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Feature Article

High-resolution infrared spectroscopy with synchrotron sources

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ABSTRACT

Most applications of synchrotron radiation lie in the ultraviolet and X-ray region, but it also serves as a valuable continuum source of infrared (IR) light which is much brighter (i.e. more highly directional) than that from normal thermal sources. The synchrotron brightness advantage was originally exploited for high spatial resolution spectroscopy of condensed-phase samples. But it is also valuable for high spectral resolution of gas-phase samples, particularly in the difficult far-IR (terahertz) range ($1/\lambda \approx 10$ – 1000 cm^{-1}). Essentially, the synchrotron replaces the usual thermal source in a Fourier transform IR spectrometer, giving a increase of up to two (or even more) orders of magnitude in signal at very high-resolution. Following up on pioneering work in Sweden (MAX-lab) and France (LURE), a number of new facilities have recently been constructed for high-resolution gas-phase IR spectroscopy. In the present paper, this new field is reviewed. The advantages and difficulties associated with synchrotron IR spectroscopy are outlined, current and new facilities are described, and past, present, and future spectroscopic results are summarized.

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1. Introduction

Synchrotron light sources are widely used to produce beams of electromagnetic radiation for scientific research over a broad range of wavelengths. There are now over 50 facilities in the world that use electron storage rings as synchrotron sources, as well as a rapidly increasing number that use linear accelerators for this purpose [1]. The majority of the applications of synchrotron radiation (SR) lie in the X-ray and ultraviolet regions of the spectrum, but it has been recognized since the 1980s that SR could also provide a useful source of infrared (IR) radiation. Conventional IR sources are usually simple thermal devices such as tungsten filament lamps or hot ($\sim 1500\text{ K}$) ceramic elements ("Globar"). In the very far-IR range ($<100\text{ cm}^{-1}$), high-pressure mercury discharge lamps offer useful gains, with effective temperatures up to $\sim 3000\text{ K}$ [2]. Compared to such thermal or quasi-thermal sources, the big advantage of SR lies not in total IR flux, but rather in brightness (or brilliance), that is, the flux emitted through a narrow aperture into a given solid angle or f/number cone. The highly collimated nature of SR means that more intensity can be focused through a small aperture, which is ideal for spectromicroscopy and other applications where it is desired to probe a sample with high spatial resolution. Infrared beamlines and the associated apparatus for such purposes have developed rapidly during the past 20 years [3–10].

It also came to be recognized that SR was useful for high spectral resolution IR spectroscopy, since a highly collimated source is

desirable here, too. This is essentially because Fourier transform spectrometers (FTS), which are based on the Michelson interferometer principle, need smaller entrance apertures for higher resolution, just as grating spectrometers need narrower slits. Although a gas-phase IR spectrum was recorded as early as 1985 using SR and an FTS at the BESSY facility near Hamburg [4], it was in the mid-1990s that the first dedicated IR beamline for high-resolution gas-phase studies was built by Bengt Nelander in Sweden [11–13]. This is beamline 73 on the Max I storage ring of MAX-lab at the University of Lund. The promising results obtained in Nelander's pioneering work [14–17], and also at LURE in France [18], stimulated the construction of a number of new beamlines dedicated to gas-phase IR spectroscopy. This relatively new and growing field of high-resolution gas-phase IR spectroscopy using synchrotron sources is the subject of the present review.

SR offers little or no advantage for low-, medium-, or even moderately high-resolution (say, 0.01 cm^{-1}) gas-phase spectroscopy through most of the IR range. The quality of a spectrum depends on the spectrometer, not the source, and it is already possible to obtain excellent results using conventional thermal sources. It is only for much higher resolution (say $\leq 0.004\text{ cm}^{-1}$) that SR becomes really advantageous. For most IR spectroscopy, the achievable resolution is limited by the Doppler width of the sample molecules being studied. This varies with temperature and molecular weight, but in most cases very high resolution cannot be used above, say, 1500 cm^{-1} . Sub-Doppler resolution at higher wavenumbers is possible using skimmed molecular beams or non-linear techniques (e.g. saturated absorption), but so far only laser spectroscopy is able to exploit these possibilities. Thus the greatest

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promise for SR tends to lie in the far-IR region, where very high spectral resolution is possible (because of small Doppler widths), where spectroscopy with conventional sources is particularly difficult, where broadly tunable lasers are less available, and where the synchrotron advantage tends to be greatest.

2. The synchrotron advantage

It is important to emphasize that SR simply provides a strong continuum IR source for absorption spectroscopy, replacing the thermal source which would normally be used in a spectrometer. Although SR has a highly-structured time profile, this has had no significance for gas-phase IR spectroscopy to date. For our purposes SR simply provides a bright continuum in the temporal and spectral domains. Thus we can regard the synchrotron as a very expensive substitute for a tungsten filament lamp, Globar, or mercury discharge lamp. Moreover, although it is more highly collimated than radiation from a thermal source, SR still falls far short of the spectral and spatial power densities available from laser sources and required for non-linear spectroscopy. In contrast, another class of accelerator-based IR source, the free-electron laser (FEL), can and does provide sufficiently high spectral brightness to enable non-linear pump/probe spectroscopy. Impressive results have been obtained in gas-phase studies with FEL sources, but to date these have been limited to relatively moderate spectral resolutions [19].

The magnitude of the synchrotron advantage (SA) relative to a conventional thermal IR source depends on a number of factors. There are the general factors of the wavelength and the degree of collimation or required aperture size. The SA generally increases with wavelength for a given aperture size, so the far-IR region is particularly favorable for SR. And of course the SA becomes larger for smaller aperture sizes – its highly collimated nature is the whole basis for the advantages of SR. The SA also depends on machine factors, in particular the storage ring current and the geometry of the extraction optics. It is important to have a sufficiently large solid angle for acceptance of the IR radiation by the extraction optics, and this becomes increasingly crucial at longer wavelengths. Although theoretical SA values of 10^2 – 10^3 or even greater are possible for small apertures in the far-IR range, the actual SA tends to be limited by source noise, which may be due to spatial or temporal fluctuations in the electron beam itself or due to mechanical vibrations in the chain of mirrors which transport the radiation from the storage ring to the spectrometer.

3. The problem of source noise

Much of the effort in design, construction, and operation of IR beamlines is concerned with minimizing this source noise [20], which can be done by eliminating the original cause of the noise (clearly the best solution), or by isolating the beamline from it. In addition, it is possible to use active optics in the beamline to minimize the effects of the noise. One or more visible or near-IR quadrature detectors monitor the position of the SR beam and this information is fed back to beamline mirrors which attempt to correct for any fluctuations in the image position. Mechanical noise tends to become worse at lower frequencies, particularly in the range around and below a few hundred Hz, and this is where active optics can be most effective. Since the typical speed of the moving mirror in an FTS is of the order of 1 cm/s, Hz in the time (i.e. acoustic noise) domain transform approximately to cm^{-1} in the spectral domain. Thus mechanical noise around ≤ 300 Hz becomes spectral noise around $\leq 300 \text{ cm}^{-1}$. Unfortunately, this is just the wavenumber range where much current interest is focused, because very high-resolution spectroscopy with conventional sources is particu-

larly difficult here and the potential SA is large. To some extent, problems of mechanical noise can be circumvented by changing the FTS mirror scan speed. But beyond a certain point, higher scan speeds are not practical, and in any case they may be limited by the relatively slow response times of thermal (bolometer) detectors commonly used in this wavelength range.

Source noise problems also limit the performance of IR spectromicroscopy beamlines. But since these usually operate in the mid-IR range (800 – 4000 cm^{-1}) the effects of mechanical noise, concentrated at lower frequencies, are not so important. On the other hand, noise effects arising from electron beam instabilities can occur at higher frequencies corresponding to the mid-IR.

In principle, it should be possible to mitigate the effects of source noise by using some sort of dual-beam technique, that is, actually measuring the noise and correcting for it. But so far this has not been tried. For example, the synchrotron IR beam can be divided into two parts using a beamsplitter after it has been modulated by the FTS. One beam passes through the absorption cell and gas sample to a detector and the other beam goes directly to a second detector. Both detector signals are recorded, and both interferograms are transformed. The ratio of the two spectra yields a transmittance spectrum which is free from source noise. Such a scheme is currently being tested at SOLEIL. Of course, there is some additional noise due to the second detector, but that's okay since we assume that source noise dominated in the first place. There is also the cost of two matched detectors, but this should be negligible compared to the cost of building a synchrotron.

As long as synchrotron source noise dominates, detector noise (which is the usual limiting factor for conventional IR spectroscopy) is not critical. This means that cheaper or more convenient (e.g. uncooled) detectors can possibly be used with no ill effects. But as source noise is reduced, the use of the best possible low-noise detectors becomes important again. When the full IR synchrotron advantage is realized, will detector noise be the limiting factor, or will another noise source like photon statistics begin to dominate? At this point, perhaps the FTS multiplex advantage will not be fully operative and it will be desirable to limit the spectral bandwidth covered in any given experiment.

4. The storage ring and beamline

Two basic parameters for SR facilities are the energy and current of the stored electron beam. Energies for modern facilities generally lie in the range ~ 0.5 to 8 GeV , and this parameter determines the high energy (short wavelength) cutoff for the X-rays that can be produced. But high electron energy is not necessary for producing IR radiation – even relatively low energy storage rings are quite suitable. Indeed, higher energy complicates the design of IR beamlines since it means that more power (in the form of X-rays) must be dissipated by the primary mirror which extracts the IR light from the ring. On the other hand, beam current is relevant since more current means more IR radiation. If, however, the signal-to-noise ratio of an IR experiment is limited by source noise (e.g. mechanical vibrations) as is often the case, then increasing the current may not result in any real improvement.

Infrared SR is usually extracted in a bending magnet section of the storage ring, where the electrons emit due to the acceleration of their curved trajectories. In contrast, beamlines for shorter wavelengths increasingly make use of so-called insertion devices (wigglers and undulators) mounted in straight sections of the storage ring, which selectively “shake” the electrons into emitting radiation. There is a further source of emission, called edge radiation [18,21,22], which is due to acceleration encountered by the electron beam passing the edges of the magnet cell. The bending magnet and edge contributions are complementary, and most very

recent IR beamline designs exploit both mechanisms [23–25]. The emittance angle of SR increases with wavelength, and a relatively large solid angle for extracting IR light is desirable, especially for the far-IR. The ring vacuum chambers for IR beamlines are therefore often specially designed to allow larger extraction angles.

The primary mirror that first intercepts the IR light emitted by the electron beam and diverts it out of the storage ring is typically labeled M1 (or sometimes M0). In most cases, this mirror must be directly water-cooled, and in higher-energy rings it must be further protected from the intense heating load imposed by UV and X-ray photons. Since these short wavelengths are highly directional, this can be done by having a relatively narrow open slot in M1 through which most X-rays can pass, or by having a water-cooled shielding tube running in front of M1 to block the X-rays. A horizontal strip at the very center of the IR beam (in the plane of the storage ring) is thus lost.

A chain of mirrors, some of which may refocus the beam, then brings the IR light to the spectrometer, through or over a thick shielding wall that protects personnel (i.e. the spectroscopist!) from harmful radiation. Located somewhere in this chain is an optical window that separates the ultra-high vacuum of the storage ring from the generally lower vacuum of the IR transport optics. This window is often made of diamond, a material which combines advantages of wide spectral transparency and high mechanical strength with the disadvantage of high cost. A fast-acting automatic valve may be included here to minimize damage to the storage ring in the unlikely event of window failure.

The energy emitted in the form of SR by the stored electron beam is constantly replenished by energy input to the storage ring in the form of radiofrequency radiation. But the beam current slowly decays over a period of hours as the total number of stored electrons drops. This decay is mainly due to collisions with residual gas molecules in the storage ring, which are still present even under ultra-high vacuum conditions of the order of 10^{-10} Torr. When the current falls below a certain value, a new beam of electrons is injected into the storage ring to restore full current. This may typically take place 2 or 3 times per day. The slow storage ring current decay means that the IR beam intensity is constantly changing, but generally this does not pose a big problem for spectroscopy with an FTS. A typical scan of a single very high-resolution interferogram may take on the order of 5–30 min, during which the change in beam intensity is not large, and many individual scans are combined to obtain the final result so the changes tend to average out. Indeed, the IFS 125 spectrometer used at most facilities (see below) usually records interferograms in pairs: the first taken from zero to maximum path difference and the second from maximum back to zero. Averaging these interferograms automatically minimizes the small apodization effects which might arise from beam current decay.

At many SR facilities there is now a trend towards “top-up mode” operation where the stored electron beam is replenished every few seconds or minutes in order to maintain a virtually constant current. Constant current is clearly a desirable goal, and top-up mode poses little or no problem for many types of beamline, but high-resolution gas-phase IR beamlines are unfortunately among those most likely to experience negative consequences. Each top-up of the electron beam inevitably introduces a slight perturbation of its orbit, to which an IR interferogram is likely to be particularly sensitive. This is not a problem if the interferogram is an average of hundreds or thousands of short ($\ll 1$ min) scans, as is the case for IR spectromicroscopy. As long as the scan time is significantly shorter than the top-up time, the relatively few bad scans contaminated by top-up can simply be omitted from the average. But for the longer scans typical of high-resolution spectra, it is possible that most or all scans will be affected by top-up. The best solution is to reduce the magnitude of the perturbation until it is insignificant. If this is not possible, then some other remedy must be devised [26]. For example, one

could omit from the final interferogram average each small “bad” section in all individual interferograms, which would be flagged by a signal from the machine control electronics. The affected portions of the average, which would be renormalized in compensation, would be numerous but short and constitute a very small fraction of the total observing time. But such ‘slicing and dicing’ of interferograms is potentially dangerous: it must be done very carefully to avoid introducing spectral artifacts.

5. The spectrometer

Spectrometers used at IR beamlines are virtually always Fourier transform instruments, both for conventional high spatial resolution work and for the new high spectral resolution facilities. At one time, there was some confusion over whether a high-resolution FTS would work at all with a synchrotron [4]. Since the SR arrives in short intense pulses with a low duty cycle, how is it possible to record an interferogram at the detector? Pulses arriving from the short stationary arm of the Michelson interferometer would have no coherent time or phase relation with pulses from the moving arm. And most of the time (between pulses) the detector would see nothing. How could an interferogram be formed? But of course experiments verified that an FTS really does operate properly with a synchrotron source, even at very high spectral resolution. It is the gas-phase sample molecules, with their sharp (we hope!) spectral lines, which impose coherence on the IR continuum radiation from the synchrotron, giving rise to structure in the interferogram even at long path differences.

The original gas-phase synchrotron investigations were done with a Bruker IFS 120 HR spectrometer at MAX-lab and a Bomem DA8 spectrometer at LURE. Today, all new gas-phase IR synchrotron beamlines have chosen the same spectrometer, the Bruker IFS125 HR. This is the successor to the IFS 120 and is now the only commercial instrument available with sufficiently high spectral resolution (i.e. $<0.002\text{ cm}^{-1}$) to be able to make constructive use of the high brightness of SR. As an alternative, we could imagine a custom-built spectrometer that would be specifically designed for use with a synchrotron source. But the big advantage of a standard instrument like the IFS 125 is the availability of commercial technical support and standardized software. These are particularly important for a user facility, since most users will have neither the time nor inclination to become thoroughly familiar with the detailed spectrometer operation.

The spectral resolution obtained using an FTS depends inversely on the optical path difference (OPD) generated in its Michelson interferometer, but the proportionality constant used in this relation may vary among users. Resolution values of $(1/\text{OPD})$ or $(0.9/\text{OPD})$ are often quoted, since these represent the approximate instrumental line width achieved with strong or medium apodization applied to the interferogram. However, apodization may not be required for high-resolution spectra when the molecular line width (from Doppler and pressure broadening) is comparable to the instrumental width – in effect the molecule provides its own apodization. In this case, it may be appropriate to quote a value as small as $(0.6/\text{OPD})$, representing the full width at half maximum of the unapodized instrument function.

6. Past, present, and future gas-phase IR results from synchrotron light sources

We are aware of seven synchrotron facilities world-wide, either in operation or under construction, with a capability for high spectral resolution gas-phase IR spectroscopy. They are summarized in Table 1. It is quite likely that more such facilities will appear in the next few years.

Table 1
Beamlines for high-resolution gas-phase IR spectroscopy.

Facility, Country	Energy/GeV	Current/mA	Beamline name	Spectrometer (maximum OPD)	Year of first published result
MAX-lab, Sweden (MAX I ring)	0.55	250	#73	Bruker IFS120HR (7.2 m)	1995
SOLEIL, France	2.75	500	AILES	Bruker IFS125HR (8.2 m)	2010 ^a
Canadian Light Source, Canada	2.9	300	Far-IR	Bruker IFS125HR (9.4 m)	2007
Australian Synchrotron, Australia	3.0	200	Far-IR and high-resolution FTIR	Bruker IFS125HR (9.4 m)	2008
Swiss Light Source, Switzerland	2.4	400	IR Branch C	Bruker IFS125HR (11.5 m)	2010
Advanced Light Source, USA	1.9	400	#5.4.3	Bruker IFS125HR (9.4 m)	
Singapore Synchrotron Light Source, Singapore	0.7	500	ISMI	Bruker IFS125HR	

^a Preliminary results from beamline SIRLOIN at LURE were published in 2001.

6.1. MAX-lab

The world's first SR facility for gas-phase IR spectroscopy was beamline 73 at MAX-lab in Lund, Sweden, installed on the Max I storage ring which operates at an energy of 550 MeV and a current of 250 mA. This beamline has enjoyed a very productive history over the past 15 years [11–17,27–44]. It is equipped with a 7-chamber Bruker IFS 120 HR spectrometer having a maximum OPD of 7.2 m. Most spectroscopic results have been obtained in the range from about 200 to 1500 cm⁻¹. Below about 150 cm⁻¹, source noise is found to become a severe problem [34], and at higher wavenumbers (i.e. 2000 cm⁻¹) there is little or no SA. In what must be the very first published high-resolution IR analysis using SR, Paso and Horneman [14] studied the ν_{10} band of CH₃CCD (propyne-d₁) around 318 cm⁻¹, achieving a remarkable standard deviation of just 0.00010 cm⁻¹ for some 1900 fitted transitions. The first figure of this paper is reproduced here as Fig. 1. Propyne continued as the subject of further papers based on MAX-lab spectra [17,31,44], and the excellent wavenumber precision which was possible in the far-IR region was utilized, together with non-SR results from other labs, to establish improved wavenumber standards based on CO₂, CS₂, and H₂O [35,36].

An important early work from MAX-lab was the 1998 study of the ν_5 band of perchloric acid (HClO₄) by Johnson et al. [15], which utilized a cooled (185 K) long path (114 m) absorption cell. This represented the first high-resolution IR analysis for this molecule, and the results had significance for atmospheric chemistry since HClO₄ is a stratospheric chlorine reservoir. The same cooled cell was employed by Wugt Larsen, Hegelund, and Nelander in notable studies of weakly-bound molecular complexes: CO–HCl [33], (HCl)₂ [34], HCN–HCl [37], and NH₃–HCN [38]. These are among the first direct high-resolution observations of the important low-frequency intermolecular vibrations of hydrogen-bonded complexes. Other molecules studied at MAX-lab include IBr [16], glyoxal [27,28], methyl silane [29], and allene [30]. Recently,

spectra of *t*-butyl hydroxide (C₄H₁₀O) and perchloric acid were recorded in the far-IR range. As well, far-IR bands of an extensive series of heterocycle ring molecules have been analyzed, including 1,2,4-triazine [32], 1,3,4-oxadiazole [39], thiophene [40], 1,3,4- and 1,2,4-thiadiazole [41,42], and pyrrole [43]. These and related non-SR results are summarized and refined in a recent review paper by Palmer et al. [45].

At the present time, the Max I storage ring is nearing the end of its life. It is planned to move the current IR facilities to Max IV, Sweden's next generation synchrotron radiation facility whose initial construction is planned to begin in 2010. As well, a new IR spectromicroscopy beamline is being constructed at the Max III ring.

6.2. LURE and SOLEIL

Extensive exploratory work on gas-phase far-IR spectroscopy was done on the SIRLOIN beamline at LURE, but little of this was published [22]. LURE was shut down at the end of 2003 as construction began on a new French light source, SOLEIL, and many personnel moved from the old to the new facility, located in Gif sur Yvette, near Orsay, south of Paris. SOLEIL is a third generation SR source of intermediate energy (2.75 GeV) with a ring current of 500 mA and a circumference of 354 m which delivered its first photons in 2006.

Design of the IR/THz beamline AILES (Advanced Infrared Line Exploited for Spectroscopy) has been described by Roy et al. [46,47]. The combined source (edge and bending magnet radiation) and the relatively large ring current offer high IR flux and brilliance for spectroscopy of both condensed matter and isolated (gas-phase) molecules. For all studies, the beamline optics are designed to allow the entire source to be used without an aperture stop (entrance iris), even at the highest spectral resolution (0.001 cm⁻¹) [47]. Like the other new gas-phase IR facilities, AILES is equipped with a Bruker IFS 125HR spectrometer. It is set up to record (short-

Fig. 1. An illustration taken from Paso and Horneman's 1995 paper [14] on propyne-d₁, the first published synchrotron-based high-resolution IR analysis. This spectrum, displaying excellent resolution and signal-to-noise ratio in the difficult 300 cm⁻¹ region, was obtained using Bengt Nelander's IR beamline at MAX-lab in Lund, Sweden.

Fig. 2. The synchrotron advantage as measured at SOLEIL in 2009. The curve illustrates the enhancement of signal-to-noise for measurements performed at 0.001 cm^{-1} resolution through a long path cell with SR versus conventional sources (globar or high-pressure mercury lamp).

er) double-sided interferograms, resulting in a maximum (single-sided) OPD of 8.2 m.

The magnitude of the synchrotron advantage was systematically evaluated at SOLEIL in 2009. Fig. 2 shows results determined for a resolution of 0.001 cm^{-1} using a long path cell with both SR and conventional sources (globar or mercury lamp). Clearly the synchrotron source allows significant enhancements through the entire far-IR range, with the largest advantage in signal-to-noise ratio being observed around 100 cm^{-1} . For higher wavenumbers, the globar emission increases and the SA enhancement is less pronounced. For lower wavenumbers, the SA decreases to about 5 at 40 cm^{-1} due to limitations imposed by electron beam and beam-line stability, as described above in Section 3. It follows that in order to reach an equivalent S/N ratio at 40 cm^{-1} , one needs to accumulate 25 times longer using a mercury lamp than with SR. At 100 cm^{-1} , an equivalent S/N ratio would be reached with a measurement duration 200 times longer!

Some of the projects being carried out at AILES are described in the following paragraphs. At an early stage of beamline commissioning, Don McNaughton (Monash University) who is closely associated with the Australian Synchrotron infrared beamline (see below) visited AILES and recorded the first high-resolution IR spectra of *N*-methyl formamide (CH_3NHCHO), in the $80\text{--}700 \text{ cm}^{-1}$ range. This is a model molecule for understanding protein folding, and analysis of the spectra is currently underway, starting with assignment and fitting of a band of the less abundant *cis* isomer around 580 cm^{-1} .

Boudon and co-workers [48] have recorded the pure rotational spectrum of methane in the $70\text{--}200 \text{ cm}^{-1}$ range using an absorption path of 150 m at room temperature. These weak “forbidden” transitions arise from the small dipole moment induced by centrifugal distortion. Transitions were observed within both the ground vibrational state ($J'' = 7\text{--}18$) and the lowest excited state $\nu_4 = 1$ ($J'' = 4\text{--}14$). This allowed accurate measurements of line intensities and precise determination of induced dipole moment parameters which will aid in the interpretation of the spectra of planetary atmospheres (e.g. Jupiter, Titan). An example showing observed and calculated spectra for the *R*(13) transition is shown in Fig. 3. In continuing work, the same group has now recorded the methane spectrum with added N_2 (5% CH_4 in N_2 for total pressures from 100 to 800 mbar) in order to determine N_2 pressure broadening coefficients and line-mixing coefficients.

The THz and far-IR spectrum of methyl formate (HCOOCH_3) is currently being investigated by Huet and coworkers with the

Fig. 3. Observed and calculated spectra showing the *R*(13) pure rotational transition of methane [48]. The spectrum was recorded using the AILES beamline at SOLEIL with a 150 m absorption path at room temperature. Note the two transitions due to water vapor impurity at the left of the trace.

purpose of characterizing this astrophysical molecule in a spectral range of interest for the Herschel and ALMA missions [49]. Preliminary assignments are underway of pure rotational transitions from 20 to 80 cm^{-1} and of the very weak torsion band, $\nu_t = 1\text{--}0$, around 130 cm^{-1} . The assignments are based on rotation-torsion energy levels calculated using the RAM approach. The particular interest in the $\Delta \nu_t = 1$ torsion-rotation band lies in achieving a more direct experimental determination of the height, V_3 , of the barrier to internal rotation, which, up to now, has been determined solely from pure rotational transitions. More generally, the aim is for a significant improvement in global knowledge of the rotational levels in the lowest torsional states of methyl formate.

Cuisset and co-workers are studying the spectrum of dimethyl sulfoxide, or DMSO ($\text{SO}(\text{CH}_3)_2$), a widely used industrial solvent, in the region of the lowest vibrational modes [50]. The spectrum of perpendicular and parallel fundamental bands associated with the asymmetric ν_{23} and symmetric ν_{11} bending modes of DMSO in the $290\text{--}420 \text{ cm}^{-1}$ region have been recorded with a resolution of 0.0015 cm^{-1} . Analysis of ν_{11} yielded accurate rotational and centrifugal distortion constants for both the ground and excited states, and a small region in the *R*-branch is illustrated here in Fig. 4. The

Fig. 4. Comparison of experimental and theoretical spectra of DMSO showing a portion of the *R*-branch of the ν_{11} fundamental band with B and C-type transitions as indicated [50]. The experiment was performed using the AILES beamline at SOLEIL with an absorption path of 150 m, a gas pressure of 8 Pa (0.06 Torr), and a resolution of 0.0015 cm^{-1} .

analysis predicts some interesting rovibrational dynamics at high rotational excitation [51]. Pure rotational spectra of DMSO have also been recorded in the 10–30 cm^{-1} region, but here the ultimate resolution available with the IFS 125 FTIR spectrometer is insufficient because DMSO is a nearly symmetric top with hindered internal rotation of the methyl groups. Thus coherent millimeter wave or opto-electronic THz [52] techniques will be required to fully resolve the pure rotational transitions.

Recently, the ν_9 fundamental band (C–C–C deformation) of propane (C_3H_8) at 369 cm^{-1} was investigated at high-resolution (0.0011 cm^{-1}) by Kwabia Tchana et al. [53]. Transitions up to $J = 65$ and $K_a = 34$ were assigned and analyzed to obtain accurate values for the band center, and the rotational and centrifugal distortion constants were obtained. These can be used to simulate synthetic spectra including hot bands of propane involving the $\nu_9 = 1$ vibrational level as the lower state in order to carry out radiative transfer calculations. In another recent study, Jacquemart and coworkers [54] have measured high-resolution spectra of acetylene between 20 and 600 cm^{-1} with the aim of providing absolute line intensities for the $\nu_4 - \nu_6$ difference band.

6.3. Canadian Light Source

The Canadian Light Source (CLS) is located in Saskatoon on the campus of the University of Saskatchewan. Its storage ring, which first entered operation in 2004, has a circumference of 171 m and operates at an energy of 2.9 GeV. At present, the maximum current is 255 mA, but this may ultimately be increased to 500 mA. There are two IR beamlines at CLS, one dedicated to mid-IR spectromicroscopy and industrial applications, and the other to far-IR spectroscopy [55]. Their construction took place in 2004 and 2005, and ‘first light’ occurred in late 2005 for the far-IR beamline spectrometer, a 9-chamber Bruker IFS 125HR.

Two multiple-reflection gas cells are in use at CLS. The smaller has a base length of 0.3 m and is used for total absorption paths up to 12 m. It has a vertical optical axis and sits directly above the spectrometer sample chamber. The second cell has a base length of 2 m and is used for total paths up to about 80 m [56]. It sits horizontally beside the moving mirror chambers of the spectrometer, and can be cooled to temperatures as low as ~ 80 K by circulating cold gas or liquid through copper tubing soldered to its outside surface. A vacuum chamber surrounding the cell provides thermal insulation. The cell windows are located at room temperature, which avoids problems associated with cold IR windows but also means that a small part of the absorption path is warmer than the rest of the cell. Transfer optics for both cells are located entirely in the spectrometer vacuum. They intercept the IR beam just before its focus in the sample chamber, direct it to the cell, and then return it back to its original path so that the IR detectors remain in their normal positions. Both cells were originally designed and constructed at the National Research Council of Canada and later moved to the CLS.

Commissioning of the far-IR beamline utilized standard molecules such as CO, CO_2 , and N_2O . In addition, acrolein (CH_2CHCHO) was chosen due to its congested rotational structure and the lack of previous high-resolution IR data. The first acrolein spectrum (summer 2006) covered the ν_{12} and ν_{17} fundamental band region, 550–660 cm^{-1} , with a nominal resolution of 0.0012 cm^{-1} . The Coriolis coupling linking these bands was analyzed and perturbations from a ‘dark’ state, $\nu_{18} = 4$, were also included, resulting in the first CLS far-IR beamline publication [57]. At that time, the observed SA around 600 cm^{-1} was about three in terms of signal-to-noise ratio. By the end of 2006, this had been doubled to ~ 7 by beamline improvements, and a smaller but still useful SA was achieved in the more difficult 100–200 cm^{-1} range. Making use of this advantage, the acrolein ν_{18} fundamental band at 157.9 cm^{-1} was then

studied [58], a significant result since hot bands originating from this vibration are ubiquitous in acrolein spectra.

Both of these initial acrolein spectra were obtained using the 0.3 m cell. When further spectra were obtained in 2007 using a path of 48 m in the 2 m cell, it was realized that line widths in the earlier results were significantly affected by pressure broadening. A greatly improved spectrum was obtained thanks to lower sample pressure made possible by the longer absorption path, as illustrated in Fig. 5. The observed width of 0.0007 cm^{-1} at 160 cm^{-1} has three contributions: unapodized instrument function ≈ 0.00064 cm^{-1} ; pressure broadening ≈ 0.00050 cm^{-1} ; Doppler width = 0.00026 cm^{-1} . Using the new results, which also included the ν_{13} and $2\nu_{18}$ bands around 320 cm^{-1} , a comprehensive analysis [59] was carried out including all 10 excited acrolein vibrational levels below 700 cm^{-1} . In retrospect, it is evident that minimizing sample pressure can be crucial for very high-resolution spectroscopy in the far-IR region. In further work on acrolein, Xu, Lees, and co-workers are engaged in studies of various bands involving vibrational levels located above 700 cm^{-1} [60].

Vibration–rotation bands of a number of organic ring molecules have been studied at CLS by Tokaryk, van Wijngaarden, and co-workers. These include thiophene [61,62], pyrrole [63], β -propiolactone [64], azetidine [65], and silacyclobutane ($\text{c-C}_3\text{H}_8\text{Si}$) [66]. This work and the closely related results from MAX-lab described above [45] illustrate how the scope of far-IR vibration–rotation spectroscopy has now expanded to include larger and heavier organic molecules whose spectra would previously have been too congested for analysis.

A study of ^{17}O methanol using SR in the 120–350 cm^{-1} region by Moruzzi, Predoi-Cross, Lees, and co-workers is currently underway [67], following earlier CLS work on the C–O stretching band of ^{18}O methanol using a global source in the 1000 cm^{-1} region [68]. As well, further observations of ^{13}C and ^{18}O methanol are being made in the 350–500 cm^{-1} range. These results are particularly significant for millimeter and submillimeter wave radio astronomy, since methanol is a strong interstellar ‘weed’ species whose transitions must be known precisely (even for the less common isotopomers) in order to recognize the rare interstellar ‘flowers’ (i.e. new or unexpected species) of importance for investigating the chemistry of stellar formation. Xu and Lees have also recorded the spectrum of the related molecule methyl mercaptan, CH_3SH , in the 150–350 cm^{-1} range. The ν_5 and ν_{12} fundamentals and the

Fig. 5. Spectra of the ν_{18} fundamental band of acrolein [58,59] from the Canadian Light Source showing improved line width obtained with lower pressures made possible by a longer absorption path in a larger gas cell.

$\nu_{12} + \nu_{18} - \nu_{18}$ torsional hot band of methyl silane (CH_3SiH_3) in the 500–700 cm^{-1} region were studied in detail by Borvayeh et al. [69]. The highly congested spectrum of thiophosgene (Cl_2CS) has been recorded and analyzed in the 500 cm^{-1} region (ν_2 and ν_4 bands) by McKellar and Billinghurst [70].

Predoi-Cross and co-workers have completed a high-resolution analysis of the very congested ν_4 band of 1,1,1-trifluoroethane, CH_3CF_3 , at 831 cm^{-1} [71]. This molecule, also known as HCF-143a, is of atmospheric interest since it is a potential replacement for CFC (chlorofluorocarbon) refrigerants. Other molecules being studied by this group with the help of CLS spectra include CO_2 (line shape studies with atmospheric applications) [72], acetic acid, and acetylene. Deuterated acetaldehyde (CH_3CDO) is the subject of an extensive analysis by Elkeurti, Coudert, and co-workers based on a CLS spectrum of the torsional fundamental around 150 cm^{-1} together with millimeter wave pure rotational data. Peebles and co-workers are currently analyzing CLS spectra of *o*- and *p*-difluorobenzene. Although these are extremely congested, rotational series are still readily identifiable. Spectra of *p*-xylene (an important volatile organic pollutant) have also been recorded recently.

6.4. Australian Synchrotron

The Australian Synchrotron is located in the suburb of Clayton, near Melbourne in the state of Victoria. It officially opened in October, 2007 with 5 of its 9 first phase beamlines in operation; the IR beamline was one of these initial 5. The storage ring measures 216 m in circumference and operates at an energy of 3.0 GeV. It can store a current of 200 mA with a lifetime of 50 h; with two injections of electrons per day, the current only drops to 150 mA. Top-up mode operation is planned by 2012. There are two branches to the IR beamline at the Australian Synchrotron which share the same front-end. One is dedicated to mid-IR spectromicroscopy (to be extended to the far-IR in 2012), and the other to far-IR spectroscopy of both gas-phase and condensed-phase samples. Both edge and bend magnet radiation are collected, with the far-IR beamline using the former and the spectromicroscopy beamline the latter [73].

The high-resolution IR beamline is equipped with a 9-chamber Bruker IFS 125HR spectrometer (maximum OPD = 9.4 m). In order to carry out high spectral resolution studies, the beamline has three multiple-reflection White-type gas cells which can be optically coupled to the IFS 125 spectrometer. Two of these are glass cells with a base length of 0.6 m which mount vertically on top of the sample compartment. One, which offers a maximum optical path length of 12–15 m, can be warmed up to 380 K and connected to a 1100 °C furnace for the study of unstable pyrolysis products. The other can only be used at room temperature but can achieve maximum paths of 35–40 m.

The third gas cell is an enclosive flow cooling (EFC) cell [74–77]. It is constructed of stainless steel, has a base optical length of 0.625 m, and offers maximum path lengths of 15–20 m. This cell can be immersed in either liquid nitrogen or liquid helium depending on the desired temperature regime, and is fitted with heaters and thermostats to achieve continuous intermediate temperatures from 4 to 79 K when using liquid helium [78,79], and from 79 to 300 K with liquid nitrogen [80–86]. In addition, the EFC is equipped with a series of solenoid gas inlet valves (which can be operated in pulse or continuous mode), and with single and multiple injection nozzle devices. These enable premixing of gases or separate injection of multiple gases to allow post-mixing inside the cell. Furthermore, it can be used in a static mode (collisional cooling) or continuous flow mode (enclosive flow cooling) in order to study clusters and supercooled gases. The EFC cell is positioned vertically on its own support frame, and is optically coupled to the IFS 125 spectrometer through its parallel exit port.

The first publication resulting from the IR spectroscopy beamline was a study of the ν_{10} and ν_{11} bands of CH_3CHF_2 in the 500 cm^{-1} region [87]. This is the molecule known as R152a, another CFC replacement whose presence in our atmosphere has consequences for climate change. Another early test molecule was formamide (HCONH_2), whose analysis was an extension of some earlier non-synchrotron work [88].

The semi-stable molecule propynal (C_2HCHO) is being studied by Robertson and co-workers, both in the range below 100 cm^{-1} dominated by pure rotational transitions, and in the range from 170 to 360 cm^{-1} where the ν_9 and ν_{11} fundamental bands occur [89]. Due to its large *A* rotational constant, propynal exhibits extensive perturbations due to Coriolis and Fermi interactions. These affect even the ground vibrational state, particularly at higher *K*-values. An example showing the overall Australian Synchrotron propynal spectrum is shown in Fig. 6. Also, high-resolution spectra have been measured for a sample of tetrafluoroethylene (C_2F_4) isotopically enriched in ^{13}C , for which preliminary work is focused on the C–F stretching modes. The analysis is of fundamental interest in that the rotational constants should allow the gas-phase structure of this molecule to be accurately determined, and it is also significant given that this molecule is involved in some laser-induced isotopic enrichment schemes.

McNaughton and co-workers have recorded spectra of the low-frequency modes of ketenimine (CH_2CNH), as well as the higher frequency section of its pure rotational spectrum in the THz range (≈ 50 –100 cm^{-1}). This short-lived species was generated *in situ* by flow pyrolysis of hydroxypropionitrile at around 1100 °C. Analysis of these bands is underway. Many interactions and perturbations are observed, in part because ketenimine, like propynal, has a relatively large *A* rotational constant. The ECF cell has been used to record spectra of some refrigerant molecules in the 1000–1400 cm^{-1} range. The species $\text{C}_2\text{F}_5\text{H}$ (FC125), CF_2Cl_2 (R12), and CHClF_2 (R22) have already been studied, and analysis of the ν_5 band of the latter is almost complete, including the weaker ^{37}Cl isotopomer. In the meantime, the ECF cell is now being further adapted for operation in the far infrared region.

6.5. NSLS/ALS

From 2003 to 2009, a Bruker IFS 125HR spectrometer (MOPD = 9.4 m) was installed on beamline U12IR at the National Synchrotron Light Source, Brookhaven, where it was mainly used for medium-resolution studies of condensed-phase samples. Its high-resolution capabilities in the range below 100 cm^{-1} were demonstrated in a paper by Carr et al. [90], but no systematic

Fig. 6. Far infrared spectrum of propynal (C_2HCHO) from the Australian Synchrotron, showing the region of the ν_9 and ν_{12} fundamentals and the onset of pure rotational transitions below 120 cm^{-1} [89]. Recorded at a resolution of 0.001 cm^{-1} with 148 co-added scans, a sample pressure of 0.5 Torr and an absorption path of 4 m. Many of the strongest lines are due to water vapor impurity in the gas sample.

gas-phase studies were carried out at NSLS. This spectrometer has now been moved to the Advanced Light Source, Berkeley, where it is currently being installed on a new IR beamline 5.4.3. An experimental program involving molecules and clusters in the gas-phase is planned.

6.6. Swiss Light Source

The Swiss Light Source (SLS) is located at the Paul Scherrer Institute in Villigen, less than 40 km north of Zürich. Its storage ring has a circumference of 288 m, an energy of 2.4 GeV, and a current of 400 mA. The output of a single IR beamline is shared among a number of end stations. One of these is equipped with an 11-chamber Bruker IFS 125HR spectrometer, the highest resolution FTS currently available. Its maximum OPD of 11.5 m gives unapodized instrumental widths as small as 0.00053 cm^{-1} , or 16 MHz! This prototype system has been built from a project grant funded by the Swiss National Science Foundation and ETH Zurich for the ETH group ‘Molecular Kinetics and Spectroscopy’ of Martin Quack. It has been fully operational since November, 2009. One current focus is the investigation of complex spectra of chiral and aromatic molecules of fundamental interest within the framework of a larger project described in [91,92]. A first conference publication has just been published [93] on the successful analysis of the spectrum of a naphthalene band centered at 782 cm^{-1} which is of some astrophysical interest and further relevance as well. Another IR end station at the SLS, intended for surface science studies, also has high-resolution capabilities. It is equipped with a Bomem DA8 spectrometer having a maximum OPD of 2.5 m.

6.7. Singapore Synchrotron Light Source

The Singapore Synchrotron Light Source is located on the campus of the National University of Singapore. Its 700 MeV Helios2 storage ring is a compact (10.8 m circumference) device with currents up to 500 mA which was originally designed as a X-ray lithography source. This scope has since broadened to include nanofabrication and a variety of analytical applications. The IR beamline (ISMI) is shared among end stations for catalysis and microscopy, as well as one equipped with a Bruker IFS 125HR spectrometer for higher resolution spectroscopy. In the future, an experimental program is planned involving vibrational spectra of atmospheric free radicals, hydrogen-bonded bio-molecules, and cyclic forms of various carbon clusters.

7. Discussion and conclusions

7.1. Coherent SR

There is considerable excitement in the synchrotron community over the prospect and potential of coherent synchrotron radiation (CSR). The idea is simple: when the wavelength of emitted SR is similar to or longer than the length of the orbiting electron bunch in a storage ring, the electrons tend to emit coherently rather than incoherently. In the incoherent case, the intensity of the SR is proportional to the number of electrons in the bunch, n . But in the coherent case, the intensity is proportional to n^2 , since the amplitudes of the individual emitted electric fields add coherently. Thus CSR may have up to n times the intensity of normal incoherent SR. In order to observe CSR, short electron bunches and/or long wavelengths are required, so it is evident that the THz or very far-IR region is of primary interest. A full survey of CSR is outside the scope of the present paper, but an overview can be obtained from the following publications and references therein [94–99]. From our high-resolution perspective, it is interesting that a relatively early observation of CSR was made using

the IR beamline at MAX-lab [94]. More recently at the CLS, May et al. [100] succeeded in recording a moderately high-resolution (0.025 cm^{-1}) gas-phase spectrum using CSR, as illustrated in Fig. 7. This spectrum shows pure rotational transitions of N_2O in a range around 18 cm^{-1} covering transitions from $R(11)$ to $R(26)$. It was obtained with an absorption path of 6 m and a pressure of 1 Torr.

What are the future prospects for CSR from the point of view of high-resolution gas-phase spectroscopy? Clearly the promise of a bright, high-power THz continuum source is attractive. However, we note that CSR is itself a non-linear effect and so may tend to be inherently noisy. As well, the usual SR source noise problems (due to mechanical noise, etc.) tend to become worse at low frequencies, as already noted. So we can expect that noise will be an issue in attempts to utilize CSR. Another factor is that there are competing techniques for high-resolution spectroscopy in the THz range. ‘Conventional’ microwave techniques [101] continue to be extended to higher frequencies using backward wave oscillators, harmonic multipliers, etc. Laser photomixing [102,103] and time-domain THz [104] techniques are becoming increasingly available. Since broad-band sources (CSR or time-domain THz) require the use of a spectrometer (i.e. FTS, time delay-line, or monochromator) it is very difficult to compete with coherent oscillators (microwave or laser mixing) in terms of high spectral resolution. High-resolution is important in the THz range because Doppler widths can be very narrow, and because high-resolution correlates with high sensitivity and low detection limits. On the other hand, the use of broad-band sources with an FTS (or delay-line) can give a huge multiplex advantage (simultaneously recording thousands of spectral lines), in contrast to coherent oscillators which must be scanned relatively slowly (particularly for very high-resolution). To summarize, if noise issues can be resolved, CSR could become a useful tool for broad-band survey spectra but perhaps not for experiments requiring the highest resolution (e.g. $<0.3\text{ MHz}$ or 0.00001 cm^{-1}) and sensitivity.

7.2. Time-resolved and non-linear spectroscopy

The comments in the preceding section apply to ‘conventional’ linear high-resolution spectroscopy. But of course the very high-power and time-structured nature of CSR may be very useful for other types of experiment. Indeed, even incoherent SR has a highly-structured time profile with relatively high peak powers. Can these attributes be utilized for IR spectroscopy? The answer is

Fig. 7. Pure rotational transitions of N_2O recorded with a resolution of 0.025 cm^{-1} using coherent synchrotron radiation at the Canadian Light Source [100].

clearly yes in the case of low- or medium-resolution pump–probe type studies of condensed matter with SR [105] and even of gas-phase samples with free-electron lasers [106]. But the potential for time-resolved or non-linear studies using SR remains to be demonstrated in the domain of high-resolution IR spectroscopy.

7.3. Future opportunities

The same attribute of brightness which makes SR advantageous for high spatial or spectral resolution can have other advantages for gas-phase IR spectroscopy. The highly collimated nature of SR essentially means that “narrower” absorption cells can be used without signal loss. For example, when using an FTS with conventional sources, it is rather difficult to achieve efficient long path lengths through supersonic jets for direct absorption studies [107]. SR should be much more suitable for this application, and indeed, a new supersonic jet apparatus (Jet-AILES) is currently under development at SOLEIL by a group led by R. Georges from the Institut de Physique de Rennes with the collaboration of laboratories in Paris (LADIR), Orsay (LPPM) and Lille (PhLAM). Other examples where a highly collimated source could be advantageous include samples subjected to high temperatures, high electric or magnetic fields, or electrical discharges.

The special requirements of IR spectroscopy tend to be rather distinct from those of other synchrotron applications at shorter wavelengths, and it is therefore attractive to think in terms of a dedicated storage ring optimized for the production of IR radiation. This would, of course, be designed for high stability and low noise, and it could be relatively compact, with relatively low energy and high current. Plans for a dedicated IR facility (utilizing CSR) at the Advanced Light Source were published a few years ago [99]. But so far it seems that the economies of scale have favored the construction of large multi-purpose storage rings. In contrast, more and more dedicated IR FEL sources are becoming available, but as noted already these are generally not useful for high-resolution spectroscopy.

It is clear that SR-based sources will have a major impact on the field of high-resolution IR spectroscopy over the next few years. This is guaranteed, because a number of new facilities will become operational and also because the performance of all IR beamlines will improve as researchers learn how best to exploit this new resource (e.g. by reducing source noise). In the longer term, the impact of SR on the field will depend on the balance between its advantages and disadvantages, as well as on the possible emergence of novel competing techniques. The main advantage of SR, as outlined in this paper, may be summarized as follows: high brightness enables the recording of IR spectra with higher spectral resolution in a shorter observing time. However, there is a disadvantage which we have not really discussed yet; it may be summarized by the word access. Since SR facilities are large, expensive, and centralized, IR spectroscopists generally need to travel and set up their experiment in an alien environment which may be far from their home laboratory. The significance of these difficulties is facility-dependent, but they still tend to cancel out some of the advantages of SR. The issue of access to IR beamline facilities may become more crucial as the number of users increases and as more exotic samples are studied (e.g. unstable molecules, supersonic jets, extreme temperatures, etc.). The ultimate success of IR beamlines may then depend not only on their spectroscopic performance, but also on their ability to accommodate and nurture new users with diverse and demanding requirements.

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