₆₀ present remains a mystery because of uncertainties in its ultraviolet absorption cross-section^[3]. Obtaining an absorption spectrum would allow the amount of C₆₀ to be determined without relying on this value.

Out of the four IR active bands of C₆₀, the F_{1u}(3) band is centered around 1185 cm⁻¹^[4], and in the region of an atmospheric transmission window. This allows for observations of this band from ground-based telescopes, which makes collecting a high-resolution absorption spectrum of C₆₀ in this region even more valuable. To pursue this goal, we have built a continuous-wave external-cavity quantum cascade laser (cw-EC-QCL) cavity ring-down (CRD) instrument. The EC-QCL, shown in **Figure 1**, allows us to achieve a tuning range of 1135 - 1220 cm⁻¹. Highly reflective mirrors form the cavity and light is allowed to build up to a user-defined intensity, at which point it is quickly shuttered. The amount of time it then takes the light to ringdown is related to the absorption of any species present within the laser path. This technique has the advantages of a large pathlength for the detection of small number densities, as well as being independent of any intensity fluctuations from the laser. By implementing

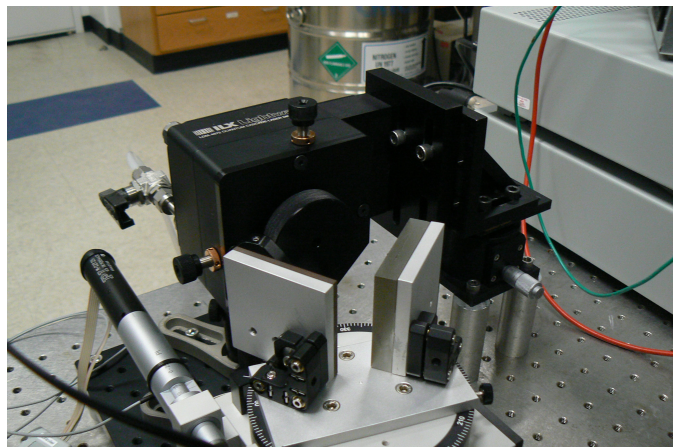


Figure 1 - The cw-EC-QCL used in our system. The resulting light is centered around 8.5 μm and allows for a scanning range of $\sim 100 \text{ cm}^{-1}$. Picture adapted from <http://bjm.scs.illinois.edu/laboratory/c60.php>.

a side-of-fringe locking setup to our system^[5], we are able to achieve sensitivities on the order of $10^{-9} \text{ cm}^{-1} \text{ Hz}^{-1/2}$ and laser frequency stability on the order of $\sim 1 \text{ MHz}$. The system has recently been utilized to obtain a gas phase spectrum of the molecule 1,3,5-trioxane^[6]. A detailed diagram of the system is presented in **Figure 2**.

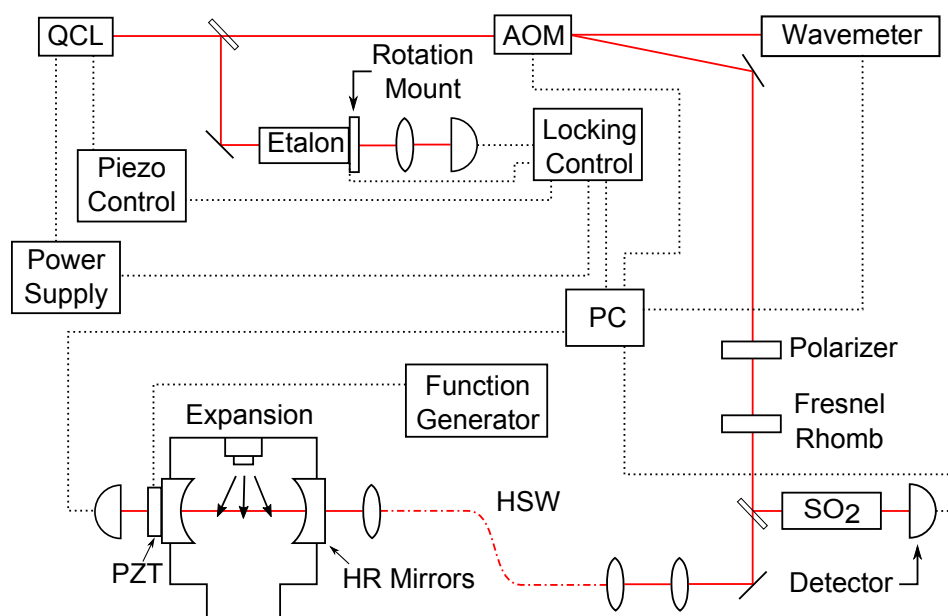


Figure 2 - Experimental layout of our EC-QCL CRD system. For details on the laser path or locking electronics, readers are directed to references [6] and [5], respectively. Figure adapted from reference [6].

The first step towards obtaining a spectrum of C_{60} was to look at a smaller PAH, in this case pyrene^[7]. Pyrene's ν_{68} band was observed between 1182.77 and 1185.06 cm^{-1} (see **Figure 3**) with a slightly older version of our system, which relied on a Fabry-Perot QCL with a tuning range of only $1180 - 1200 \text{ cm}^{-1}$. In order to obtain cooled gas phase pyrene, solid pyrene was heated in an oven to around 420 K and supersonically expanded, using argon as the carrier gas, through a slit and into the path of the laser. By comparing simulations to the observed spectrum, a rotational temperature of around 23 K was determined and the vibrational temperature was estimated to be between 23 and 111 K .

The first attempt to observe gas phase C_{60} was completed in a similar fashion to pyrene^[8]. However, since C_{60} has negligible vapor pressure at room temperature, it must be heated to much higher temperatures than pyrene in order to vaporize a significant amount. C_{60} was thus heated up to $\sim 955 \text{ K}$ and supersonically expanded through a slit using a number of different expansion conditions and a mass flow rate of ~ 2 grams per hour. Although these conditions give a predicted S/N of ~ 130 for the strongest transitions, as can be seen in **Figure 4**, a spectrum was never observed with our setup. A large factor in the ability to observe a spectrum is having a significant portion of the population in the ground state. Since we start at a relatively high temperature of the gas, C_{60} must be efficiently cooled in the expansion in order to achieve this. One difficulty with C_{60} is that it has 174 vibrational modes, which results in a large partition function even at relatively low temperatures. In addition, the lowest excited vibrational mode lies 267 cm^{-1} above the ground state. This is much higher than most PAHs and since the cooling efficiency of collisions decreases as the energy gap increases, it becomes more difficult to completely cool these modes with a similar number of collisions.

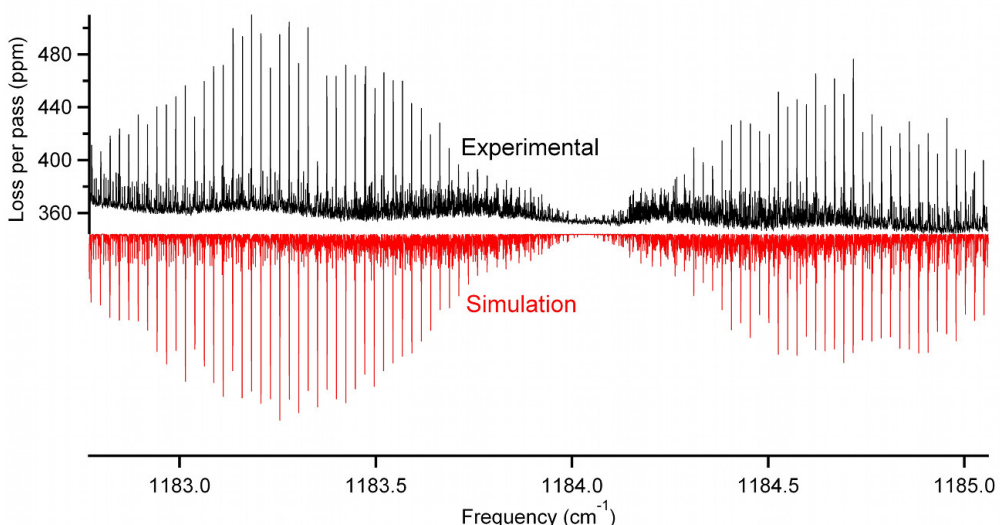


Figure 3 - Experimental and simulated spectrum of the ν_{68} band of pyrene. Figure adapted from reference [7].

The results and analysis from the oven-heated supersonic expansion of C_{60} showed that a new approach was going to be needed if a spectrum was to be observed. To this end, we designed a supercritical fluid (SCF) source based on designs for SCF chromatography by Sin et al.^[9] This allows for the production of C_{60} vapor at much lower temperatures which decreases the partition function. A SCF mixture of CO_2 and toluene was chosen since CO_2 alone is a poor solvent for C_{60} but pure toluene has a high critical temperature of 592 K. By creating a 7:3 mole fraction ratio (CO_2 :toluene), the mixture only needs to be heated to a critical temperature of 445 K.^[10] One iteration of the SCF expansion source has already been tested with D_2O in SCF CO_2 ^[11] and a second-generation source, pictured in **Figure 5**, has recently been built to fix a few minor problems we found with the first one. With this, we have already observed 1,3,5-trioxane dissolved in a CO_2 :toluene (7:3 v/v) SCF mixture. Based on the solubility of C_{60} in these mixtures, we estimate that we will see a mass flow rate of a few milligrams of C_{60} per hour^[9].

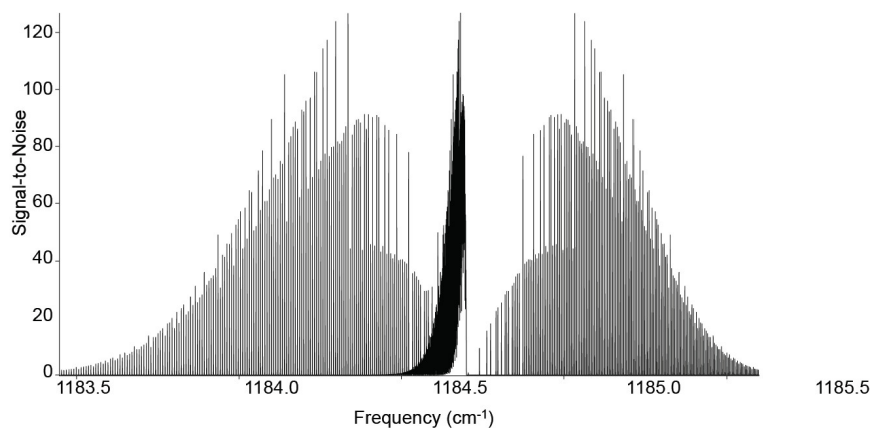


Figure 4 - The expected S/N of the different transitions in the $F_{1u}(3)$ band of C_{60} based on the mass flow rate of C_{60} and the sensitivity of the instrument. Figure adapted from reference [8].

Since the number density of C_{60} in our expansion will be much lower than previous attempts, we will have to increase the sensitivity of our instrument. Currently the intensity of light for ringdown is built up by dithering one of the cavity mirrors by greater than one free spectral range (FSR), which allows for the cavity to be on-resonance with the laser twice per pass. By locking the laser frequency to our cavity with the Pound-Drever-Hall technique, we can achieve almost continual constructive interference of the light since the cavity will be on-resonance with the frequency of the laser. Since sensitivity is based in part on the ringdown rate, increasing ringdown events from 100 Hz to over 10 kHz will allow us to do high-repetition rate ringdown and provide an increase in sensitivity of at least 10-fold to $\sim 10^{-10} \text{ cm}^{-1} \text{ Hz}^{-1/2}$. This sensitivity and the ability to average over many ringdown events should allow us to observe a spectrum of C_{60} even with the decrease in mass flow rate.

Although obtaining an absorption spectrum of C_{60} poses some difficult challenges, the sample introduction and improvements to our instrument make this an attainable goal in the near future. The implementation of a SCF source for C_{60} will encourage vibrational cooling of the molecule; and the addition of high-repetition rate ringdown should make up for loss from the lower mass flow rate. These factors in combination with each other should allow a rotationally-resolved absorption spectrum of C_{60} to finally be observed in the laboratory, and the results will be extremely helpful in the continual search for C_{60} in other regions of the ISM from ground-based telescopes.

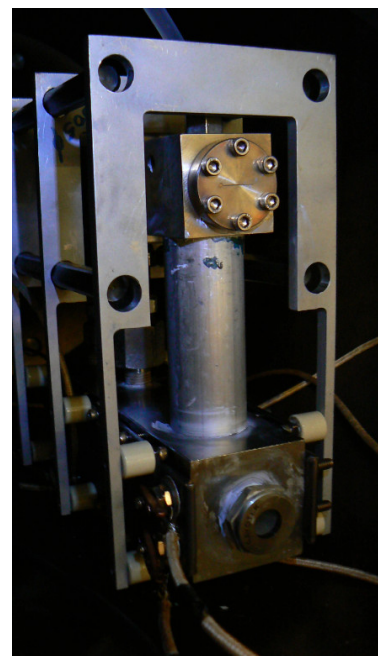


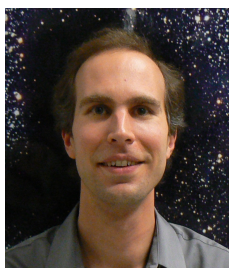
Figure 5 - The second-generation SCF expansion source built for the observation of C_{60} vapor.



Nicole Koeppen: is a graduate student in Physical Chemistry at the University of Illinois at Urbana-Champaign.
E-mail: nkoeppe2@illinois.edu.



Brad Gibson: is a graduate student in Analytical Chemistry at the University of Illinois at Urbana-Champaign.
E-mail: bmgibso2@illinois.edu.



Ben McCall: is a Professor of Chemistry and Astronomy at the University of Illinois at Urbana-Champaign.
E-mail: bjmccall@illinois.edu.

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