Application of Terahertz Spectroscopy to Time-Dependent Chemical-Physical Phenomena

Plinio Innocenzi,*[,†] Luca Malfatti,[†] Massimo Piccinini,[‡,⊥] Diego Sali,[§] Ulrich Schade,[‖] and Augusto Marcelli*[,⊥]

Laboratorio di Scienza dei Materiali e Nanotecnologie, D.A.P., Università di Sassari, CR-INSTM, Palazzo Pou Salid, Piazza Duomo 6, 07041 Alghero (Sassari), Italy; Bruker Optics, s.r.l., Via Pascoli 70/3, 20133 Milano, Italy; Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Elektronenspeicherring BESSY II, Albert-Einstein-Strasse 15, D-12489 Berlin, Germany; and INFN-Laboratori Nazionali di Frascati, Via E. Fermi 40, 00044, Frascati, Italy

Received: March 19, 2009; Revised Manuscript Received: June 15, 2009

We present here a "proof of concepts" experiment that has been realized to show that time-dependent phenomena can be successfully studied in the terahertz region in a non pump−probe configuration. We have built-up an original analytical setup that has allowed following the evaporation of a deuterated water droplet cast on a CVD diamond substrate simultaneously in the near-middle infrared region and in the terahertz range. We have used a synchrotron light source in the terahertz region and a conventional thermal source in the infrared range. The results demonstrate that it is possible to study time-dependent phenomena simultaneously in the middle and terahertz ranges monitoring the entire chemical-physical process that occurs in the time domain of minutes.

Introduction

An important current trend in research is the development of experimental methods based on concurrent and simultaneous time-resolved capabilities.[1] It has been shown that it is possible to combine different types of time-resolved analytical techniques using different sources, such as synchrotron light.[2] In particular, it is expected that in a near future the realization of concurrent spectroscopic experiments investigating complex phenomena on a time scale that ranges from the subsecond to the microsecond time domain will make it possible to study multiscale and time-dependent phenomena in an unprecedent way. An example is the combination of X-ray and infrared beams to perform time-resolved experiments.[2] However, although in the X-ray domain the idea of time-resolved studies started at the end of the 70s and triggered the development of the dispersive geometry in many synchrotron radiation facilities all around the world, infrared time-resolved experiments were mainly confined to laboratories and limited in time resolution by the available sources and detectors.

Stimulated by the availability of infrared (IR) synchrotron sources and by the unique characteristics of synchrotron radiation also in the IR domain, we selected a simple chemical-physical system to realize a "proof of concepts" experiment to verify the possibility of performing time-resolved analysis in the terahertz (THz) region with a rapid scan method.[3,4] It should be underlined that time-resolved experiments performed in the THz region are typically realized by a pump-and-probe configuration with picosecond resolution.[5] These experiments are performed by generation and detection of THz pulses in a synchronous and coherent way by visible or near-IR laser pulses. In the present experiment, we have used the THz emission of the synchrotron radiation, a pulsed source that is characterized by bunches from tenths of picoseconds to a few nanoseconds long. The advantage of using a nonthermal high-brilliance synchrotron source coupled with sensitive bolometers is also the high signal-to-noise ratio that can be achieved in particular in the far-infrared region. In this case, it is possible to extend the application of THz spectroscopy in the linear framework to time-dependent phenomena that are not limited by pump-and-probe configurations in a short time scale.

The system is composed of a deuterated water droplet; obtaining direct chemical-physical information during an evaporation process is however in general quite a difficult task because several experimental problems need to be solved. This is a typical time-dependent chemical-physical phenomenon, and in situ time-resolved experiments by infrared spectroscopy represent a suitable solution. A strong drawback is however represented by the signal saturation of water bands in the mid-IR region. Even a few micrometer thickness droplet of water cast on an infrared transparent substrate can easily give a saturated signal, especially at the first stage of the evaporation process. We have solved this problem optimizing, in a previous work, the experiment in the near-IR region;[6] the water overtone and combination bands have been well resolved, and not saturated signals from the beginning of the process have been recorded. We have obtained an indication of the effect of relative humidity (RH) in the process and a good description of the phenomenon with time. We have now extended this experiment to the terahertz region; our goal is to use the previous results as a reference to check the capability of performing such kind of experiments in the terahertz region. In order to achieve the target, we have set up a special experimental optical layout that has allowed us to perform a simultaneous measure of the evaporation phenomenon in the whole infrared range using a conventional source in the near- and middle-infrared region and a synchrotron light in the terahertz region.[7]

---

* To whom correspondence should be addressed.

[†] Università di Sassari.

[‡] Present address: Porto Conte Ricerche, Laboratorio Imaging, SP 55 Porto Conte-Capo Caccia km 8, 400, Loc. Tramariglio - 07041 Alghero (SS), Italy.

[§] Bruker Optics.

[‖] Elektronenspeicherring BESSY II.

[⊥] INFN-Laboratori Nazionali di Frascati.

10.1021/jp902502z CCC: $40.75

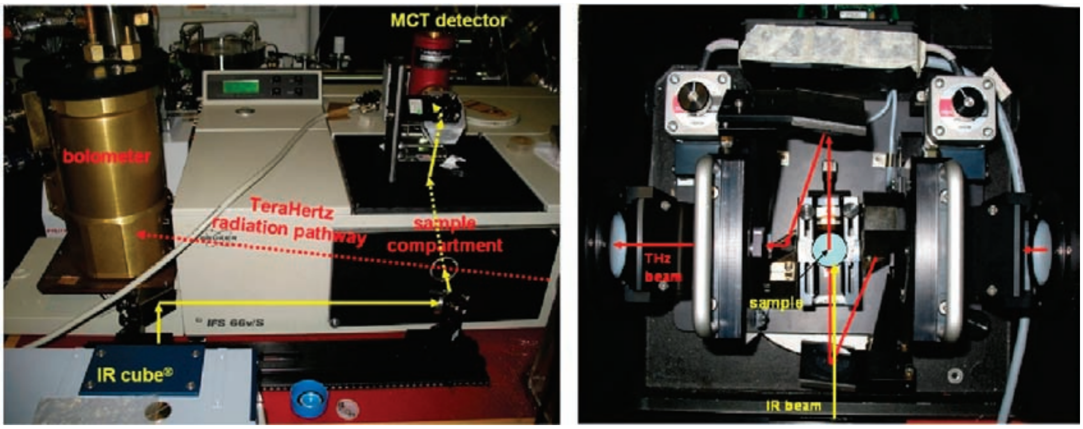

Figure 1. Images of the experimental setup built at the infrared-terahertz beamline at BESSY. The path of the infrared beam is shown in yellow, and the path of the terahertz beam generated by the syncrothron is in red (left figure). A detail of the sample compartment is shown in the right figure.

Experimental Section

We built a special experimental setup able to perform simultaneous measurements in the far-infrared region (600−30 cm^{-1}) and in the near- and mid-IR range (6500−600 cm^{-1}) combining the emission of a synchrotron light source and a conventional thermal (Globar) source.

The experiments in the far-infrared energy domain were performed using the emission of the IRIS beamline of the BESSY synchrotron facility (Berlin, Germany). We installed a grazing incidence reflectance accessory (A513/Q Bruker) inside the interferometer (Bruker IF-66v/S) available at the beamline. It is a high performance variable angle reflection accessory optimized for the Bruker FT-IR spectrometers. We used the base accessory that allowed manually adjusting both the incidence and collection angles, independently, and we modified it to work in the transmission geometry (Figure 1). A CVD wedged diamond window was placed horizontally with respect to the sample position, and the focused IR beam was hitting the surface of the window at an incidence angle of 60° (respect to the vertical). Reflectivity spectra of the CVD diamond substrate can be found in ref 8. A FIR broadband beam splitter was used, and all of the interferometer operated in a vacuum of about 3 mbar, except the sample compartment that was maintained at room pressure and in conditions of controlled temperature and relative humidity by a nitrogen gas flux. Two windows of polyethylene were placed at the entrance and the exit of the sample compartment. The spectral resolution was 8 cm^{-1}, and each spectrum has been obtained by averaging 16 scans at a scanner velocity of 0.633 cm s^{-1}. As a reference spectrum, we used the average of 150 scans collected measuring the substrate before the deposition of the drop.

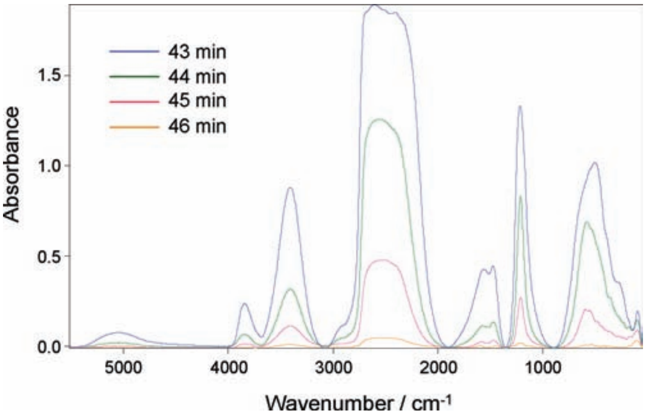

Figure 2. The infrared−terahertz spectrum of deuterated water obtained at different evaporation times.

Mid-infrared and near-infrared acquisitions were performed simultaneously to the far-infrared measures by means of a Bruker IR-cube interferometer installed at the side of the IF-66v/S sample compartment (see Figure 1, left). The IR-cube was equipped with a conventional Globar source and a KBr beam splitter. The IR beam from the interferometer was deflected in the horizontal plane by a plane mirror toward the sample compartment of the Bruker IF-66v/S interferometer. Light entered the sample compartment through a NaCl window and was focused at the sample position by a parabolic mirror before being reflected vertically by a plane mirror placed at 45° just below the substrate (see Figure 1, right). The spectral resolution of the mid-IR spectra was again 8 cm^{-1}, and each spectrum was obtained by averaging 16 scans at the same scanner velocity of 0.633 cm s^{-1}. Also, in this case, the reference spectrum was collected on the window substrate averaging 150 scans before the deposition of the drop.

All measurements started simultaneously, although the acquisition times for the two data sets (e.g., the two interferometers) were slightly different. Indeed, two different computers were used, and it was impossible to have absolutely coincident acquisitions for each couple of spectra. As a matter of fact, the time delay between the beginnings of two consecutive measurements in the mid-IR was 10 s, while in the far-IR was 12 s. Acquisition parameters were chosen to have the best signal-to-noise ratio and to optimize the time coincidence between simultaneous mid- and far-IR acquisitions.

The experiment was realized depositing a droplet of deuterated water of ~50 μL volume on a CVD diamond substrate and studying the evaporation process by infrared spectroscopy in the entire IR domain from the near-IR to the THz. The temperature and the relative humidity were maintained at 25 °C and 7%, respectively, during the experiment.

Results and Discussion

We have followed the evaporation of a droplet of deuterated water by using synchrotron light in the terahertz region and a conventional source in the middle- and near-IR range. The experiment has been simultaneously performed using the instrumental setup that has been described in the Experimental Section. For the first time, this original configuration has allowed us to record simultaneous spectra of different IR regions that

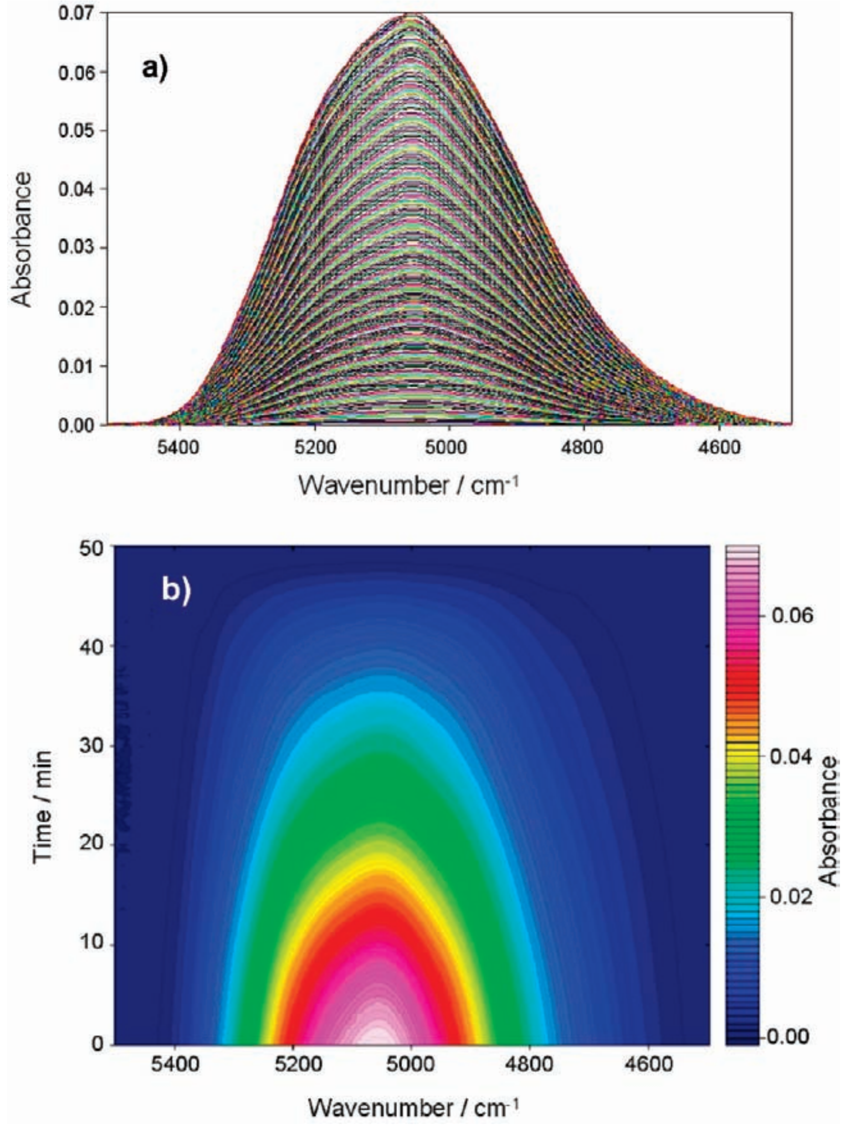

Figure 3. (a) Rapid-scan time-resolved FT-IR spectra in the 5500−4500 cm^{-1} range (near-infrared) of an evaporating deuterated water droplet. (b) 3D FT-IR time-resolved spectra (absorbance−wavenumber−time); the absorbance variation is represented by false color change.

because of the limitations of the available commercial instruments is otherwise impossible to obtain. The use of synchrotron light in the far-infrared/terahertz region has relevant advantages with respect to conventional sources in terms of stability, brilliance, and flux, which is reflected in a much higher signal-to-noise ratio; especially in the case of time-resolved experiments in the second and millisecond range, this represents a significant improvement. The chemical-physical phenomenon that we have chosen as the case study has a time scale of several minutes; the average evaporation time of a 50 μL water droplet at room temperature with a constant relative humidity of 7% is around 50 min, although other solvents or mixtures of solvents are characterized by shorter time scales down to <1 min such as ethanol.[9] This time scale has a good compatibility with the instrumental time-resolved capability; indeed, we could record a single spectrum within a few milliseconds, an interval that is perfectly suitable or well below what is needed for these type of processes (e.g., evaporation of water). Figure 2 shows the whole spectra in the 5500−30 cm^{-1} wavenumber range that is obtained by performing simultaneous acquisitions during the evaporation of a deuterated water droplet. Four spectra recorded at different instants of time (43, 44, 45, and 46 min) of the evaporation process are shown as an example. Three different regions of the wide infrared domain can be studied at the same time: the near-infrared range in the 5500−4000 cm^{-1} interval that shows the overtones and combinations bands; the mid-infrared region, 4000−600 cm^{-1}, that contains vibrational modes; and the terahertz range in the 600−30 cm^{-1} region, where the rotational and translational motion bands appear. The spectra have been obtained by adding the corresponding data

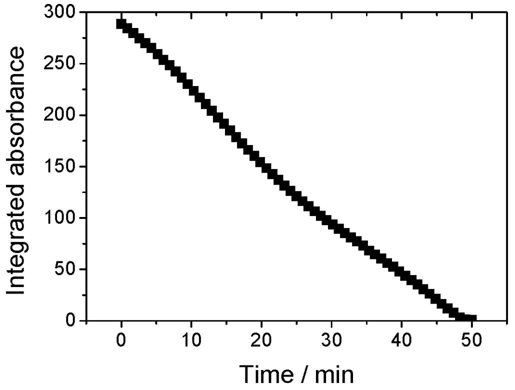

Figure 4. Integrated absorbance of the 5100 cm^{-1} band as a function of the evaporation time.

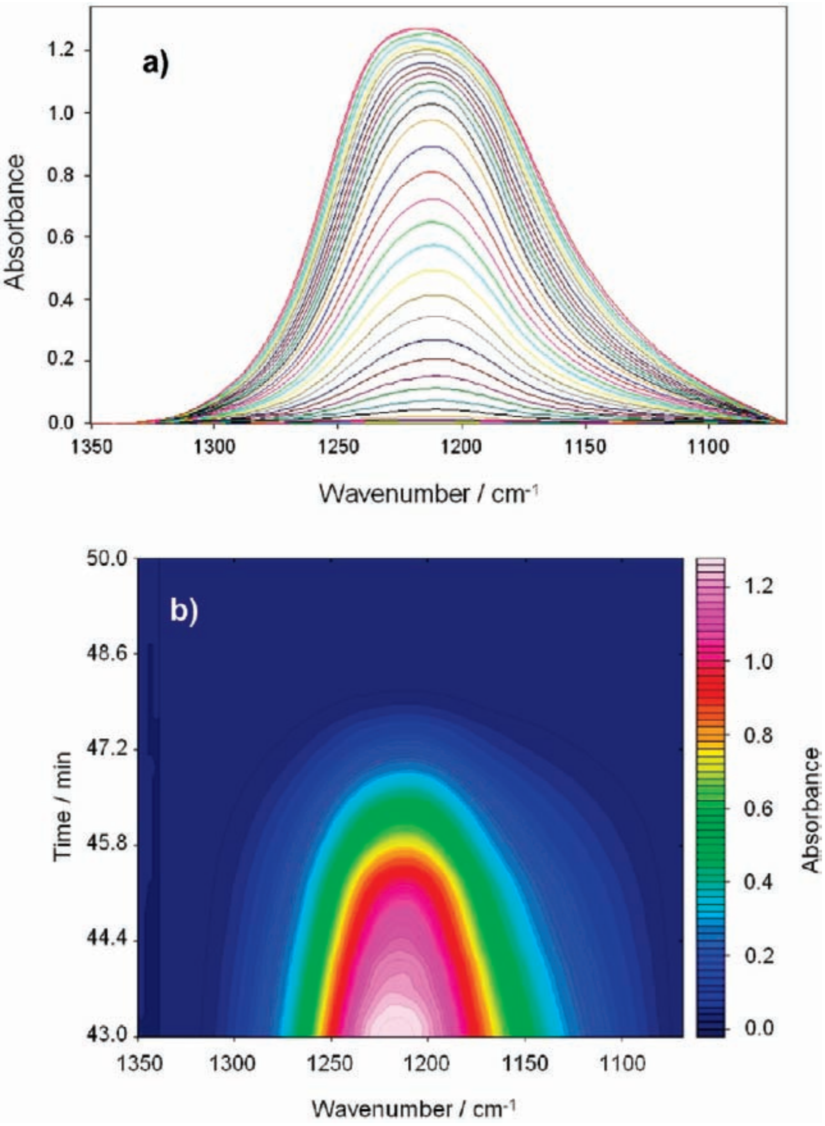

Figure 5. (a) Rapid-scan time-resolved FT-IR spectra in the 1350−1050 cm^{-1} range (mid-infrared) of an evaporating deuterated water droplet. (b) 3D FT-IR time-resolved spectra (absorbance−wavenumber−time); the absorbance variation is represented by false color change.

at the same time of the process in the near-middle infrared and the THz regions in only one data set. For these spectra, the baseline has been calculated by a rubberband algorithm using 64 points. All structures appear well-resolved in the entire IR range and at this stage of the experiment, which is almost at the end of the evaporation process of the deuterated water droplet; the structures in the near- and mid-IR do not exhibit saturation. The latter is however the main problem to be faced during this type of experiments, and in a previous work, we have observed that only the near-IR interval is well suitable to monitor not saturated bands during the entire process.

Figure 3a shows the near-IR spectra recorded during the evaporation of a droplet of deuterated water cast on a CVD diamond substrate at 7% RH. The FT-IR spectra range from 4500 to 5500 cm^{-1} and show an absorption maximum around 5050 cm^{-1}, which is assigned to the first overtone of the stretching mode of D_2O.[10] However, the 2D spectra (wavenumber−absorbance) do not allow identifying of a clear time-dependent trend; then, we have used visualization of the data by 3D spectra (absorbance−wavenumber−time) to obtain a direct indication of the time dependency of the phenomenon (Figure 3b). The absorbance is shown in a false color scale on the right of the figure; the evaporation, in the time interval shown in the figure, appears as a continuous process, which is well-resolved in this time scale. The curve of the integrated absorbance as a function of time gives a clear indication that, in these experimental conditions of low RH, the evaporation is linearly correlated with time (Figure 4).

We have also tried to obtain for comparison the same type of spectra using the data extracted from the mid-infrared region. Figure 5a shows the wavenumber−absorbance FT-IR spectra in the 1350−1050 cm^{-1} interval; the spectra show an absorption band peaking at 1210 cm^{-1} that is assigned to the stretching mode of the deuterated water. 3D FT-IR spectra (Figure 5b) show the same continuous trend that we have observed in the near-IR range (Figure 4) in the same time interval, which is an indication that data have not been affected by the baseline correction. In this figure, we have shown only the last 7 min of evaporation, as the absorption bands due to the deuterated water in the mid-IR range are saturated for the first 43 min. On the other hand, we could follow all of the evaporation process in spectra shown in Figure 6a (29−58 cm^{-1}) in the terahertz domain. An absorption peak at 44 cm^{-1} (1.32 THz), which is assigned to translational OOO bending of the deuterated water, clearly decreases in intensity with time. The detection of this band in water is still controversial, and there is not consensus in the literature,[11−13] likely because the band is weak and

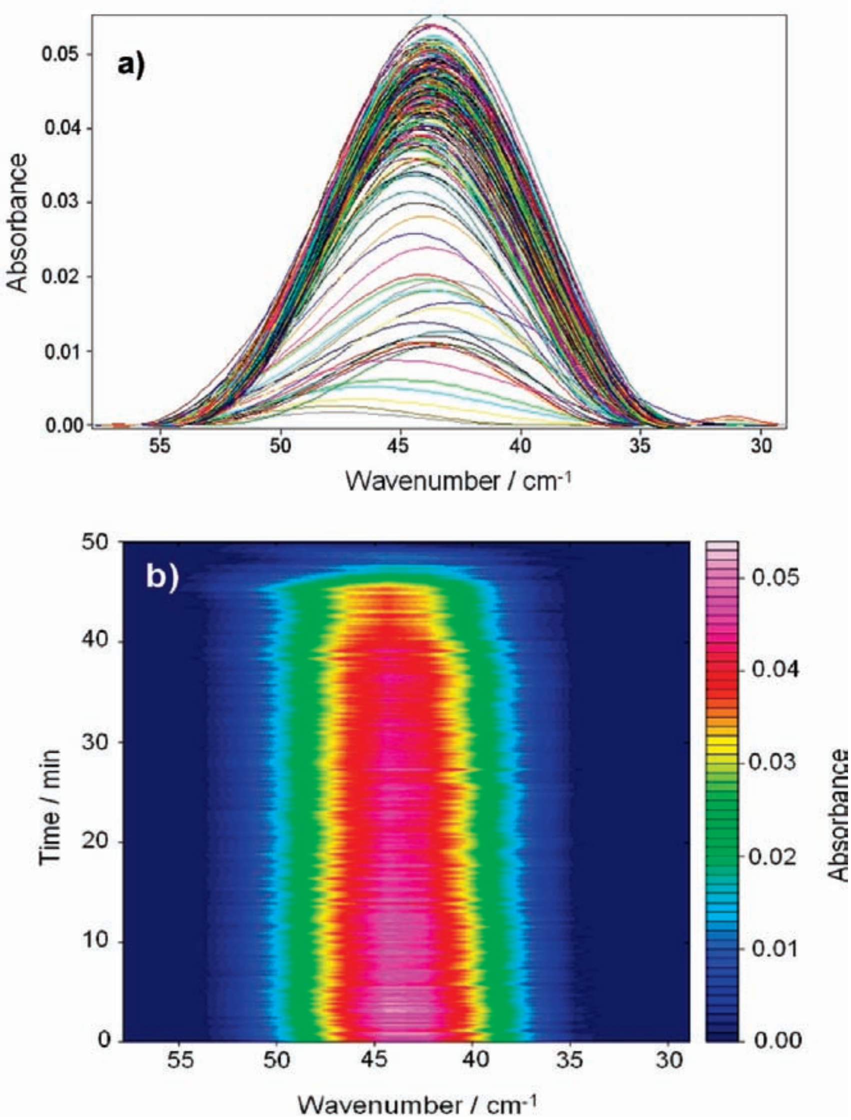

Figure 6. (a) Rapid-scan time-resolved FT-IR spectra in the 58−29 cm^{-1} range (terahertz) of an evaporating deuterated water droplet. (b) 3D FT-IR time-resolved spectra (absorbance−wavenumber−time); the absorbance variation is represented by false color change.

conventional sources do not guarantee the necessary resolution to resolve the signal. We observe however a band peaking around 44 cm^{-1} that even if of weak intensity is sharp and well-resolved that we assign to the OOO bending of deuterated water. On the other hand, the evolution of this band with time, which continuously decreases in intensity following the evaporation, supports the attribution to a deuterated water band; at the end of the process, the intensity of this band goes to zero. In the THz region, we may also recognize a wide and intense band of deuterated water whose intensity changes continuously with time. This band is assigned to another translational motion (OO antisymmetric stretching) of deuterated water. Even if theory suggests a negligible isotopic shift so that no significant differences should be observed, this band is found at lower wavenumbers with respect to water, which is generally detected in the 160−180 cm^{-1} range. A reference spectrum of deuterated water in the 30−160 cm^{-1} range measured with IR synchrotron radiation is shown in Figure 7.

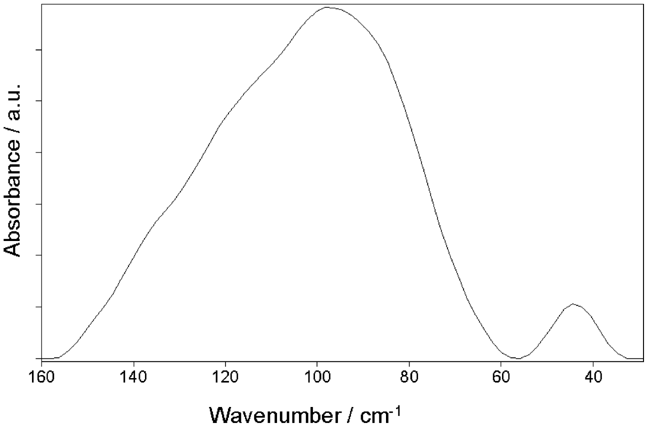

Figure 7. The terahertz spectrum of deuterated water obtained by syncrothron light in the 30−160 cm^{-1}.

Finally, we show 3D FT-IR spectra (Figure 6b) that give a direct visualization of the overall evaporation phenomena. Time-dependent spectra in 3D demonstrate that the evaporation is a continuous process and that, also in the THz region, it is possible to monitor all the process, such as in the near-IR, avoiding signal saturation. However, the THz 3D image appears slightly noisier with respect to the corresponding figures in the near-IR and mid-IR range (Figures 4 and 5) likely because of instabilities of the source that introduce noise in THz spectra. Better data could be certainly obtained using more intense THz sources such as those available by the coherent synchrotron sources now available or proposed.[14]

Our experiments have shown that rapid-scan acquisitions in the second domain can be performed simultaneously in the extended infrared range; we also have shown that the THz region may offer some advantages in the investigation of evaporation processes where the vibrational signal is saturated in the mid-IR domain. Studies in low frequency modes are continuously growing in number with new observations and validation of THz frequency biomolecules vibrational spectra, as well as identification of full compounds.[15] Moreover, the vibrational modes corresponding to protein tertiary structural motion lay in the far-infrared and THz frequency range. It is well-established that these collective large scale motions depend on the global protein structure although they felt perturbations induced by ligand binding phenomena. Our results suggest that, in addition to investigation on biological systems, THz−IR experiments can be performed to study dynamic processes or phase transitions and more in general, when is required monitoring phenomena in which vibrational (molecular) modes are partially or totally masked by the vibrational contribution of the water.

Conclusions

We have realized an experiment of evaporation of a deuterated water droplet using a special analytical setup that has allowed recording time-resolved infrared absorption spectra in a wide interval that ranges from the near-infrared up to the terahertz region. The experiment has been realized combining for the first time two different sources, a conventional thermal source in the near−mid-IR range and synchrotron radiation in the far-IR region performing a simultaneous analysis in the near−mid-IR regions down to the THz region. The experiment shows that rapid-scan acquisition can be performed and that the terahertz region is really suitable to investigate time-resolved processes, such as evaporations or phase transitions that occur in a time scale of several minutes, and could be used to monitor complex experiments that require a good separation of the vibrational modes during the evolution of a process involving water.

The method also addresses the possibility to monitor other physical-chemical processes where the simultaneous acquisition of vibrational spectra in the entire IR domain may return information both at the intramolecular level and at the "lattice level" (i.e., the intermolecular level probed by the terahertz spectroscopy). Actually, by combining the acquisition in many chemicals and organic molecules, we should measure intramolecular modes in the mid-IR region and intermolecular vibrations that probe the dynamics of large biomolecules in solution with THz spectroscopy.

Acknowledgment. This research was supported by the Italian Ministero dell'Università e della Ricerca (MiUR) through FIRB2003 (RBNE033KMA) grant. Cosmolab Consortium is also acknowledged for financial support. We acknowledge the BESSY synchrotron facility for the support during experiments and Dr. A. Simon and F. Koschine of BRUKER Optics Germany who provided us the IR-cube FT-IR interferometer used for the experiments and helped us during the installation. Pierangelo Morini of Bruker Optics Italy and Michele Ortolani of the Institute of Photonics and Nanotechnology (CNR, Rome) are acknowledged for fruitful discussions.

References and Notes

(1) Marcelli, A.; Hampai, D.; Xu, W.; Malfatti, L.; Innocenzi, P. *Acta Phys. Pol.* **2009**, *115*, 489.

(2) Innocenzi, P.; Malfatti, L.; Kidchob, T.; Falcaro, P.; Costacurta, S.; Piccinini, M.; Marcelli, A.; Morini, P.; Sali, D.; Amenitsch, H. *J. Phys. Chem. C* **2007**, *111*, 5345.

(3) Innocenzi, P.; Kidchob, T.; Malfatti, L.; Costacurta, S.; Takahashi, M.; Piccinini, M.; Marcelli, A. *J. Sol-Gel Sci. Technol.* **2008**, *48*, 253.

(4) Innocenzi, P.; Kidchob, T.; Mio Bertolo, J.; Piccinini, M.; Cestelli Guidi, M.; Marcelli, A. *J. Phys. Chem. B* **2006**, *110*, 10837.

(5) Beard, M. C.; Turner, G. M.; Schmuttenmaer, C. A. *J. Phys. Chem. B* **2002**, *106*, 7146.

(6) Innocenzi, P.; Malfatti, L.; Piccinini, M.; Marcelli, A.; Grosso, D. *J. Phys. Chem. A* **2009**, *113*, 2745.

(7) The THz spectroscopy conventionally covers the spectral range from about 3 cm^{-1} to about 600 cm^{-1}; this frequency interval is also indicated as the far-IR domain. (1 THz is 33.33 cm^{-1}, and the THz domain ideally falls within the ~0.1−20 THz interval).

(8) Dore, P.; Nucara, A.; Cannavò, D.; De Marzi, G.; Calvani, P.; Marcelli, A.; Sussmann, R. S.; Whitehead, A. J.; Dodge, C. N.; Krehan, A. J.; Peters, H. J. *Appl. Opt.* **1998**, *37*, 5731.

(9) Innocenzi, P.; Malfatti, L.; Costacurta, S.; Kidchob, T.; Piccinini, M.; Marcelli, A. *J. Phys. Chem. A* **2008**, *112*, 6512.

(10) Khoshtariya, D. E.; Dolidze, T. D.; Lindqvist-reis, P.; Neubrand, A.; Van Eldik, R. *J. Mol. Liq.* **2002**, *96−97*, 45.

(11) Balbuena, P. B.; Blocker, W.; Dudek, R. M.; Cabrales-Navarro, F. A.; Hirunsit, P. *J. Phys. Chem. A* **2008**, *112*, 10210.

(12) Gaiduk, V. I.; Crothers, D. S. F. *J. Mol. Liq.* **2006**, *128*, 145.

(13) Hasted, J. B.; Husain, S. K.; Frescura, F. A. M.; Birch, J. R. *Chem. Phys. Lett.* **1985**, *118*, 622.

(14) (a) Abo-Bakr, M.; Feikes, J.; Holldack, K.; Wüstefeld, G.; Hübers, H.-W. *Phys. Rev. Lett.* **2002**, *88*, 254801. (b) Abo-Bakr, M.; Feikes, J.; Holldack, K.; Kuske, K.; Peatman, P.; Schade, W. B.; Wüstefeld, G.; Hübers, H.-W. *Phys. Rev. Lett.* **2003**, *90*, 094801. (c) De Santis, S.; Byrd, J. M.; Li, D.; Sannibale, F. *CIRCE Note LSCN-IF- 1*; Lawrence Berkeley National Laboratory: Berkeley, CA, 2003. (d) Sannibale, F.; Marcelli, A.; Innocenzi, P. *J. Synch. Radiat.* **2008**, *15*, 655.

(15) Choi, M. K.; Taylor, K.; Bettermann, A.; Van derWeide, D. W. *Phys. Med. Biol.* **2002**, *47*, 3777.

JP902502Z