Molecules in Space & Laboratory, Paris, 2007
J.L. Lemaire & F. Combes (eds)

A LABORATORY AND OBSERVATIONAL SEARCH FOR THE VIBRATIONAL SPECTRUM OF C_{60}

S. L. Widicus Weaver[1], B. E. Brumfield[1], S. Howard[2], C. Gmachl[2] and B. J. McCall[1]

Abstract. We are conducting laboratory and observational searches for the 8.5 μm rovibrational band of C_{60}. We have constructed a continuous-wave cavity ringdown spectrometer using a quantum cascade laser, and we have tested this spectrometer with the ν_8 band of CH_2Br_2. The results of this study indicate that the C_{60} experiment should be feasible once laser mode hop difficulties are overcome. We are currently testing new optics that should soon eliminate these mode hops, allowing us to begin our search for the C_{60} spectrum. We have also begun an observational search for this C_{60} band toward four sources, though no obvious spectral features have been observed. We report here on our progress toward obtaining the first cold, resolved gas phase spectrum of C_{60} for comparison to observational spectra.

1 Introduction

Buckminsterfullerene (C_{60}) was serendipitously discovered during experiments designed to simulate the conditions of carbon star outflows (Kroto et al. 1984). C_{60} is stable against photodissociation, is expected to be present in the interstellar medium, and has four infrared active modes that should be observationally detectable. Since its laboratory discovery, C_{60} has been detected in craters on NASA's Long Duration Exposure Facility (Radicati di Brozolo et al. 1994) and in sediments related to meteorite impacts (Becker et al. 2001).

Laboratory gas phase emission spectra of C_{60} have been obtained at high temperatures (Frum et al. 1991), and infrared absorption studies in a parahydrogen matrix have also been conducted (Sogoshi et al. 2000). Yet a cold, high resolution gas phase spectrum is required for direct comparison to observational spectra. To this end we are utilizing continuous-wave cavity ringdown spectroscopy (cw-CRDS) to investigate the rovibrational spectrum of C_{60} using an 8.5 μm continuous-wave quantum cascade laser (cw-QCL). In addition to the laboratory studies, we have conducted observational searches for the C_{60} 8.5 μm mode. We present here an overview of our cw-CRDS laboratory study and observational search for C_{60}.

[1] Departments of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

[2] Department of Electrical Engineering, and the Princeton Institute for the Science and Technology of Materials, Princeton University, Princeton, New Jersey 08544, USA

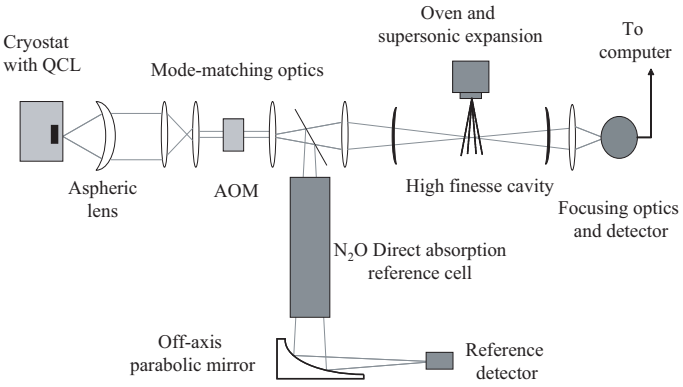

Fig. 1. Schematic diagram of the C_{60} cw-CRDS experiment.

2 Laboratory Spectroscopy of C_{60}

We are performing cw-CRDS on gas phase C_{60} using the instrument shown in Figure 1. The output of a continuous-wave quantum cascade laser is matched to the focal properties of a high finesse cavity with a series of mode matching optics. The beam is passed through an acousto-optical modulator (AOM), and the first order diffraction is selected. This beam is coupled into a cavity formed from two highly reflective mirrors ($R \sim 0.9999$). A piezo dithers one of the mirrors, changing the length of the cavity, and the light couples into the cavity when the cavity length is in resonance with the laser frequency. Intensity builds up in the cavity when resonance is achieved, and some of this intensity is transmitted by the cavity on each pass. This transmission is observed with a HgCdTe detector, and the output of the detector is monitored by a comparator circuit. When a given threshold intensity is reached, the TTL output of the comparator switches to high, modulating the amplitude of the RF drive to the AOM by -38 dB. This suppresses the first order diffraction and allows ringdown to occur. The exponential decay of the intensity transmitted out of the cavity is recorded, and the time constant for this decay is proportional to the cavity absorption. The ringdown times for 100 ringdown events are averaged and the absorption coefficient (α) is determined from this value at each frequency setting, yielding a molecular spectrum. Wavelength calibration is achieved by simultaneously recording the direct absorption spectrum of N_2O.

The high finesse cavity is placed around a supersonic expansion containing gas phase C_{60}. To achieve this expansion, solid C_{60} is heated to >600 °C in a sample oven, and the resultant vapor is expanded with argon through a pinhole. We have obtained gas phase C_{60} from this source, confirmed by the fact that the front flange of the vacuum chamber becomes coated with a layer of C_{60} once the oven reaches full temperature. We have tested the spectrometer and the supersonic expansion by observing the ν_8 band of CH_2Br_2, and have observed a rotational temperature of ∼20 K, a Doppler linewidth of 60 MHz, and a minimum detectable absorption of 2×10^{-9} cm^{-1}. An example spectrum is shown in Figure 2. These conditions should provide full resolution of the C_{60} rotational transitions, which are expected to be separated by ∼180 MHz.

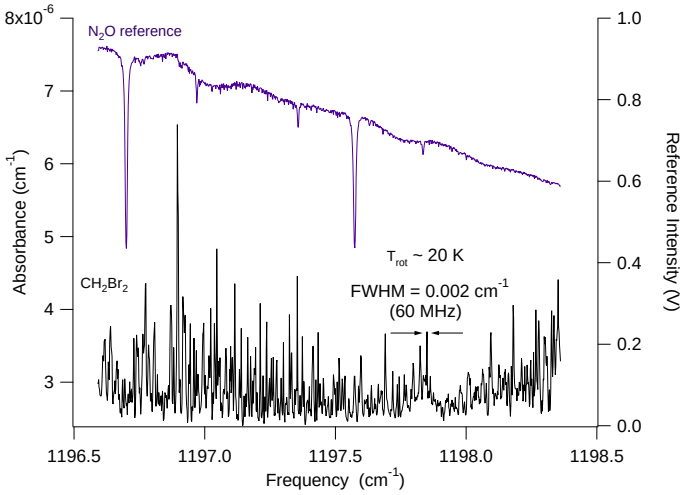

Fig. 2. Spectrum of the ν_8 band of CH_2Br_2, used to test the cw-CRDS spectrometer designed for the C_{60} experiment.

It was found during the CH_2Br_2 experiment that the laser beam position moved as the level of the liquid nitrogen in the cryostat changed. We therefore constructed an armature that rigidly connects the laser mount to the body of the cryostat. Thermal breaks were included to isolate the laser mount and cold head from the cryostat wall. The laser mount was attached to the cold head through copper ribbons, which allow for sufficient cooling of the laser mount but mechanically isolate the mount from the cold head.

This is only the third cw-CRDS experiment to use a QCL, and we have faced some difficulties with operation of the laser that have delayed completion of the C_{60} experiment. These devices are custom grown through molecular beam epitaxy to yield the desired wavelength, and are known to have a short tuning range, typically $\leq$10 cm^{-1}. QCLs also have a tendency to mode hop, which has been the major difficulty faced in our experiment, and we have discovered that back reflection from the ringdown cavity increases the likelihood for mode hops. We have recently obtained a Faraday isolator to protect the QCL from this back reflection, and this isolator should allow mode hop free tuning with these lasers. We have successfully obtained CH_2Br_2 spectra in the 1197 cm^{-1} frequency range, as is illustrated in Figure 2, and we are optimistic that we will soon achieve similar success in the 1184 cm^{-1} range required for the C_{60} experiment. We are currently testing the isolator, and soon will resume our search for the C_{60} spectrum.

3 Observational Searches for C_{60}

In addition to the laboratory studies of C_{60}, we have also conducted preliminary observational searches in three molecular clouds and one variable star, namely AFGL 2136, AFGL 2591, NGC 7538 IRS 1, and R Coronae Borealis, respectively. The data were obtained in June 2003 with the Texas Echelon Cross Echelle Spectrograph

(TEXES) on NASA's InfraRed Telescope Facility (IRTF). No obvious C_{60} spectral features were observed, and a column density upper limit of 3×10^{15} cm^{-2} was calculated from these results. More dedicated searches for the C_{60} band will follow completion of the laboratory experiment.

4 Conclusion

We have constructed an 8.5 μm cw-CRDS spectrometer for investigation of the gas phase spectrum of C_{60}. This is the largest and most symmetric molecule to ever be studied with high resolution spectroscopy, and this challenging laboratory experiment requires the use of prototype QCLs and a high temperature sample oven combined with a supersonic expansion. We anticipate that we will soon overcome the experimental difficulties faced thus far, and will then resume our search for the laboratory C_{60} spectrum. In addition to the laboratory work, we have conducted preliminary searches for C_{60} in several astronomical sources. No spectral features were observed, and a column density upper limit of 3×10^{15} cm^{-2} was calculated. Additional observational searches will be conducted once the laboratory spectrum is obtained.

We wish to acknowledge financial support from the NASA Laboratory Astrophysics program, the American Chemical Society, and the Dreyfus Foundation. We would also like to thank Matthew Richter and Dana Nuccitelli for their work on the observational studies, and Richard Saykally for the loan of laboratory equipment.

References

Kroto, H. W., Heath, J. R., O'Brien, S. C., Curl, R. F., & Smalley R. E. 1985, Nature, 318, 162

Radicati di Brozolo, F., Bunch, T. E., Fleming, R. H., & Macklin, J. 1994, Nature, 369, 37

Becker, L., Poreda, R. J., Hunt, A. G., Bunch, T. E., & Rampino, M. 2001, Science, 291, 1530

Frum, C. I., Engleman, R., Hedderich, H. G., Bernath, P. F., Lamb, L D., Huffman, D. R. 1991, Chem. Phys. Lett., 176, 504

Sogoshi, N., Kato, Y., Wakabayashi, T., Momose, T., Tam, S., DeRose, M. E., & Fajardo, M. E. 2000, J. Phys. Chem. A, 104, 3733