

ASTROPHYSICS AND ATMOSPHERIC SCIENCES AT THE CLS: THE FAR INFRARED BEAMLINE

BY BRANT E. BILLINGHURST, RONALD M. LEES, A. ROBERT W. MCKELLAR, AND ADRIANA PREDOI-CROSS

With the commissioning in 2007 of the Far-Infrared (FIR) Beamline at the Canadian Light Source (CLS), the molecular spectroscopy community in Canada has joined their high energy and astronomy colleagues in the world of Big Science, with keen competition for access to large facilities at the leading edge of international research. Building on the legacy of Gerhard Herzberg's Spectroscopy group at the National Research Council (where most team members had worked as staff members, postdocs or visiting researchers) the FIR Beam Team has embarked on a wide range of projects relevant to molecular astrophysics throughout the universe as well as to atmospheric studies closer to home on Earth and within the Solar System. Like Herzberg's group, which was notable for its international connections, many of our programs involve partnerships with researchers from around the world (see below).

Our knowledge of the composition and other properties of worlds outside our own (stars, planets, comets, interstellar space, ...) comes primarily from remote sensing in which electromagnetic radiation from the remote body is analyzed using spectroscopy. The same is true for probing the vastness of the earth's atmosphere, since we often can't be there in person. Infrared (IR) and longer (millimeter, microwave) wavelengths are especially important for sensing molecular matter in "cooler" regions like the earth and other planets (as contrasted to warmer regions like stars where atoms and plasmas dominate). Start-up of the CLS FIR Beamline coincides with the dawn of a new "Golden Age" for FIR astronomy. The launch in 2009 of the Herschel Space Observatory carrying HIFI, the Heterodyne Instrument for the Far Infrared, heralds a quantum jump in sensitivity and frequency coverage for molecular astronomy and the spectacular results now coming in confirm that a huge effort is needed to compile lab-

oratory spectral databases in order to exploit these observations. 2010 also saw the first flight of SOFIA, the Stratospheric Observatory for Infrared Astronomy, which is a modified 747 jetliner carrying an IR telescope to above 99% of atmospheric water vapor and turbulence. As well, the Atacama Large Millimeter Array (ALMA) will reach full capability in the near future, generating spectral data with very high spatial resolution and sensitivity, again underscoring the need for extensive databases for known and potential interstellar and protostellar molecules. Accurate laboratory data are crucial for interpretation of the results of these missions, but in many cases these are inadequate or entirely missing. Thus, a vital function of the CLS FIR beamline is to provide "fingerprint" IR lab data as a key to molecular identification for astrophysics. The need for high-quality data and modeling to support international investments in satellite-based atmospheric remote sensing is equally acute. To model climate change and greenhouse effects it is essential to have precise knowledge of spectroscopic band strengths and line shapes over a range of pressures and temperatures, in addition to line positions. Work is underway at CLS on important species such as methane, carbon dioxide and certain of the CFC molecules with high greenhouse potentials. As well, the capability to rotationally resolve the dense spectra of relatively big molecules opens the door for study of larger organic species involved in complex chains of atmospheric chemical reactions leading to pollution.

It has been recognized since the 1980s that synchrotron radiation (SR) represents a powerful source of IR radiation in addition to its more common applications in the ultraviolet and x-ray ranges. Conventional IR sources are simple thermal devices such as tungsten filament lamps or hot ceramic glowers. By comparison, the advantage of SR lies not in total IR flux, but rather in brightness, that is, in the flux that can be focused through a small opening into a given solid angle. The highly collimated nature of SR makes it ideal for applications probing a sample with high spatial resolution, like spectro-microscopy. Synchrotron IR beamlines for such purposes have developed rapidly during the past twenty years.

But highly collimated SR is also useful for IR spectroscopy with very high spectral resolution, because



Brant Billinghamurst
<brant.billinghurst@lightsource.ca>, Canadian Light Source Inc., University of Saskatchewan

Ronald Lees, Department of Physics, University of New Brunswick

Robert McKellar, Steacie Institute for Molecular Sciences, National Research Council of Canada

Adriana Predoi-Cross, Department of Physics and Astronomy, University of Lethbridge

SUMMARY

The Canadian Light Source is helping to pioneer the relatively new application of synchrotron radiation to enhance the capabilities of high-resolution far-infrared spectroscopy with important applications in astrophysics and atmospheric sciences.



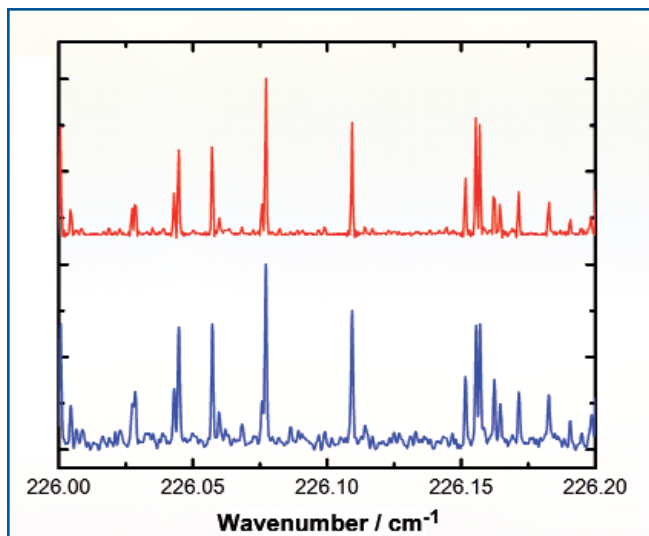


Fig. 1. Absorption spectra of methyl mercaptan (CH_3SH) obtained with equal collection times using synchrotron radiation (upper trace) and using a conventional Hg discharge lamp source (lower trace) using the full spectrometer resolution of 0.00064 cm^{-1} (unapodized). An even greater synchrotron advantage is achieved at the CLS in the $400 - 700 \text{ cm}^{-1}$ range.

Fourier transform (FT) spectrometers, based on the Michelson interferometer principle, need small entrance apertures for high resolution, just as grating spectrometers need narrow slits. In the mid-1990s the first IR beamline for gas-phase studies was built at MAX-lab in Sweden^[1,2]. Promising results obtained there, and at LURE in France^[3], stimulated the construction of

a number of new dedicated beamlines for high-resolution gas-phase IR spectroscopy, including the CLS Far IR Beamline. These developments are described in a review paper by one of us^[4], parts of which have been adapted for the current article.

The greatest promise for SR lies in the far-IR wavelength region, partly overlapping with the now trendy Terahertz frequency region. Although there is no strict definition, we can characterize the far-IR approximately in terms of various wavelength, wavenumber, frequency, and energy units as follows: $\lambda \approx 10 - 1000 \mu\text{m}$; $1/\lambda \approx 10 - 1000 \text{ cm}^{-1}$; $\nu \approx 0.3 - 30 \text{ THz}$; $E \approx 1.3 - 125 \text{ meV}$. Here, very high spectral resolution is possible in gases because of small Doppler widths, but spectroscopy with conventional sources is particularly difficult and broadly tunable lasers are not easily available. For the gas phase spectroscopy carried out to date, the synchrotron simply replaces the thermal source, providing a very bright IR continuum for otherwise conventional linear absorption spectroscopy (the structured time profile of SR has not been exploited so far). In contrast, a different accelerator-based IR source, the free-electron laser, provides high spectral brightness as required for nonlinear pump/probe spectroscopy, but so far only with modest spectral resolution. Relative to a conventional thermal IR source, the “synchrotron advantage” can in principle be as large as $\sim 10^3$ for a small aperture in the far-IR range, but in practice this tends to be limited by source noise due to fluctuations in the electron beam or due to vibrations of the mirrors which transport the radiation from the storage ring to the spectrometer. Figure 1 illustrates the synchrotron advantage currently achieved at the CLS in the difficult 200 cm^{-1} region: the synchrotron spectrum has a signal-to-noise ratio about 2.6 times better than the conventional spectrum for equal observation times.

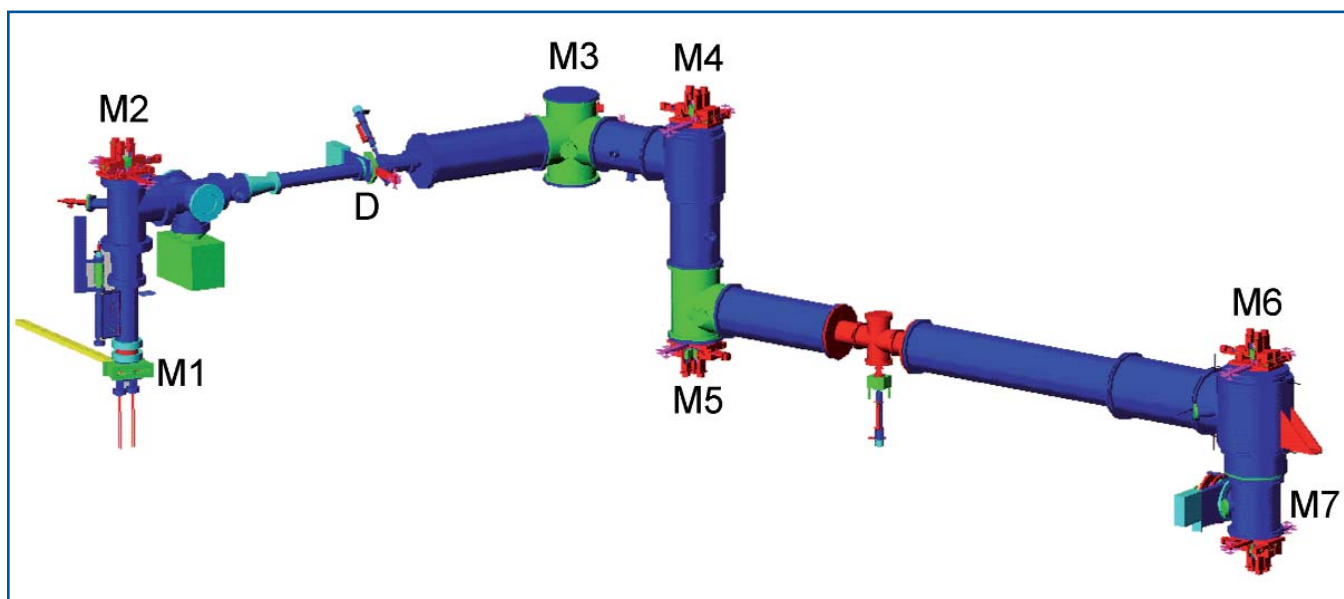


Fig. 2. Illustration of the vacuum system enclosing the mirrors which direct infrared radiation from the CLS electron storage ring (starting with mirror M1 on the left) to the entrance port of the high resolution spectrometer for the far-infrared beamline (mirror M7). D indicates the location of the diamond window.

Planning for the CLS Far-IR beamline began at a meeting organized by Tom Ellis at Université de Montréal in 1998. A letter of intent was submitted to the CLS at the end of 1999, followed by a more detailed proposal, and ultimately Far-IR was chosen as one of the six original (Phase I) beamlines. A large part of the cost of the spectrometer was covered by an NSERC Major Installation Grant received in 2002, the idea being that NSERC would fund the incremental cost of adding ultra-high spectral resolution (required for gas-phase studies) to the already-planned FIR beamline. The spectrometer was ultimately installed at the end of 2003, and “first light” for synchrotron radiation into the spectrometer occurred in late 2005.

The chain of mirrors which comprises the beamline (Fig. 2) collects light from a bending magnet section of the electron storage ring through an angular aperture of 55 by 37 milliradians. The first mirror is planar and has a 6 mm central slot that allows the more directional high energy (ultraviolet and x-ray) photons to pass through to an absorber, thus reducing the heat load on the mirror (and losing a small amount of IR radiation at the center of the beam). An ellipsoidal mirror then focuses the collected infrared radiation through a diamond window that separates the ultra-high vacuum of the storage ring from the rough vacuum of the beamline. A further series of 3 flat and 2 ellipsoidal mirrors direct it to a focus at the entrance aperture of the spectrometer located in the users’ experimental area, the “Far-IR hutch” – see Fig. 3. The FT spectrometer is a Bruker model IFS 125HR, whose maximum optical path difference of 9.4 m gives instrumental widths as narrow as 0.00064 cm^{-1} or 19 MHz (before apodization). The IR radiation is first modulated by the spectrometer, then passed through an absorption cell containing the gas being studied, and finally recorded by a cooled (77 or 4 K) detector which may be photoconductive (e.g. copper-doped germanium) or thermal (e.g. silicon bolometer).

Two gas cells are in routine use at CLS. Both use multiple-reflection optics to increase absorption path and hence sensitivity. One cell has a base length of 0.3 m and is used for total path lengths up to 12 m. It has a vertical optical axis and sits directly above the spectrometer sample chamber. The second cell (see Fig. 3) has a base length of 2 m and is used for total paths up to about 80 m. It sits horizontally beside the spectrometer, and can be cooled to temperatures as low as $\sim 80\text{ K}$ by circulating cold gas or liquid through copper tubing soldered to its outside surface. This is monitored by sensors inside and outside the cell, but at lower temperatures the uniformity is limited to a few K by the large size of the cell. Thermal insulation is provided by a vacuum chamber surrounding the cell. Transfer optics for both cells are located in the spectrometer vacuum to avoid the strong IR absorption caused by atmospheric H_2O and CO_2 . A third cell, now being tested, is 1.5 m long and can incorporate various types of electrical discharge in order to study unstable molecules such as free radicals and ions.

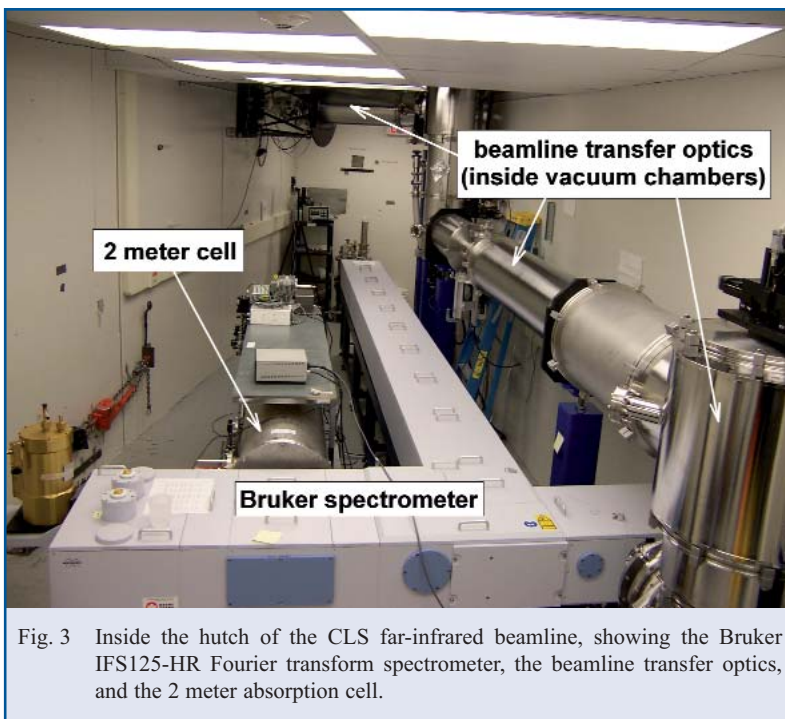


Fig. 3 Inside the hutch of the CLS far-infrared beamline, showing the Bruker IFS125-HR Fourier transform spectrometer, the beamline transfer optics, and the 2 meter absorption cell.

The members of the Far-IR Beamline Team, many of whom have been active since the early days of the beamline proposal, extend from coast to coast and are drawn about equally from both Physics and Chemistry departments. The Team Leader is Robert McKellar, Researcher Emeritus at the Steacie Institute for Molecular Sciences, National Research Council, Ottawa, while some of the other main users include Irving Ozier from UBC, a strong Alberta contingent with Wolfgang Jaeger and Yunjie Xu from the U. of Alberta, Nasser Moazzen-Ahmadi from the U. of Calgary and Adriana Predoi-Cross from the U. of Lethbridge, Jennifer van Wijngaarden from the U. of Manitoba, and the UNB CLAMS group (Centre for Research in Laser, Atomic and Molecular Sciences) including Dennis Tokaryk, Li-Hong Xu and Ron Lees. In addition to these users, there are other vital contributors to the development and operation of the beamline. Tom Ellis was a key early promoter for both infrared beamlines and is now the Director of Research at CLS. Peter Bernath, also an early supporter, is now at the University of York, UK. Tim May was responsible for design and construction of the IR beamlines, which he now manages and further develops. Dominique Appadoo was the original Far-IR beamline scientist, before departing at the end of 2007 to assume the same duty at the Australian Synchrotron. His replacement, Brant Billinghurst, came from a background of laser and FT spectroscopy and has rapidly and enthusiastically adapted to high resolution techniques.

Initial commissioning of the far-IR beamline in 2006-2007 utilized not only the “standard” test molecules CO , CO_2 , and N_2O , but also the more challenging acrolein (or propenal, CH_2CHCHO). This molecule was chosen due to its very rich rotational structure (requiring high resolution for meaningful analysis), the relative lack of previous IR data, and its intrinsic

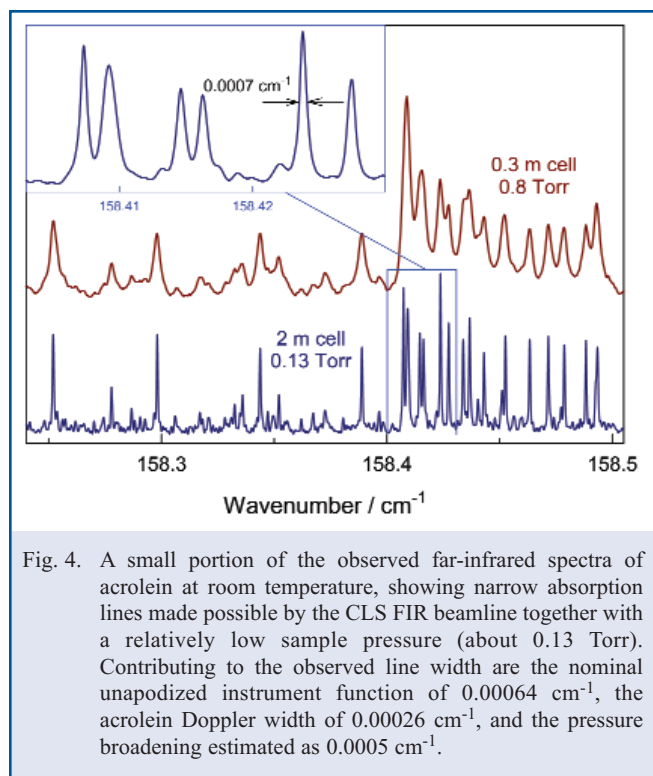


Fig. 4. A small portion of the observed far-infrared spectra of acrolein at room temperature, showing narrow absorption lines made possible by the CLS FIR beamline together with a relatively low sample pressure (about 0.13 Torr). Contributing to the observed line width are the nominal unapodized instrument function of 0.00064 cm^{-1} , the acrolein Doppler width of 0.00026 cm^{-1} , and the pressure broadening estimated as 0.0005 cm^{-1} .

spectroscopic interest in several areas. Acrolein is of importance in astrophysics as an interstellar molecule, and a significant species in combustion chemistry, air pollution, and industry. Combustion of fossil fuels (and of tobacco) contribute to the environmental prevalence of acrolein, which is identified as one of the 32 main Hazardous Air Pollutants by the American Environmental Protection Agency (EPA) and as one of six priority mobile source air toxics by the U.S. Federal Highway Administration. Detailed knowledge of the spectrum provides a key to its detection in the atmosphere.

Our first acrolein spectrum, recorded in summer 2006, covered the $550 - 660 \text{ cm}^{-1}$ region with a spectral resolution of 0.0012 cm^{-1} , including the ν_{12} and ν_{17} vibrational bands. These bands were analyzed in detail, including the Coriolis interaction which couples them as well as perturbations from a “dark” state, $\nu_{18} = 4$, resulting in the first CLS far-IR publication^[5]. At that time, the observed synchrotron advantage around 600 cm^{-1} was about a factor 3 in terms of signal-to-noise ratio for equal observation times. By the end of 2006, this advantage had been doubled to ~ 7 by beamline improvements, and a smaller but still useful advantage was achieved in the more difficult $100 - 200 \text{ cm}^{-1}$ range where another acrolein band, ν_{18} , was studied^[6]. These initial acrolein spectra were obtained with the 0.3 m cell, but a great leap forward was achieved with the mounting of the 2 m cell in 2007 when we realized that pressure broadening could be greatly reduced and remarkably improved spectra obtained^[7] thanks to the low sample pressures made possible by the longer absorption paths, as highlighted in Fig. 4. Several of the dense bands above 700 cm^{-1}

have also been successfully analyzed as groundwork for diode laser detection of acrolein in tobacco smoke^[8].

A notable variety of molecules has been studied so far at CLS, with a common thread being relevance to astrophysics and the atmosphere, in addition to fundamental interest in terms of molecular structure, internal motions, coupling, and dynamics. In the astrophysical area, Xu, Lees and Predoi-Cross have programs on methanol, methyl mercaptan (see Fig. 1) and methylamine, all having particularly dense and complex spectra due to internal rotation. Methanol is found throughout the universe in interstellar clouds and star-forming regions, and is known as an interstellar “weed” due to the strength, richness and omnipresence of its spectrum in astronomical sources. The FIR study at CLS has extended the range of known energy levels of CH_3OH to high torsional levels of interest in protostellar “hot core” regions^[9], and is also expanding spectral information on isotopic species such as O-18 and O-17 that are likely to be observable with the powerful new astronomical instruments^[10,11]. Deuterated acetaldehyde is a related molecule under study by Moazzen-Ahmadi and McKellar in a broadly-based international collaboration^[12]. Spectra of the ethane and methyl silane internal rotor molecules are also being studied by Moazzen-Ahmadi’s group, shedding new light on the internal coupling between the torsion and the other vibrational modes^[13], while Predoi-Cross and international colleagues have identified new FIR bands in several isotopic forms of acetylene^[14,15]. Ethane and acetylene are of current interest in planetary atmospheres, notably the atmosphere of Titan as probed by the Cassini spacecraft.

In atmospheric physics, CLS contributions fall in two main areas, the accurate determination of absorption band strengths and line broadening behaviour of major atmospheric species and the resolution and assignment of FIR bands of molecules of importance in atmospheric chemistry, notably large ring molecules whose dense spectra can only now be resolved through the synchrotron advantage. In support of atmospheric remote sensing, the Predoi-Cross group at Lethbridge is exploring techniques for more accurate modeling of molecular line shapes, collisional dynamics and radiative transfer, and is developing novel tools combining spectroscopic investigations of molecular structure and interactions with line shapes. A detailed study of weak bands of CO_2 was recently completed^[16], as well as an investigation aimed at improving the accuracy of line strength and shape measurements by removal of channeling (standing waves) from the spectral background^[17].

In initial exploitation of the advantages provided by synchrotron radiation at the CLS in molecular physics experiments, Dennis Tokaryk demonstrated a striking improvement in signal-to-noise ratio (nearly a factor of 10 around $400 - 800 \text{ cm}^{-1}$) at the highest spectral resolution, enabling spectra of relatively large molecules to be analyzed, many for the first time, and expanding the scope of far-IR vibration-rotation spectroscopy to include larger and heavier organic molecules whose spectra would previously have been far too congested for analysis.

Tokaryk and van Wijngaarden have now investigated numerous species, including thiophene^[18,19], pyrrole^[20], β -propiolactone^[21], azetidine^[22], silacyclobutane (c-C₃H₈Si)^[23] and, most recently, p-xylene (an important volatile organic pollutant). Together with the study of thiophosgene (Cl₂CS) by McKellar and Billinghurst^[24], 1,1,1-trifluoroethane (HFC-143a) by Predoi-Cross and co-workers^[25], and o- and p-difluorobenzene by international visitor Rebecca Peebles and co-workers, these CLS results contribute significantly towards understanding of the spectroscopy of VOC trace species of potential importance in global warming or in chemical reaction pathways contributing to atmospheric pollution and ozone depletion.

The last few years have been exciting times for the FIR Beamline team members, with major new research capabilities afforded by the coupling of bright synchrotron light to a high resolution Fourier transform spectrometer and the novel transition from the confines of one's own laboratory to the "suitcase" science world of visits to the busy CLS facility. The synchrotron community has seen explosive growth in recent years with new and upgraded installations coming into service all around the world. Many of these have included infrared beamlines, so the potential for friendly rivalry and competition is heating up.

The CLS FIR Beamline was the first of a new generation of dedicated far-infrared facilities to complete commissioning, giving us an initial lead internationally in exploiting the synchrotron advantage to push the boundaries of resolution and sensitivity for gas-phase spectroscopy, and we have been working hard to maintain this position. The strong world-wide interest in synchrotron and free-electron laser development has led to a series of significant international meetings and a highlight for us, as well as a recognition of our international prominence, was the invitation to host WIRMS2009, the 5th International Workshop on Infrared Microscopy and Spectroscopy with Accelerator Based Sources, held at the Banff Conference Centre in September, 2009. This meeting served to showcase the IR work at CLS and to strengthen links among the international community. With recent modifications to introduce active optics to the FIR Beamline mirror system and the addition of a new absorption cell for unstable molecules, we are looking forward to even better spectra in the near future and extension of our work from stable gases into the glamorous world of unstable and ionic species of great interest and importance in the astrophysical and atmospheric domains. Like the synchrotron itself, the future for the FIR beamline is bright!

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