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Water Evaporation Studied by In Situ Time-Resolved Infrared Spectroscopy

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Evaporation of water is a fundamental and ubiquitous process that is on the ground of different types of nanoscience phenomena such as evaporation induced self-assembly. Even if water evaporation is a very basic phenomenon, there is still a lack of experiments that give a direct insight of the process. In situ application of rapid scan time-resolved infrared spectroscopy to an evaporating droplet has allowed monitoring the process at different relative humidity conditions. The experiments have been performed in the near-infrared range using water and deuterated water. The water evaporation appears as a continuous process that is not affected by changes of relative humidity in the external environment. This result, however, is affected by the impossibility to discriminate the contribution of the adsorbed water. The same experiment repeated with a deuterated water droplet has allowed, instead, a direct observation of the contribution during the evaporation process from water in the external environment. The time-resolved analysis has shown that at higher relative humidity the water adsorption is enhanced and that this process is time delayed with respect to the beginning of the evaporation process.

Introduction

Fabrication of films from liquid phase and self-organization processes of nanomaterials, such as evaporation induced self-assembly (EISA), are strongly dependent on evaporation phenomena.[1] Sol−gel processing of thin films is a typical example; solvent evaporation drives the hydrolysis and polycondensation reactions during the deposition process, typically by dip-coating or spin-coating. The precursor sol contains an alcohol as solvent and water for the hydrolysis, which evaporate at different rates during film deposition. Controlling the external conditions in the deposition environment is very important because the relative humidity strongly affects the overall process. Evaporation of solvents plays an even more crucial role in the so-called evaporation induced self-assembly, which is a technique employed to push and drive self-organization of nanostructures. Several examples are reported in the case of mesoporous materials and different types of colloidal structures.[2] In particular, EISA has been used to organize colloids that are drawn to the meniscus by convective transport; the capillary forces push organization into close-packed structures.[3] An aligned film of carbon nanotubes can be formed simply by evaporation on a hydrophilic substrate[4] of a water drop containing dispersed carbon nanotubes. Another very important example is represented by mesostructured materials that are obtained through self-assembly of supramolecular templates.[5] The fast evaporation of the solvent drives the formation and organization of micelles, whereas the polycondensation reaction of building blocks (inorganic or hybrid oligomeric species) at the micelle surface forms the mesostructure backbone.

Our attention has been driven by the importance of water and solvent evaporation during deposition of films from liquid phase; understanding these phenomena is a mandatory step to increase the reproducibility and to develop applications. Evaporation of water is very important for nanochemistry but is a fundamental general process that is ubiquitous in ordinary life. Several aspects of this very basic process have still to be understood; the main limitation is represented by the lack of time-resolved techniques that can be applied to monitor in situ the evaporation processes. Most of the studies have used contact angle changes as a function of time to follow the water evaporation process. This method, however, gives only a limited set of information and does not allow to investigate the details of the chemical−physical features associated to the process.[6−8] An alternative technique to study evaporation−adsorption phenomena is rapid scan time-resolved (RSTR) infrared spectroscopy.[9] Recent developments in the technique have allowed reaching by ultra rapid scan a time resolution of few milliseconds, which is a good time scale to study in situ evaporation processes of liquids. The evaporation of a water droplet is a time-dependent phenomenon whose length is a function of the droplet dimension; bigger droplet volumes need more time for a complete evaporation. Even with a small droplet of few microliters, several minutes are necessary for evaporation to go to completion. Time-dependent studies by FTIR are limited by mechanical movement of the mirror to a millisecond scale for rapid scan but this time scale is well suitable to study chemical−physical phenomena with subsecond time resolution, such as evaporation of small droplets. In previous works, we have used rapid scan time-resolved FTIR spectroscopy to study the chemical−physical processes during EISA of silica and hybrid thin films,[10,11] formation of wrinkled structures,[12] and ethanol evaporation.[13] The technique has shown to be a very powerful tool to follow reversible and irreversible time-dependent phenomena that can be observed using interferometric methods in a millisecond time scale. We have also demonstrated that if the time scale of the evaporation process is on the order

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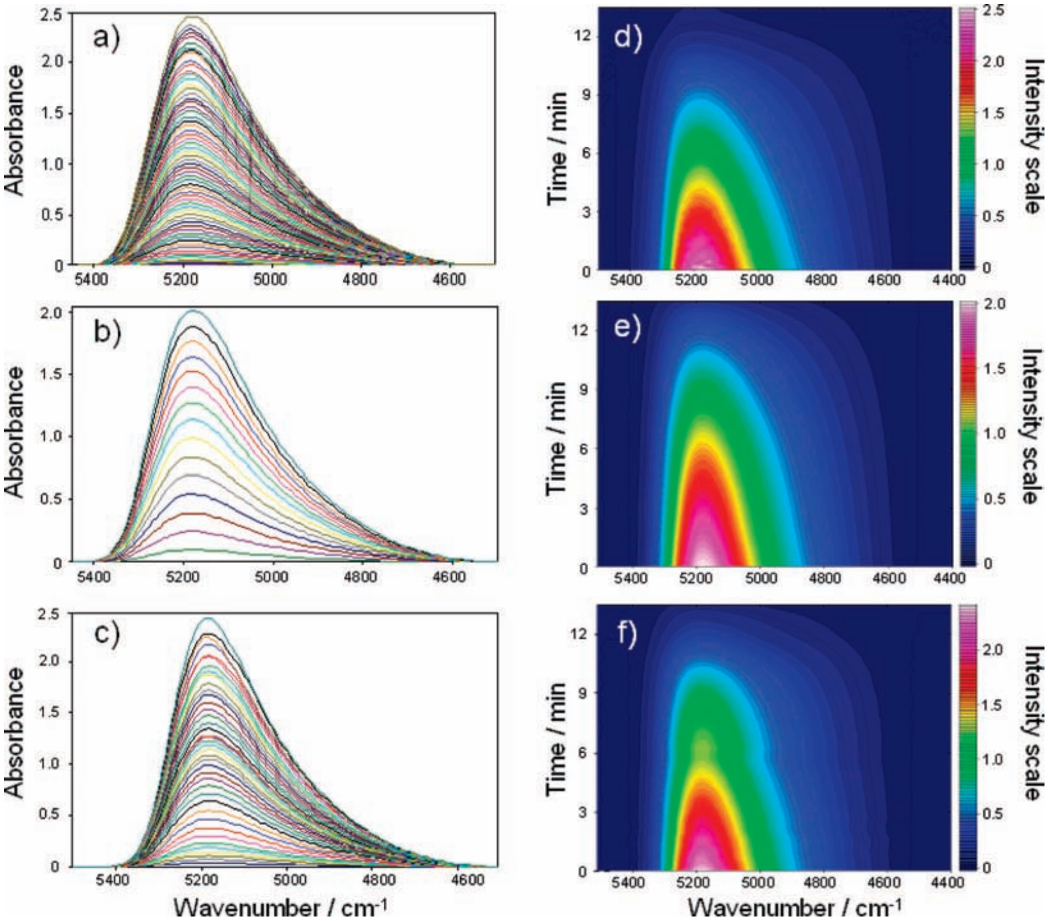

Figure 1. Rapid-scan time-resolved FTIR spectra in the 5500−4500 cm^{-1} range of an evaporating water droplet, a) 45% RH, b) 30% RH, and c) 15% RH. 3D FTIR time-resolved spectra (absorbance−wavenumber−time), d) 45% RH, e) 30% RH, and f) 15% RH; the absorbance variation is represented by false color change.

of several minutes even time-resolved infrared imaging can be applied such as in the case of stain effects.[14] We have applied in the present work RSTR infrared spectroscopy to observe the evaporation of a water droplet cast on a solid substrate as a function of the relative humidity in the external environment. The technique has allowed getting a direct time-resolved observation into the evaporation of water.

Experimental

Deuterated water (D_2O) and double-distilled water were used for the evaporation experiments. Time-resolved in situ infrared (IR) analysis was performed at the synchrotron infrared beamline (SINBAD) at the Laboratori Nazionali di Frascati (Frascati, Italy) of the Istituto Nazionale di Fisica Nucleare (INFN) using a Bruker Hyperion 3000 microscope coupled to a Bruker Equinox 55 interferometer modified to work in high vacuum; a conventional Globar source was used. The IR measurements were performed in the 1000−12 000 cm^{-1} wavenumber range with a resolution of 16 cm^{-1}. An MCT detector (250 × 250 μm^2 size) cooled to the nitrogen temperature and a KBr beam splitter were used. Rapid-scan time-resolved (RSTR) measurements were performed by averaging 8 interferograms per spectrum for a total acquisition time of 1.23 s, the time delay between the beginning of each acquisition was 10 s. These parameters are the best compromise in terms of signal-to-noise ratio and resolution compared to the typical evaporation time of the investigated samples. Another experimental parameter that we have optimized is the water droplet size; if the water droplet is too large the infrared signal will be saturated for most of the measurement time; however, smaller droplets show a very fast evaporation and are not suitable for time-resolved studies. The experimental conditions that we have selected are optimized for an evaluation of the physical changes of the system but do not allow us to extract quantitative data, for example about the evaporation rate. We have repeated the experiment for several runs (up to 10 for each experimental condition) to ensure reproducibility, and the experimental trend has been always the same; on the contrary, the time scale has been more difficult to reproduce because of the limited control of drop dimensions.

The relative humidity (RH%) and temperature during the experiment were carefully monitored and a cabinet was built around the microscope to control the experimental conditions. Evaporation experiments were run at three different RH: 15, 30 and 45%, at 25 °C and at room pressure.

In a typical experiment, a small droplet of H_2O or D_2O (50 μL) was cast on a ZnSe substrate and the measurement started at the same time. The substrate is not thermally controlled and the experiment was run at the conditions of the experimental room. The experiments were performed in transmission configuration, using a double-sided, forward−backward acquisition mode of the interferometer. The background spectrum of the ZnSe substrate was recorded as the average of 40 interferograms in the air.

The results were analyzed by *Bruker Opus 6.5* software. The baseline was calculated by rubberband correction[15] using 64 points.

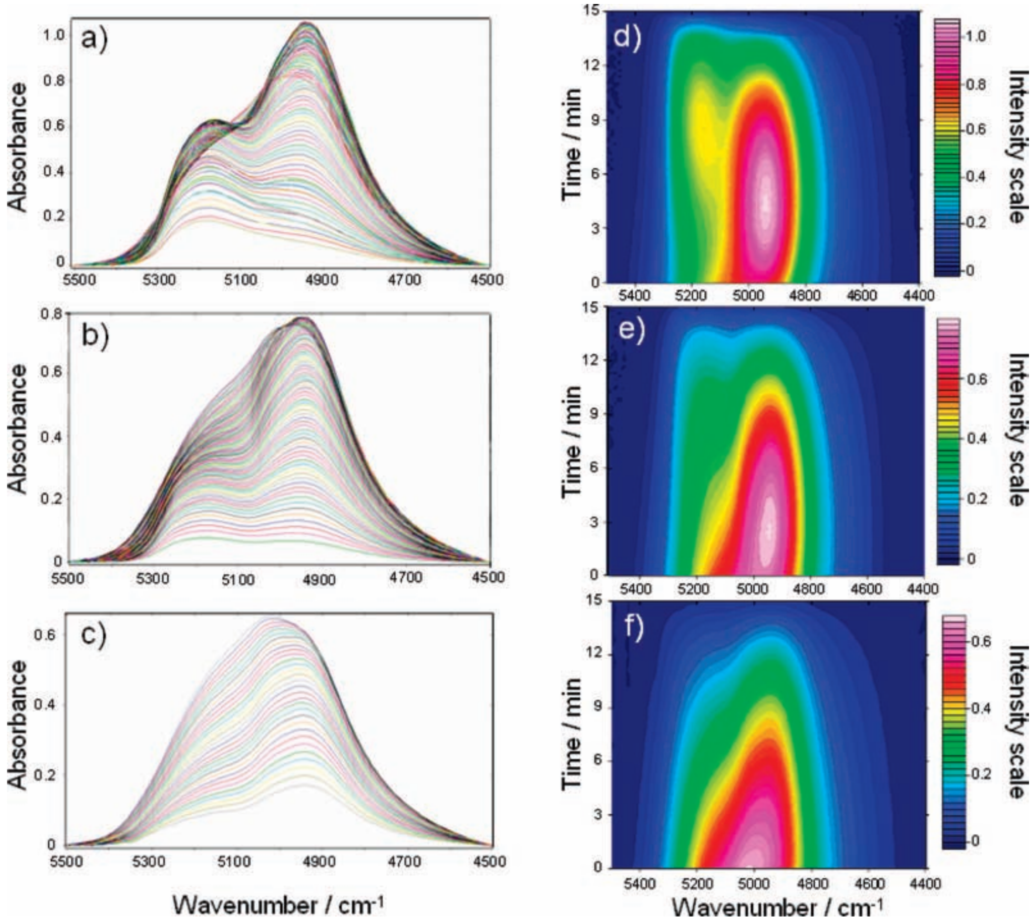

Figure 2. Rapid-scan time-resolved FTIR spectra in the 5600−4400 cm^{-1} range of an evaporating droplet of deuterated water, a) 45% RH, b) 30% RH, and c) 15% RH. 3D FTIR time-resolved spectra (absorbance−wavenumber−time), d) 45% RH, e) 30% RH, and f) 15% RH; the absorbance variation is represented by false color change.

Discussion and Results

Obtaining direct chemical−physical information on the water evaporation process is in general a difficult task because several experimental problems have to be solved. In situ time-resolved experiments by infrared spectroscopy can offer a good solution but a strong drawback is represented by the signal saturation of water bands in the mid-IR region. Even a few microns 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 faced this problem optimizing the experiment in the near-IR region, the water overtone, and combination bands have been well resolved and not saturated signals from the beginning of the process are obtained.

1. Evaporation of Water at Different Relative Humidities. The evaporation of a water droplet cast on a ZnSe substrate has been followed using the ~5200 cm^{-1} band in the near-IR region, which is assigned to the second order combination of OH stretching (~3350 cm^{-1}) and OH bending vibrational modes (~1650 cm^{-1}), $\nu_s^{01}(\mathrm{OH}) + \delta^{01}(\mathrm{OH})$.[16] The 5200 cm^{-1} band ranges from 4600 to 5400 cm^{-1} and has a maximum at 5190 cm^{-1}; the band is strongly asymmetric with a long tail at low wavenumbers and appears formed by different components (Figure 1, left column).[17] There is a general consensus in literature to assign this overtone band of water to several overlapped species; however, a detailed analysis of this combination band has failed to distinguish the substructures that are correlated to the vibrational sub-bands.[14] Our experiments of evaporation performed at different RH have given the FTIR spectra in Figure 1 (left column: 1a, 45% RH; 1b, 30% RH; 1c 15% RH). The different spectra exhibit a similar trend, even if the evaporation experiment is performed at different relative humidity values: a decrease in absorbance with no shift in the absorption maxima. A better representation of the time dependence of the phenomenon is given by 3D FTIR time-resolved spectra (absorbance−wavenumber−time) shown in Figure 1 (right column: 1d, 45% RH; 1e, 30% RH; 1f, 15% RH); the absorbance intensity is represented by false color change. The evaporation of the water droplet appears as a continuous process and no significant differences emerge if the experiment is performed at different RH conditions. These experimental conditions have not allowed discriminating any contribution of water from the external environment, and there is not direct evidence of the effect of relative humidity on the droplet evaporation process.

2. Evaporation of Deuterated Water at Different Relative Humidities. The water evaporation experiments performed by time-resolved FTIR spectroscopy have not shown any discontinuity in the process, even if exchange of water from external environment should have been expected, at least at the higher RH conditions. The water adsorption is likely balanced by the evaporation of water at the first stages, this means that the process is slower at higher RH, but this effect is hard to detect, at least in the present experimental conditions because it is impossible to discriminate between evaporating and adsorbed water molecules. We have, therefore, performed evaporation experiments with deuterated water; because of the good separation between the vibrational modes of water and D_2O, this

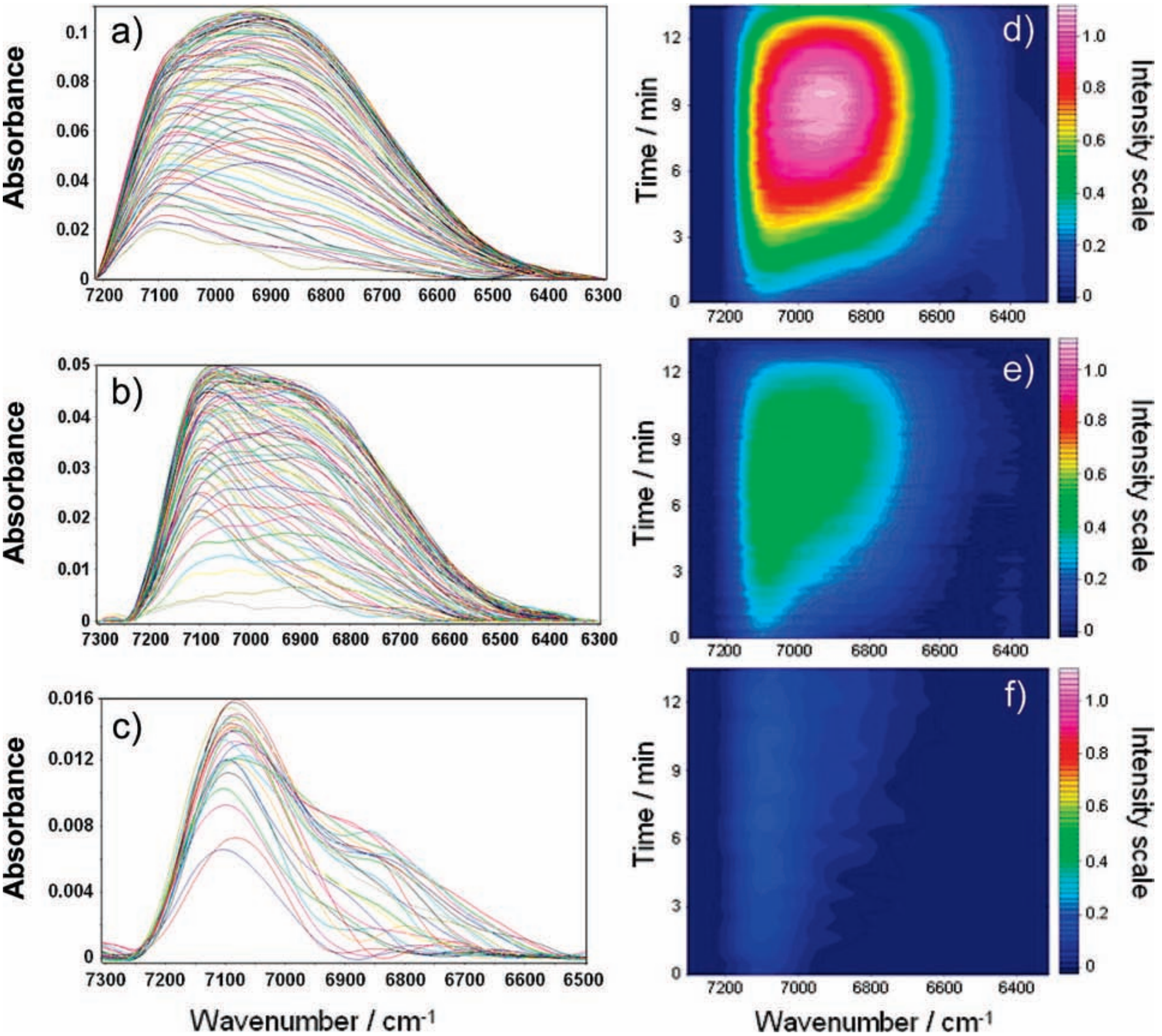

Figure 3. Rapid-scan time-resolved FTIR spectra of an evaporating droplet of deuterated water a) 45% RH, b) 30% RH, and c) 15% RH. 3D FTIR time-resolved spectra (absorbance−wavenumber−time) in the 7300−6300 cm^{-1}, a) 45% RH, b) 30% RH, and c) 15% RH; the absorbance variation is represented by false color change.

should allow, in principle, distinguishing contributions from the water molecules from the external environment during the evaporation process.

Figure 2 (left column: 2a, 45% RH; 2b, 30% RH; 2c, 15% RH) shows the FTIR spectra recorded during the evaporation of a droplet of deuterated water cast on a ZnSe substrate at different RH conditions. The FTIR spectra range from 4500 to 5500 cm^{-1}, and are strongly asymmetric; a strong difference is observed in the spectra recorded at different RH, which appear formed of different overlapped vibrational modes. The main band shows an absorption maximum around 5000 cm^{-1}, which is attributed to the first overtone of the stretching mode of D_2O.[18] This band has shown to be sensitive to temperature variations and up to five components have been separated by Gaussian fitting.[16] An overlapped band of medium-strong absorbance is detected around 5200 cm^{-1}, which is attributed to the combination band of water (vide supra); this band has a different absorbance as a function of evaporation time and relative humidity conditions. The 2D spectra (wavenumber−absorbance) do not allow, however, identifying a clear time dependent trend; visualization of the data by 3D spectra (absorbance−wavenumber−time) gives, instead, a direct indication of the time dependency of the phenomenon. We attribute the 5200 cm^{-1} water component to water adsorbed from the external environment, which is supported by the trend shown in Figure 2 (right column: 2d, 45% RH; 2e, 30% RH; 2f, 15% RH): the absorbance of the water combination band is getting stronger with the increase of the RH in the experimental room, only a small perturbation of the signal is observed at 15% RH, whereas at 45% RH another peak appears in the middle of the evaporation process. The H_2O combination band (5200 cm^{-1}) and D_2O stretching first overtone band (5000 cm^{-1}) appear enough separated in the 3D spectra to give a direct visualization of the different trends during the evaporation process. We have not tried any deconvolution analysis because both of the bands are formed by several water and deuterated water components that are difficult to resolve. If we use a simple water model (three main water species), we should assume at least six components, three of each one for water and D_2O, and with a high uncertainty due to the high overlapping of the bands. If we look to the maximum of absorbance of deuterated water (5000 cm^{-1}), we observe that is shifted to longer times when the evaporation process occurs at higher RH values. It is difficult to state if this is a true phenomenon or if it is generated by the overlapping of the adsorbed water, which causes a translation of the peak to longer times; on the other hand the 3D spectra clearly show that a higher RH induces a stronger water exchange. Some interesting observations about the time scale of the water adsorption can be also drawn on the basis of the present results: the more the evaporation of deuterated water proceeds, which means also spreading of the drop and increasing of the evaporation rate, the more water is adsorbed on the drop surface. The maximum of water adsorption is, in fact, observed after that more than half of the evaporation process has been completed (part d of Figure 2, 45% RH).

3. Water Adsorption During Evaporation of Deuterated Water. As we have previously pointed out, the partial overlapping of water combination band and deuterated water first overtone stretching mode does not allow a clear separation between the water adsorption and deuterated water evaporation phenomena. We have, therefore, used the band around 7000 cm^{-1} to follow directly the water adsorption process. Figure 3 (left column: 2a, 45% RH; 2b, 30% RH; 2c, 15% RH) shows the evolution of this band during the evaporation of a droplet of deuterated water at different RH conditions. The band ranges between 7200 and 6500 cm^{-1} and is assigned to the second overtone of the water stretching mode; it has a lower intensity in comparison with the 5000 cm^{-1} band and appears also strongly asymmetric with a tail at the lower wavenumbers but is well separated from other overtones and combination bands of deuterated water and can be used to follow the kinetics of the water adsorption process. The 3D FTIR spectra in the 6400−7300 cm^{-1} range are reported in Figure 3 (right column: 3d, 45% RH; 3e, 30% RH; 3f, 15% RH); they show the absorbance changes as a function of time of the second overtone stretching band of water. The spectra show that the water adsorption from the external environment does not follow a sudden mechanism but it increases with the time to reach a maximum after two-thirds of the process; after that, the evaporation of the adsorbed water starts, as addressed by the decrease in the absorbance of the associated band.

The adsorption−evaporation process of water, as shown by the experiments with deuterated water, is a complex phenomenon whose kinetics is environment dependent in terms of temperature, pressure, and RH. In the present experiment, we have only changed one parameter, the RH, and water exchange on evaporating droplets appears to play an important role. A simple modeling of the process through a classical physical-chemical theory[19] is added in the Supporting Information.

Conclusions

Rapid-scan time-resolved infrared spectroscopy has been used to study the evaporation process of water and deuterated water droplets in the near-infrared region. The method, which allows monitoring time-resolved processes on the millisecond scale, has shown to be a very effective tool to get a better insight into the water evaporation−adsorption processes, which occurs at different RH conditions. This method can be extended to study a wide range of time-dependent chemical phenomena on the millisecond scale time resolution, such as different types of evaporation process.

The water evaporation appears as a continuous process and no significant changes are observed as a function of the RH in the external environment. Monitoring the evaporation of a deuterated droplet cast on a ZnSe surface allows, however, a direct observation of the contribution from external water. The separation in the near-infrared range of the water and deuterated water bands gives, in fact, a clear indication of the different processes behind the evaporation phenomenon of water and how this is affected by external conditions of relative humidity. The time-resolved 3D images show that at higher RH the adsorption of water is significantly enhanced and the process is time delayed with respect to the beginning of the evaporation process.

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Supporting Information Available: Equations, figure, and table regarding theoretical prediction of H_2O adsorption in a D_2O drop during evaporation. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Rapid scan and step scans are two different techniques that can be used to record real time-resolved infrared spectra. In the rapid scan technique, the time-dependent evolution of the infrared active species is observed by recording the spectra in sequence. In this acquisition mode, the time resolution is limited to about 20 ms because of the scanning speed of the moving mirror. In the step-scan mode, instead, the position of the moving mirror is fixed at a particular position, and a complete time run is recorded at this particular mirror position. This procedure is repeated at all other mirror positions, and a 3D representation of the temporal evolution of the entire interferogram is obtained by combining the respective time traces. Fourier transformation yields the corresponding 3D representation of the time evolution of the IR difference spectra.

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