Reflections on the Early Days of THz Spectroscopy

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Early struggles in the development of THz spectroscopy are reviewed. The field, covering an important spectral region for material characterization, suffered badly from poor lightsources and detectors in the old days, but blossomed rapidly after the arrival of femtosecond lasers. It provides another example how advances of laser technology revolutionize a field.

THz Spectroscopy was known as far-infrared or sub-mm spectroscopy in the old days. It was recognized very early that the spectroscopy is most important for probing low-frequency excitations in material characterization. In condensed matter physics, it was used to study, for example, manybody excitations such as magnons, plasmons, and superconducting gaps. In molecular physics, it was employed to probe molecular rotation, conformation, and association, as well as molecular interaction with substrate. Compared to spectroscopy in other spectral regions, unfortunately, conducting far-IR spectroscopy was extremely challenging. Both light sources and detectors encountered severe limits, rendering spectroscopic measurements very difficult and not easily accessible. As sources, commonly used blackbody radiation from globars or incandescent lamps in this spectral range was miserably weak. As detectors, bolometers, photoconductors and pyroelectric detectors were poor in detection sensitivity. In the absence of any prospects of finding sources brighter than blackbody radiation, researchers in the field directed their effort more towards developing more sensitive detectors. Dramatic improvement on detection sensitivity facilitated far-IR spectroscopy, making difficult measurements such as far-IR fluorescence spectroscopy of adsorbed molecules on surfaces feasible. It allowed mapping of the distribution of the cosmic blackbody radiation background possible that has created great excitement in astrophysics.[1]

The need of better light sources to advance far-IR spectroscopy was well noticed. The advent of lasers naturally brought hope to this issue. In the 1971 laser physics symposium in Esfahan, Iran, there was a panel discussion on the future of lasers presided by 9 panelists.[2] In the discussion, three leaders (Townes, Prokhorov, and Lax) in laser physics specifically mentioned the importance of far-IR spectroscopy and expressed hope that lasers would help in its development. Optically pumped far-IR lasers were already available at the time, but they were not tunable.

Soon after nonlinear optics was born in 1961, it was realized that wave mixing is an effective means to extend coherent light sources to new frequencies. Naturally, difference frequency generation (DFG) in nonlinear crystals that converts laser outputs to lower frequencies was considered a possible means to generate coherent radiation in the far IR. It was first demonstrated in quartz by Zernike and Birman using a free running, multimode, Nd:glass laser,[3] but limited by technology at the time, characterization of the far-IR output turned out to be non-trivial. Furthermore, to use DFG to construct a tunable far-IR source, tunable lasers were needed.

The first experiment on tunable far-IR generation by DFG was conducted in $LiNbO_3$ using temperature-tuned Q-switched ruby lasers.[4] A series of difficulties arose in the experiment. (1) Q-switched ruby lasers could be fired only once in a few minutes. (2) Two ruby lasers with different lasing frequencies must be fired synchronously with little time jitters between the two ns laser pulses. (3) Far-IR output was highly diffracted. The signal that could be collected by a detector was low. To have sufficient signal-to-noise ratio, the detector must be cooled down to 1.5K. (4) The slow response of photodetectors allowed only measurement of integrated pulse energy of the far-IR output. (5) Interferometric measurement of the output spectrum was not a simple task. Nevertheless, the difficulties were overcome, and tunable far-IR output was observed. Tunability from 1.2 to 8.0 cm^{-1} was demonstrated. The tuning range could be extended to ~50 cm^{-1} if the temperature of the lasers could be tuned down to 77K and the lasers could be selected to lase at either the R_1 or the R_2 transition. The spectral purity of the far-IR output directly reflected the spectral quality of the ruby lasers. The peak power generated in a 0.47-mm $LiNbO_3$ crystal under the phase-matching condition reached ~1 mW. Such a far-IR source was of course far from being practically useful even when tunable dye lasers later became available and could conveniently replace ruby lasers in DFG and generate far-IR over a wide spectral range.[5,6]

Optical rectification of short pulses can be considered a special case of DFG. Frequency components of a pulse can mix with one another in a nonlinear medium and generate fields with a band of frequencies, coherent combination of which produces a rectified pulse in the time domain. If there is no dispersion in DFG, the rectified pulse is simply the envelope of the input pulse. Otherwise, it is distorted and lengthened. This was recognized as a means to generate broadband THz radiation.[7] In the early 1970s, femtosecond pulsed lasers had not yet been invented, so the experiment had to be carried out with ps laser pulses, and accordingly, the generated THz radiation had a fairly limited bandwidth. With 2-ps input pulses from a mode-locked Nd:glass laser, the observed spectra of THz output from $LiNbO_3$ crystals covered a range up to ~10 cm^{-1}(0.33 THz). The spectra exhibited considerable dispersion although resonant absorption of $LiNbO_3$ is not significant in this region. It mainly came from the spectra content of the input pulse as well as the frequency dependence of dipole radiation efficiency and phase matching of DFG. The experiment was comparatively easier than the ruby laser case, but still suffered from the low rep-rate (1 per 2 minutes) of laser shots. Laser damage and crystal quality of $LiNbO_3$ were also a problem. While such a system appeared

promising as a THz source, it was not nearly practical for spectroscopy use. The situation changed completely with the arrival of highly stable, high rep-rate, fs Ti:sapphire lasers.

Optical rectification of ~20 fs pulses in nonlinear crystals can generate THz radiation with a bandwidth of ~1000 cm^{-1}, subject to dispersive effects mentioned earlier as well as possible complications arising from other nonlinear optical effects that may distort the input fs pulses as they propagate in a nonlinear medium. Auston and coworkers showed that a picosecond pulse propagating in a nonlinear medium could induced a moving rectified polarization pulse that would generate Cherenkov THz radiation at a cone angle.[8] The THz radiation appears as fs or sub-ps coherent pulses. It is remarkable that the time-varying optical field of such pulses is usually high enough to be directly measured by electro-optical modulation effect, which is the inverse of optical rectification. Thus the temporal trace of the field of a THz pulse can be mapped out by co-propagating the THz pulse with a time-shifted fs visible pulse in a nonlinear crystal.[8] In another important development, Auston and coworkers showed that THz pulse radiation could also be generated from a Hertzian dipole in the form of a localized transient photocurrent created by fs pulse excitation of a photoconductor.[9] The radiating power could be optimized by proper antenna design. Again, the inverse process could be used to detect the time variation of the THz pulse field. Although the THz spectral range, limited by the photocurrent response, was less than what can be achieved by optical rectification, simplicity, high rep-rate of pulses, and excellent signal-to-noise ratio of the scheme made it most attractive. Grischkowsky and coworkers[10] in 1989 set up a THz spectroscopy system based on such a scheme and demonstrated that they could obtain the THz spectrum of water vapor in air with 0.03 cm^{-1} spectral resolution and a signal-to-noise ratio of 3000. Unlike other optical spectroscopy techniques, Fourier transform of the THz field pulses after interrogation of a medium yields not only the absorption spectrum, but also the dispersion of the refractive index of the medium. Soon after, the THz field exploded. Continuing progress of the field in the past decades in advancing the technology and in finding wide ranges of applications in many disciplines has turned the field into one that is known even to common people. It is certainly a great pleasure to witness the birth and growth of the THz field.

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