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PAPER

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Broadband cw-terahertz spectroscopy for characterizing reactive plasmas

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Abstract

Terahertz spectroscopy is seeing increasing use in analytical chemistry because of its ability to access ground state molecular rotational and vibrational transitions. Experiments reported on the use of THz spectroscopy to the studies of low pressure plasmas have focused on the use of pulsed sources, which have limited spectral resolution. These are suitable in the characterization of plasma parameters such as electron density, but somewhat inadequate in the study of molecular absorption spectra. The recent commercial availability of continuous THz sources with much higher spectral resolution has afforded the detailed probing of molecular absorption features but they have not yet been exploited in studies of low pressure plasma chemistry. One of the major benefits of continuous-wave THz spectroscopy (cw-TS) compared to optical and infrared methods is its applicability to the study of both plasma chemistry as well as parameters, i.e. electron density and collision frequency. In this article, we provide first insights into the use of cw-TS as a plasma diagnostic, and demonstrate the opportunities and challenges by example measurements in a low-pressure argon-methanol radio frequency inductively coupled plasma in which we estimate both the plasma-induced dissociation in the precursor methanol concentration, as well as the electron density and momentum scattering collision frequency.

Keywords: cw-terahertz spectroscopy, ICP plasma discharge, electron density, collision frequency

(Some figures may appear in colour only in the online journal)

1. Introduction

Terahertz (THz) electromagnetic radiation, spanning a wavelength range of 1 mm–100 μ m, accesses rotational and vibrational transitions within an electronic state in polar molecules making them suitable for ground-electronic state spectroscopic diagnostics.

Examples include the pure rotational transitions of heteronuclear diatomic molecules such as HCl [1], asymmetric rotor molecules such as light hydrides (e.g. XH_n , with $n = 1, 2$) [2], and highly reactive molecules such as radicals and molecular ions [3]. The low rotational–vibrational bending modes of large molecules with internal motion, such as carbon-chain molecules (e.g. $\text{CH}_3\text{CH}_2\text{OCH}_3$) also have absorption features in the THz range [3]. Small biomolecules, which usually have

intramolecular vibrational resonances in frequency regions above 10 THz, often form weak hydrogen bonds when interacting with other biomolecules. Vibrational modes mediated by these hydrogen bonds result in resonant frequencies that are lower than typical intramolecular resonant frequencies [3], resulting in absorption at even lower-frequency (<10 THz). Finally, heteronuclear diatomic molecules such as HCl exhibit unique spectral signatures arising from transitions between rotational quantum levels [1]. Such unique molecular absorption signatures are complementary to the more well-established mid-IR signatures. For quite some time, there was a lack of practical sources and detectors that operate in this range, sometimes called the THz gap [4]. In recent years, there has been a filling of this gap, in part due to the development of laser-based THz generation. Typically, there are two ways in which THz radiation has been generated and tailored for use in spectroscopic applications. The first one is

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time-domain THz spectroscopy (TDTS). TDTS is based on the use of intense femtosecond laser pulses in either semiconductor or non-linear crystals to drive collective oscillations in free charge carriers or bound electrons to THz bursts [5]. A fast Fourier transform is then performed to convert the temporal signal into a broadband frequency spectrum (ranging from a few tens of GHz up to 10 THz) [5]. The second method has only been available more recently, and is the one used in this study. It is continuous-wave THz spectroscopy (cw-TS) where two near-infrared cw-lasers, with their difference frequency equal to the desired THz frequency, are superimposed and focused onto GaAs or InGaAs photo-mixers producing narrow-band THz radiation [6]. With these technological developments, THz spectroscopy has seen increasing use in various disciplinary areas ranging from analytical chemistry to combustion [7, 8]. Furthermore, since most non-polar materials are transparent to THz radiation these sources are suitable for solid-state characterization of material properties such as the complex dielectric function or the moisture content of hygroscopic materials such as plastics or clothes [9]. THz spectroscopy is a versatile technique that can also be employed in the characterization of chemistry and its evolution in plasma processing systems that sometimes involve both gaseous and solid substances. To our knowledge, there are relatively few, if any, studies that exploit either TDTS or cw-TS to study plasma chemistry. This paper serves to outline some of the basic opportunities and challenges, and to demonstrate, as an example, the use of cw-TS to make measurements in a low pressure argon-methanol (CH_3OH) inductively-coupled plasma discharge.

The most common quantitative spectroscopic techniques used in reactive plasmas include, for example, laser absorption spectroscopy (LAS) which favors the use of tunable diode lasers (TDL) [10] and, most recently, quantum cascade lasers (QCL) [11]. Other spectroscopic methods of studying plasma chemistry include wide-band Fourier transform infrared (FTIR) spectroscopy [12], laser induced fluorescence (LIF) spectroscopy [13] (particularly of the two-photon variant [14]), cavity ring-down spectroscopy [15], Raman scattering spectroscopy [16], Rayleigh scattering [17] and optical emission spectroscopy (OES) [18]. These diagnostics are relatively robust and reliable methods that can achieve high sensitivity, spectral, and temporal resolution for molecule detection and quantification. THz spectroscopy is complementary to these methods. With a broadband or widely tunable THz source, a number of important precursor molecules used in plasma processing, and their by-products, can be detected simultaneously with TDTS or with a single tunable cw-TS source. Some of these precursor molecules that have relatively strong transitions in the THz spectral region (0.1 THz to a few THz), are presented in table 1 along with typical strong line strength transitions (according to HITRAN database [19]) and their application to plasma processing.

THz spectroscopy is particularly suitable for probing plasma processes that nucleate nano- and micro-scale dust particles, such as silane and hydrocarbon plasmas that are used in silicon and carbon thin film deposition, respectively. THz radiation has relatively long wavelengths in comparison

to the particle sizes (0.01 μm to a few μm) produced during these plasma processes and is therefore less prone to scattering and extinction. For example, Hsieh *et al* have compared IR absorption to THz absorption in spectroscopic studies of gas cells containing smoke dust, delineating the benefits of reduced scattering associated with the use of much longer wavelengths [20].

Another interesting aspect of using THz spectroscopy in plasma applications lies on the possibility of determining fundamental plasma parameters such as electron density, n_e , and the electron momentum scattering collision frequency, ν . The sensitivity of such measurements in processing plasmas in comparison to infrared sources is that their frequency is much closer to the plasma cut-off frequency $f_p = \omega_p/2\pi$ (e.g. tens to hundreds of GHz) with the plasma frequency,

$$\omega_p = (n_e e^2 / m_e \epsilon_0)^{1/2} \quad (1)$$

where e , m_e , and ϵ_0 represent the electron charge, mass, and vacuum permittivity, respectively. In this range, the shape of the broadband attenuation of the electromagnetic waves is sensitive to both n_e , and ν . Typically, for low pressure RF and pulsed plasmas, n_e ranges from $\sim 10^{11} \text{ cm}^{-3}$ to at most 10^{14} cm^{-3} , corresponding to $f_p \sim 3 \text{ GHz}$ to 90 GHz .

Being a non-intrusive method, THz measurements of n_e are better suited than electrostatic probes which are also commonly employed in this plasma density range, particularly in reactive plasmas, or when a line-of-sight measurement is acceptable. As the electron density usually increases with working gas pressure the use of Langmuir probes may be difficult to interpret as the plasma becomes collisional. Stark broadening of hydrogen lines, a commonly used emission-based spectroscopic signature for extracting n_e , is usually limited to plasma densities higher than $\sim 10^{13} \text{ cm}^{-3}$. THz spectroscopy is therefore complementary with the previous mentioned methods and other well-established techniques such as microwave interferometry [21] as well as Thomson scattering [22].

Measurements of plasma parameters using TDTS have been performed by a few groups [23–27], for example, in HiPIMS discharge [28], and, more recently in both ICP discharges and pulsed discharges with microsecond temporal resolution [29].

The literature for using THz spectroscopy and, more specifically, cw-TS (which affords high spectral resolution) for studies of chemistry in reactive plasmas suggests that cw-TS for plasma diagnostics is largely an unexplored field. That may be because of only the recent commercial availability of cw-THz sources. The major difference between TDTS and cw-TS is that the former offers sub-microsecond temporal resolution (at the expense of spectral resolution of only 10s of GHz) whereas the later offers MHz spectral resolution at the expense of temporal resolution (fractions of seconds). TDTS can be a suitable diagnostic tool to characterize chemistry occurring during transient plasmas, such as a plasma ignition event or perhaps the chemistry of the direct-afterglow following plasma extinction. In contrast, cw-TS can achieve a spectral resolution needed to study narrow molecular features

Table 1. Example of species that can be measured with THz spectroscopy (with typical position of strong line strength transitions [19]) and examples of plasma applications that can benefit from THz spectroscopy.

Species [example of spectral position in THz]	Plasma applications
Ammonia (NH ₃) [0.573, 1.214]	Nitride deposition [30] Ammonia synthesis [31, 32]
Hydrofluoric acid (HF) [1.232]; hydrochloric acid (HCl) [0.626, 1.251]	Semiconductor etching [33, 34]
Acetylene (C ₂ H ₂) [1.010, 0.653]; methane (CH ₄) [1.022, 1.619]	Carbon based material deposition [35] Hydrocarbon dusty plasmas [36]
Methanol (CH ₃ OH) [0.636, 0.890]; acetone ((CH ₃) ₂ CO) [0.132]; water (H ₂ O) [0.557, 1.097]; hydrogen peroxide (H ₂ O ₂) [1.038, 1.587]; nitric oxide (NO) [0.950, 1.252]; nitrogen dioxide (NO ₂) [1.132]; nitrogen oxide (N ₂ O) [0.679, 0.804]; carbon monoxide (CO) [1.037, 0.693]/dioxide (CO ₂) [0.550]; hydroxyl radical (OH) [1.392], ozone (O ₃) [0.656] ...	Atmospheric pressure plasma: – Pollutant abatement [37] – Plasma medicine [38] – Plasma–liquid [39]

with higher sensitivity. Thus, cw-TS is a versatile technique that is suitable for performing absorption spectroscopy on low density plasmas while also enabling measurements of plasma parameters.

This paper introduces cw-TS for the characterization of low pressure reactive plasmas. We present its main features, addressing the opportunities as well as its limitations. We also provide an example of its application to characterize an argon-methanol low pressure inductively coupled discharge. The paper is intended to provide just a first assessment of a plasma diagnostic that has the potential to become an important tool in studies of reactive chemistries in gas discharges.

2. Description of the plasma and cw-THz spectrometer

This section provides a description of the plasma source as well as the salient features of the cw-THz spectrometer. Figure 1 is a schematic of the experimental arrangement. The plasma reactor consists of a typical RF-ICP discharge (40 MHz). The vacuum chamber is fabricated using a stainless-steel cross connected to a pumping plant (roots blower/mechanical pump combination) through its bottom port. One of the side flanges is mated to a high-density polyethylene (PE) window (2 mm thick and 4 cm of diameter) chosen for its high transmission properties at THz frequencies. The opposite flange supports a cylindrical quartz tube 2 cm in diameter and 25 cm long. A two-turn, 2.5 cm diameter copper antenna surrounds the quartz tube. The antenna is connected to a custom-fabricated impedance matching network to optimize the transmitted power delivered by a 40 MHz RF generator. A stainless steel chamber is mounted at the other end of the quartz tube for introducing the reactants (which in this case, is a mixture of argon and methanol) and to house the second PE window for THz transmission measurements. The transmission path length, i.e. the distance between the two PE windows, is ~ 37.5 cm. The plasma ignites in the region of the copper coil antenna for pressures, P , ranging from 0.5–6 Torr at a total gas volume flow rate, Q , of 50 sccm and RF power, P_{RF} , of 30–200 W. The active plasma occupies a volume within the region of a coil that spans a length, L_p , from ~ 8 –15 cm, depending on the operating conditions, as determined approximately by its luminous spatial emission.

Terahertz absorption is performed using a commercial cw-THz spectrometer (Toptica Photonics model TeraScan 1550). We briefly describe the pertinent working features of the system here and refer to the paper of Roggenbuck *et al* [40] for details. The cw-TS device generates linearly polarized incoherent THz EM waves using a pair of tuned distributed feed-back (DFB) lasers ($\lambda = 1546$ and 1550 nm). The laser beat frequency can be tuned continuously from 60 GHz to 1.2 THz by reducing the temperature of the first laser while raising that of the second laser. Interferometric control of the laser frequency results in a spectral resolution and frequency stability of tens of MHz [41]. The two laser beams are launched into a dual fibre array and delivered to a tapered amplified. Once amplified, the dual-frequency beam is split into two beams, one of which is electronically modulated at kHz frequencies (for phase-sensitive detection, described below) and carried to an InGaAs photomixer which serves as the THz emitter to produce nearly-collimated THz radiation (see schematic depicted in the insert of figure 1). As mentioned earlier, the THz are generated by the optical heterodyne method [42] in which the beat frequency field excites collective carrier oscillations in the InGaAs, which then drives current to flow in an integrated broadband spiral antenna that radiates THz waves at the laser beat frequency. The second beam is fiber guided to the second InGaAs photomixer which serves as the THz receiver. Here, the THz signal from the transmitting photomixer (which passes through the device to be studied) and beating lasers interfere in driving the collective charge oscillations in the InGaAs resulting in a signal generated in its corresponding spiral antenna that is proportional to the field strength of the transmitted THz source, but modulated due to the phase shift of the transmitted THz source [40] at a frequency $f_M = L/c$. Here, L is the added path length from the transmitter to the receiver and c is the speed of the THz wave along this path.

Because the contribution of the THz wave to the receiver signal is expectedly weak, phase sensitive detection is used to extract the contribution of the detected signal at the modulated frequency, f_M . The extracted amplitude of the signal is proportional to the THz field transmitted through the path between the transmitter and receiver. The modulation carries with it information on the phase shift introduced as the THz waves traverse this path, which can have a refractive index other than unity when a plasma is present. In its construction, the

Figure 1. Experimental arrangement used for cw-THz spectroscopy in an inductively coupled plasma reactor. PE: polyethylene, OAP: off-axis parabolic and DFB: distributed feed-back.

THz radiation generated at the transmitter is focused into and collected from the plasma chamber using two 90°, 76.2 mm diameter, off-axis parabolic mirrors (OAP), each with an effective focal length $f = 152.2$ mm. In our experiment, the distance between the two mirrors is fixed at 80 cm.

3. Typical cw-THz photocurrent features and reference gas absorption

A typical measured photocurrent signal from the spectrometer is shown in figure 2. Figure 2(a) presents a representative signal when the chamber has a finite partial pressure of methanol (CH_3OH) recorded over the relatively short frequency range of 610–690 GHz. Apparent in this figure is the underlying high frequency modulation at $\sim f_M$, which is clearly resolved in the expanded region shown in figure 2(b). Also apparent is the envelope of this modulated signal, which represents the attenuation of the transmitted beam due to the presence of strong methanol lines (see CH_3OH vertical arrows in figure 2(a)).

As described above, the frequency-dependent photocurrent extracted from the phase-sensitive detection,

$$I_{pc}(f) = E_{\text{THz}} \cos(2\pi Lf/c) \quad (2)$$

where E_{THz} is the amplitude of the terahertz electric field (red curve in figure 2(a)), obtained, for example, from the extrema of the photocurrent oscillations. The phase shift introduced by the path length traversed by the THz waves when a plasma is present is determined from the frequency-dependent change in f_M that is introduced when a plasma is ignited, relative to that without the plasma. The detected THz photocurrent is thus used to reconstruct the transmission spectra over the whole spectral range.

A typical broad spectrum (300 GHz–1000 GHz, i.e. 10 cm^{-1} – 33.35 cm^{-1}) obtained with the reactor chamber filled with methanol vapour (without the plasma) at atmospheric pressure and ambient temperature is shown in figure 3.

For this spectrum, the reactor is simply used as a calibration reference with all parameters controlled and known. Except for a few weak water absorption lines (centered at 557 GHz, 752 GHz and 988 GHz) due to traces of water vapour in the space between the antennas and the chamber windows, the majority of the molecular absorption features are those of methanol as verified using the HITRAN database [19]. The scan duration required to collect this broadband spectrum was typically ~ 5 min. A spectrum acquired over a more restricted range large enough to encompass an isolated molecular line of interest takes much less time, typically only several seconds.

The experimental transmission spectrum of figure 3 is converted into an absorbance spectrum ($-\ln(I/I_0)$) as shown in figure 4(a). Here I_0 and I are the signals obtained before and after introducing the methanol into the reactor, respectively. Figure 4(a) shows the recorded experimental broadband absorbance spectrum, as well as that calculated using the SpectraPlot software that interfaces to the HITRAN database [43]. We see that the agreement between the predicted and measured absorbance is quite good.

Experiments were conducted over a range of methanol pressures (from 0.5–80 Torr) as shown in figure 4(b). We see that the molecular lines of methanol centered at approximately 530 GHz are easily detected at pressures as low as 0.5 Torr, as one can see from the inset to figure 4(b). The narrowing of the spectral lines with reductions in pressure is due to the reduced collision broadening. In principal, collision broadening coefficients can also be determined from these data by fitting the synthetic spectra to those measured over a range in pressure using the broadening coefficient as a fitting parameter, although we have not yet carried out this analysis on these data. If the collision broadening coefficients are well known, both density and temperature can be extracted by resolving the distinct contributions to the lineshape from collision (which is largely Lorentzian in shape) and Doppler broadening (which is Gaussian in shape). Even lower detection limits can be obtained

Figure 2. (a) Measured THz photocurrent signal over a short frequency range obtained with the chamber filled with methanol at atmospheric pressure and room temperature (no plasma). The shape of the red line that contours the modulated signal represents the attenuation of the transmitted THz beam due to strong methanol absorption. (b) Expanded region from 651 GHz to 656 GHz that shows the frequency modulation of the signal and at the same time, the typical resolution that is achieved with the cw-THz spectrometer.

Figure 3. Measured broadband spectrum of methanol vapor (no plasma) at atmospheric pressure and room temperature obtained with the cw-THz spectrometer.

(below 0.5 Torr) by studying the transitions of higher line strengths which appear at high THz frequency. The broadband nature of this cw-TS allows choosing the most suitable spectral region for a particular study. Note that the experimental results presented in this section (and below) were performed using a single pass configuration.

For our conditions, we expect a detection limit of about $\sim 4 \times 10^{14} \text{ cm}^{-3}$. This value is determined from the lowest pressure (0.1 Torr) at which the strongest line strength transition is still detected with reasonable certainty within our accessible THz spectral window. This detection limit is not quite as low as that of well-established mid-IR spectroscopy that uses multi-pass cells, such as TDLAS that can achieve $\sim 10^{13} \text{ cm}^{-3}$ for methanol [44]. Note that our detection limit can be further improved by also using a multi-pass cell configuration, which may be especially desirable for very low pressure conditions.

With extended tuning (to a few THz) line strengths are higher, particularly for smaller molecules, and sensitivities can be increased substantially. As an example, using a custom-fabricated cw-THz spectrometer with high spectral resolution ($\sim 5 \text{ MHz}$) and a large tuning (0.3 to 3 THz), Bigourd *et al* was able to measure HCN concentrations as low as about 10^{12} cm^{-3} [45].

4. Plasma characterization

This section introduces the opportunities and limitations encountered in using broadband cw-TS for reactive plasma characterization. When traversing the plasma, THz waves with angular frequency higher than the plasma frequency, ω_p , may experience frequency-dependent changes in propagation related to the electron's contribution to the refractive index, $n(\omega) = \sqrt{\epsilon}$. Here, ϵ is the complex plasma dielectric constant,

$$\epsilon(\omega) = \epsilon_R + i\epsilon_I = \left(1 - \frac{\omega_p^2}{\omega^2 + \nu^2}\right) - i\left(\frac{\omega_p^2}{\omega^2 + \nu^2} \frac{\nu}{\omega}\right), \quad (3)$$

and ν is the total electron momentum transfer collision frequency. The frequency-dependent modifications of the detected THz photocurrent are seen, particularly in the sub-THz frequency range, close to the plasma frequency. Figure 5 plots the raw photocurrent over a narrow range of frequency centered about 109.5 GHz for a 6 Torr argon discharge at two values of the discharge power, P_{RF} . For comparison, we include the reference spectrum acquired with the plasma off. Apparent in the photocurrent is a progressive evolution in both the attenuation of the amplitude (envelope) as well as a shift in the phase, $\Delta\Phi$, of the modulation (relative to the reference) as plasma power increases. From the evolution of the photocurrent spectrum, i.e. before and after plasma ignition, one can obtain information about plasma properties. If the collision frequency is known, the plasma density, n_e , can be determined

Figure 4. (a) Absorbance spectrum fitted with a simulated spectrum that has been obtained with SpectraPlot that uses the HITRAN database [43] (atmospheric pressure and room temperature). (b) Measured absorbance spectrum as a function of methanol pressure (no plasma) at room temperature. The inset represents lowest pressure conditions studied in order to better appreciate the potential detection limit encountered in our studies.

from the measured phase $\Delta\Phi$ [26]. The phase shift can also be determined from the difference in the real part of the refractive index, $\Delta n_R(\omega)$, for cases with and without the plasma,

$$\Delta\Phi(\omega) = \Delta n(\omega) \omega L_p / c \quad (4)$$

where L_p is the length of the plasma in the discharge tube, which we assume to be uniform. If we take the refractive index of the medium when the plasma is off to be ~ 1 , and the electron collision frequency $\nu \ll \omega$, then it is relatively easy to show that

$$\Delta\Phi(\omega) \approx \frac{\omega L_{pl}}{c} \left[\sqrt{1 - \frac{\omega_p^2}{\omega^2}} - 1 \right]. \quad (5)$$

We find that at the highest power, the measured phase shift is $\Delta\Phi(\omega) \approx 2.3$ radians, resulting in a plasma density of $\sim 3 \times 10^{12} \text{ cm}^{-3}$ which is consistent with the values typically measured in RF-ICP discharges [46]. This plasma density corresponds to a plasma frequency, $\omega_p = 9.8 \times 10^{10} \text{ rad} \cdot \text{s}^{-1}$ (15.5 GHz).

To estimate ν from the experimental THz spectra, we examine the spectrally dependent attenuation of the transmitted THz waves after plasma ignition.

Figure 6(a) shows broadband spectra of both the reference (taken before plasma ignition) and that for a 6 Torr Ar plasma at $P_{RF} = 60$ and 90 W. We see that increasing P_{RF} leads to a favoring of the attenuation at lower frequency, i.e. closer to the plasma frequency. At frequencies $\omega \gg \omega_p$, typically higher than ~ 600 GHz for these conditions, the THz wave transmission is no longer significantly affected by the plasma as evidenced in the inset of figure 6(a). With n_e determined from the phase shift as described above, ν can be estimated by calculating the frequency-dependent absorption coefficient, $\alpha = \omega n_I / c$, which depends linearly on the imaginary contribution to the refractive index, $n_I = \text{Im}(\sqrt{\epsilon_R + i\epsilon_I})$, which, for $\nu \ll \omega$ (or $\epsilon_I \ll \epsilon_R$), reduces to $n_I \approx \sqrt{\epsilon_I^2 / 4\epsilon_R}$. This absorption coefficient therefore becomes [47],

Figure 5. Measured THz photocurrent signal before (reference) and after argon plasma ignition (6 Torr at both 60 and 90W) in a short sub-THz frequency region.

$$\alpha \approx \sqrt{\frac{\omega^2}{4c^2} \left(1 - \frac{\omega_p^2}{\omega^2} \right) \left[\frac{\nu \omega_p^2}{(\omega^2 - \omega_p^2) \omega} \right]^2}. \quad (6)$$

Considering that $I_{pc}(\omega) \propto E_{THz}(\omega)$, one can theoretically synthesize the plasma transmission spectra from the reference spectrum I_{REF} (plasma off) using the Beer-Lambert law [23]:

$$I_{pc}(\omega) = I_{REF}(\omega) e^{-\alpha L_{pl}}. \quad (7)$$

Since the electron density (and hence the plasma frequency) is known from the measured phase shift, we use just the collision frequency as a fitting parameter until agreement is obtained between the calculated and the measured spectrum. Figure 6(b) shows the comparison between the calculated and measured spectrum (at 60 W of RF power) for a collision frequency of $\nu \sim 1 \times 10^{10} \text{ s}^{-1}$. A relatively good agreement is obtained over the entire spectral range. For these plasma conditions, electron-neutral collisions are expected to

Figure 6. (a) Broadband measured spectrum before (reference) and after argon plasma ignition (6 Torr at both 60 and 90 W). (b) Measured plasma spectrum obtained at 60 W compared to the calculated spectrum obtained using (7).

contribute most to the electron momentum transfer collision frequency. If the average rate at which electrons collide with Ar atoms is represented as

$$\nu_{en} \approx n \langle \sigma \rangle_{en} v_{th} \quad (8)$$

where n is the neutral argon density, $\langle \sigma \rangle_{en}$ is the velocity averaged momentum transfer cross section and v_{th} the mean electron speed. A 6 Torr discharge in relatively cold (room temperature) argon gives $n \approx 2 \times 10^{23} \text{ m}^{-3}$. If we assume that the electron temperature is $T_e \approx 3 \text{ eV}$ ($v_{th} \approx 10^6 \text{ m s}^{-1}$), then the measured collision frequency gives $\langle \sigma \rangle = \nu_{en}/nv_{th} \approx 5 \times 10^{-20} \text{ m}^2$ which is quite reasonable [48], adding confidence to the measured collision frequency.

We see then that the plasma parameters determined from the THz spectra are consistent with values expected from RF-ICP discharges [46]. However, we should mention that these plasma parameter measurements were obtained in pure argon discharges, and we might expect that in reactive plasmas, the THz spectral region could be affected by both plasma attenuation/phase shifting and molecular absorption. This would suggest that where it is desired to extract both molecular concentrations and plasma parameters, the theoretical synthesis of molecular spectra should guide in the identification of potential features that might interfere in the spectra at low frequencies, from which plasma parameters are extracted. Furthermore, molecular absorption measurements should be carried out in the upper part of the THz spectral region to avoid interference from the attenuation and phase shift introduced by the plasma electrons. Fortunately, the majority of the molecules of interest to processing plasmas (see table 1) have strong lines in higher spectral region ($\sim 600 \text{ GHz}$ to a few THz), a range that can be now easily accessed with these commercially-available cw-TS systems.

Finally, we demonstrate that cw-TS can be used to monitor the dissociation chemistry of a gaseous reactant, such as CH_3OH , by the plasma. As a line-of-sight diagnostic, THz absorption spectroscopy (as well as any laser or optical absorption spectroscopic methods) is confronted with the challenge of determining accurately, the molecular density, as the probed media spans a spatially inhomogeneous distribution of molecular density and gas temperature. Some assumptions have been adopted here to estimate degree of dissociation through line-of-sight concentration measurements. For gas temperature, we have assumed a mean temperature of 400 K as the plasma length is much lower than the total optical path. Stable methanol molecules are assumed to be present in the entire optical path especially in the coolest zone of the plasma reactor (300 K). The absorbance spectra are then simulated using the Spectraplot [43] that contains database of calculated temperature-dependent line strengths for the estimation of CH_3OH concentration. Figures 7(a) and (b) show the investigated methanol absorption transitions over a narrow range of frequency ranging from 610 to 640 GHz before and after operation of the plasma at 60 in an Ar/ CH_3OH mixture at 6 Torr as well as degree of dissociation of methanol as a function of plasma power (c). The degree of dissociation D is determined by:

$$D = \left(1 - \frac{[\text{CH}_3\text{OH}]}{[\text{CH}_3\text{OH}]_0} \right) \times 100 \quad (9)$$

where $[\text{CH}_3\text{OH}]_0$ and $[\text{CH}_3\text{OH}]$ are the mean methanol concentration before and after plasma, respectively. Note that the results of dissociation degree are subject to errors coming from the assumptions mentioned previously.

We see that there is an increase of degree of dissociation with increased plasma power. These results are somewhere similar to

Figure 7. A zoom into the 610–640 GHz region of the upper part of the THz spectrum (where the plasma is no longer affecting the spectrum) showing the measured versus simulated (using spectraplot [43]) absorption lines before (a) and after plasma ignition (b) at 60 W (argon/methanol mixture at 6 Torr). (c) The estimated methanol concentration and the degree of dissociation as a function of plasma power.

the dissociation degree found by Hempel *et al* that have carried out plasma experiment in same range of pressure [44].

5. Summary

We have introduced in this paper the potential use, including opportunities and challenges, of cw-THz spectroscopy for the characterization of reactive plasmas. Experiments are carried out with commercially-available THz spectrometers applied to a laboratory RF ICP discharge. We have shown that cw-THz spectroscopy enables access to both electron density and electron momentum scattering frequency by studying the plasma-induced frequency dependent propagation and attenuation experienced by the THz waves. These spectrally-dependent changes to transmission affect the spectrum in the sub-THz region, i.e. regions within an order of magnitude of the plasma frequency (typically in the 100 GHz–600 GHz region). Studies of molecular absorption of plasma species should therefore be carried out in the upper part of the THz spectrum (typically above 600 GHz) to avoid any interference from the plasma electrons. We see, through the exploitation of the full broadband THz spectrum, one can measure important plasma parameters as well as plasma-induced modifications of constituent chemistry to understand reactive plasma processes. We demonstrated, by way of example using a mixture of CH₃OH and argon, that THz spectroscopy can be used to characterize the electron-impact dissociation of gaseous

precursor molecules. With simultaneous characterization of both electron and molecules, one may gather insight about the processes that induce dissociation, i.e. one might differentiate between electron impact processes or pure thermal process. THz waves are particularly advantageous over optical waves when characterizing dust-generating plasma chemistries as their relatively long-wavelengths are less susceptible to extinction due to direct particle scattering. As a perspective, one may also characterize thin films that are produced during plasma process using THz spectroscopy and then be able to access to a complete set of data from plasma, to molecule and thin film properties.

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