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Regular article

Transmission and photoacoustic spectroscopy of organosulphur and aromatic hydrocarbons using coherent synchrotron radiation

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This work is dedicated to the memory of Dr. J.C. Bergstrom.

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ABSTRACT

This article describes transmission and photoacoustic spectroscopy experiments performed using coherent synchrotron radiation (CSR) at the Canadian Light Source. The storage ring was operated at energies of 1.0 and 1.5 GeV, with currents between 0.8 and 8.6 mA and synchrotron frequencies from 4.0 to 7.7 kHz. Relationships among these parameters and the associated energy curves were characterized in detail. Spectra of organosulphur and aromatic hydrocarbon compounds acquired using CSR exhibited absorption bands near 20 cm^{-1}, likely due to translational and rotational motion in dimers. The location and extent of usable CSR can be modified through adjustment of the ring energy, synchrotron frequency, and ring current, making this radiation suitable for acquisition of spectra at very low wavenumbers.

1. Introduction

Coherent synchrotron radiation (CSR) is emitted when the lengths of the electron bunches in a storage ring are reduced to dimensions similar to the radiation wavelength, typically about 1 mm [1,2]. CSR has been investigated in considerable detail at the Canadian Light Source (CLS) during the last decade. This research, extending from the microwave region to about 30 cm^{-1} (~1 THz), has characterized superradiance [3], and wakefields and resonances [4], using a high-resolution Fourier transform infrared (FT-IR) spectrometer. Practical applications of CSR at CLS include photoacoustic (PA) and transmission spectroscopy studies of solid materials [5,6]. CSR has similarly been employed for spectroscopy measurements at several other synchrotron facilities since 2004 [7–14], particularly at BESSY (Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung mbH) [7,8] and synchrotron Soleil [10–14]. Much of this work is motivated by the scarcity of radiation sources at very low wavenumbers, where rotational and translational vibrations of many compounds occur.

The present article describes the results of a transmission and PA spectroscopy study of organosulphur and aromatic hydrocarbons based on the use of CSR at CLS. The storage ring was operated at energies of 1.0 and 1.5 GeV in this investigation, in contrast with the usual 2.9 GeV energy employed for day-to-day (incoherent radiation) operation. Absorption bands were observed below 25 cm^{-1} for several hydrocarbon compounds in the transmission and PA spectra, consistent with the previous CSR studies at CLS. Relationships among CSR energy distribution and machine conditions were also examined in this work, by varying the ring energy, synchrotron frequency and beam current. The locations and profiles of the CSR energy curves in these tests provide important information that can be used in future CSR spectroscopy studies.

2. Experimental

2.1. Spectroscopy measurements

Spectra were acquired using the Bruker IFS 125 HR FT-IR spectrometer at the CLS far-infrared beamline. A 75-μm multilayer Mylar beamsplitter was installed in the interferometer. The resolution was set at 0.2 or 0.5 cm^{-1}; spectra were also recalculated at lower resolution (4 cm^{-1}) where necessary. The scan frequency, referenced to the He-Ne laser wavenumber, was 30–80 kHz for the transmission measurements and 5 kHz for the PA spectra. A liquid helium-cooled bolometer served as the detector for transmission, while a gas-microphone cell was utilized for the PA work.

Polyethylene (PE) pellets were analyzed in the transmission experiments. Because low-wavenumber absorption is very weak for the hydrocarbon compounds studied here, the pellets were prepared at sample concentrations as high as ~50 per cent by weight. Typical pellet thickness was about 1 mm. Molecular weight was not taken into

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consideration during pellet preparation; hence, exact concentrations were not calculated for these pellets and comparisons of the spectra are somewhat qualitative in nature. Blank PE pellets were scanned to create reference (background) spectra.

2.2. Storage ring conditions

Currents in the storage ring during CSR studies are typically between one and two orders of magnitude lower than the 220 mA value presently used for standard synchrotron operation at CLS. As mentioned above, the ring was operated at energies of 1.0 and 1.5 GeV in this study. Very low currents (0.7–1.7 mA) were necessary for stable operation at 1.0 GeV, where the natural bunch length is shorter than at higher energies. As the bunch length is reduced, electrons are lost due to Touschek scattering [15]; RF noise also causes beam loss at low synchrotron frequencies. Except for one experiment, currents ranged from 3.2 to 8.3 mA during the more extensive 1.5 GeV tests. The ring was filled with 210 electron bunches at both 1.0 and 1.5 GeV, yielding continuous CSR emission.

3. Results

3.1. CSR characterization

3.1.1. 1.0 GeV experiments

Fig. 1 presents a series of energy curves measured with the bolometer. These empty-instrument spectra were recorded at 0.2 cm^{-1} resolution and calculated using boxcar apodization. The ring energy was 1.0 GeV, with a synchrotron frequency of 4.8 kHz. The current diminished from 1.734 to 0.970 mA during the 15-min interval in which these data were recorded. Where necessary, the scan frequency and aperture of the spectrometer were adjusted to avoid saturation of the detector signal. The resulting spectrum intensities therefore differed significantly, accounting for the dissimilar ordinate scales in most of the five figure panels.

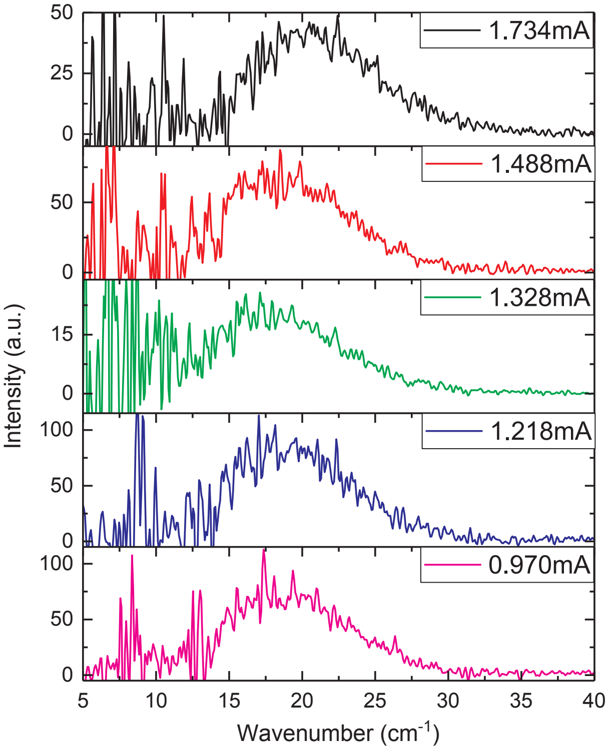

Fig. 1. CSR energy curves observed at a storage ring energy of 1.0 GeV and the currents shown in each panel. The synchrotron frequency was 4.8 kHz. An FT-IR spectrometer and bolometer were utilized to acquire these data at 0.2 cm^{-1} resolution.

Although the spectra in Fig. 1 are quite noisy (partly due to the high resolution and choice of apodization function), the data clearly confirm the existence of CSR from about 12 to 30 cm^{-1}. The maxima in these energy curves shifted from approximately 20.5 to 17.5 cm^{-1} as the current diminished from 1.734 to 1.328 mA. By contrast, the maxima increased to about 18.7 cm^{-1} at the lower currents of 1.218 and 0.970 mA. These 1.0 GeV spectra are noticeably different from previous results at the higher energies of 1.5 and 2.9 GeV [5,6], where CSR extended from about 5 to 25 cm^{-1} with maximal intensity near 10 cm^{-1}. To summarize, reduction of the ring energy to 1.0 GeV shifted the CSR emission to higher wavenumbers by about +5 to +10 cm^{-1} as compared with CSR operation at higher energies.

After the spectra in Fig. 1 were recorded, the synchrotron frequency was reduced to 4.0 kHz and the ring current fell to 0.799 mA. The energy curve obtained under these conditions was very similar to the 4.8 kHz, 0.970 mA (bottom panel) result in Fig. 1, i.e., reduction of the synchrotron frequency had little noticeable effect on CSR production at 1.0 GeV.

3.1.2. 1.5 GeV experiments

The storage ring was operated at 1.5 GeV after the 1.0 GeV experiments were completed. Results at the higher energy were significantly different from those described in the preceding section, but similar to findings in previous CLS studies at higher energies. As an example, Fig. 2 shows the energy curve acquired at 1.5 GeV with the synchrotron frequency at 4.7 kHz and a ring current of 0.862 mA. CSR is observed from about 4 to 12 cm^{-1} in this spectrum, with greatest intensity occurring near 7 cm^{-1}. It should be noted that the narrow peaks in this curve are genuine CSR features, likely due to the vacuum chamber [4], rather than noise; all of these peaks appeared in a series of eight spectra recorded immediately after the spectrum in this figure. The beam current diminished by 0.03 mA during this 15-min experiment, causing the integrated CSR intensities (interferogram peak amplitudes) to fall by about eight per cent. This reduction in intensity was approximately proportional to the square of the current, as expected for coherent radiation [2,4].

Fig. 3 reports results from further 1.5 GeV tests, with ring currents at more typical values of several milliamperes. These energy curves show that CSR intensity increased by a factor of about 90 as the synchrotron frequency was reduced from 7.7 to 4.7 kHz (upper panel), despite the accompanying current reduction of 1.1 mA. In this series of measurements, CSR was observed from about 4 to 12 cm^{-1} at frequencies down

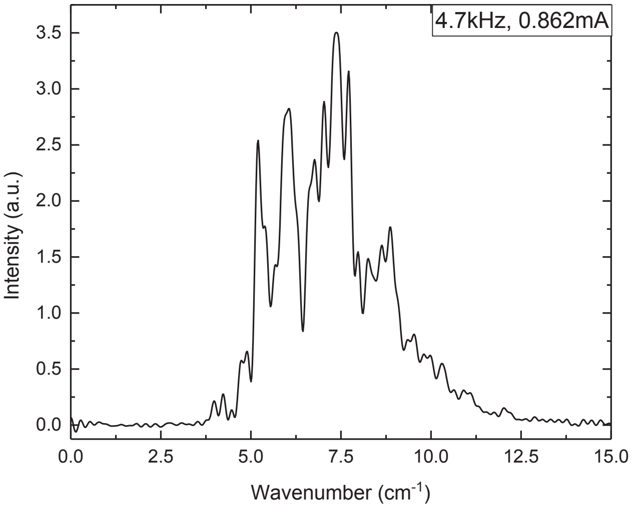

Fig. 2. Energy curve observed at 1.5 GeV, 0.862 mA, and 4.7 kHz. The spectrum resolution was 0.2 cm^{-1}.