Terahertz absorption spectrum of *para* and *ortho* water vapors at different humidities at room temperature

X. Xin, H. Altan, A. Saint,[a)] D. Matten, and R. R. Alfano[b)]
Institute for Ultrafast Spectroscopy and Lasers, Physics Department, The City College of the City University of New York, New York, New York 10031

Terahertz time-domain spectroscopy has been used to measure the absorption of water vapor in 0.2–2.4 THz range from low to high humidity at room temperature. The observed absorption lines are due to the water molecular rotations in the ground vibrational state. We find that the absorption strength of *para* transitions increases as humidity increases, while the absorption strength of *ortho* transitions increases and then decreases in intensity with increasing humidity. We explain this difference based on the nuclear spin statistics based ratio of *ortho* to *para* water monomer populations at room temperature. The preferential adsorption on the solid surfaces of *para* water leads to an *ortho* dominated vapor cloud whose monomer rotational absorption intensity decreases due to the effects of dimerization, molecular collisions, clustering, and interactions with liquid droplets at high concentrations. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2357412]

INTRODUCTION

Over the past two decades, the water vapor absorption spectrum in the low terahertz frequency range has been investigated at fixed relative humidity by using time-resolved terahertz spectroscopy.[1,2] The observed absorption profile is primarily due to the molecular rotational transitions in the vibrational ground or excited state. From the detailed study of individual rotational transitions, it is possible to extract various properties including parameters such as molecular structure and rotational constants. These time-resolved terahertz studies often use sophisticated techniques to accurately measure each individual transition, which can be better observed using narrow band terahertz methods that have higher frequency resolution. The advantage of a broad band technique such as time-resolved terahertz spectroscopy is that the entire spectrum of the absorbing species can be analyzed at once.

Traditionally, the absorption profile for water vapor is derived from the Beer-Lambert-Bouguer law, which states that the absorption cross section per molecule is independent of intensity of the incident radiation or the concentration of the absorbing species. However, at very high concentrations the absorption by a molecule is no longer independent of the surrounding molecules. For powerful sources, the absorption cross section per molecule is not independent of the intensity due to the nonlinear effects. In contrast, the absorbance is linearly dependent on the concentration of the absorbing species. Thus, for increasing concentrations the absorption cross section per molecule should remain constant while the absorbance should increase. Furthermore, the absorption cross section for H_2O vapor depends nonlinearly on pressure and temperature leading to an absorption profile that can skew from a Beer-Lambert-Bouguer model with respect to environmental conditions.

The absorption for water vapor is further complicated since it is a mixture of two components, *para*-H_2O and *ortho*-H_2O when considering the nuclear spin effect of hydrogen atoms in water molecule, which results in an *ortho* to *para* ratio (OPR) of 3:1.[3] Previous studies on water vapor have shown that due to the nonrotational ground state of *para* water, solid surfaces will have preferential adsorption of *para* water.[4] Consequently, the *ortho* to *para* monomer population ratio will not remain 3:1. Adsorptions of *para* water onto solid surfaces, as well as interactions amongst water monomers themselves (dimer formation and clustering) and with liquid water droplets for highly saturated environments, have all been shown to decrease the absorption intensity.[5]

In this paper, the absorption profile of water vapor was measured using terahertz time-domain spectroscopy in the frequency range from 0.4 to 2.4 THz with increasing relative humidity. The unexpected decrease in absorption intensity for *ortho* rotational transitions with increasing concentration is attributed to the interactions between monomers, dimers, and clusters in the terahertz beam path.

METHODOLOGY

The design of the terahertz spectroscopy system used in our measurements has been discussed previously[6] and is shown in Fig. 1. An Er-doped mode-lock fiber laser (IMRA Inc., F-100) is used as the source of the terahertz generation. The laser pulse has center wavelength of 810 nm, pulse width of 120 fs, and average power of 100 mW at a repetition rate of 75 MHz. A 1.5 mm thick (110) ZnTe crystal is used for generating terahertz through optical rectification.[7–10] The terahertz beam is collected by two parabolic reflectors and focused collinearly with the probing beam on a second (110) 2 mm thick ZnTe crystal. The terahertz electrical field

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a)Also at Benjamin N. Cardodo High School, Bayside, NY 11364, NASA COSI high school program.
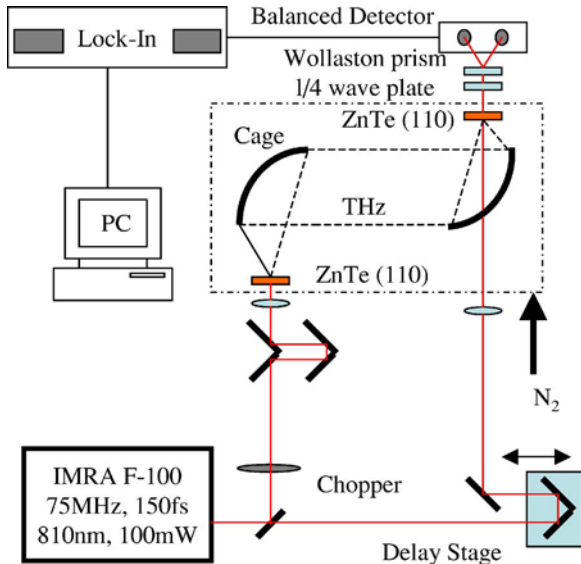b)Electronic mail: ralfano@ccny.cuny.edu

FIG. 1. (Color online) Time-resolved terahertz spectrometer driven by IMRA Inc. model F-100, mode-locked Er-doped fiber laser.
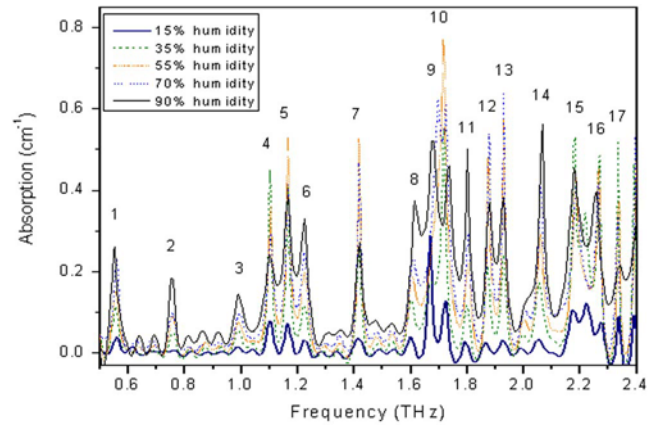

FIG. 2. (Color online) Water vapor absorption profiles at different humidities at room temperature. The details for each numbered transition are given in Table I.

is detected using electro-optic detection technique, where differential changes in the intensity between the orthogonal polarizations of the gating beam are detected with a balanced photodetector. The signal is measured with a lock-in amplifier referenced to a mechanical chopping frequency of 3.5 kHz. The terahertz beam path is enclosed in a cage to be purged with nitrogen to drive away water vapor for a reference signal. The thickness of the ZnTe crystal limited the scans to about 20 ps after the main pulse in the time domain due to the back reflection, resulting in a resolution in the frequency domain of 0.05 THz. The overall usable bandwidth limited the measurements to frequencies from 0.4 to 2.4 THz.

Various quantities of 99.5% pure, drinking water were evaporated inside the cage to reach desired humidity levels of 15%, 30%, 50%, 70%, and 90% with an accuracy of ±5%. All measurements were performed at an ambient temperature of 296±2 K. The humidity was measured by using a hygrometer with an accuracy of 0.1% in 0%–100% range.

RESULTS

All measurements were referenced to the dry nitrogen purged cage. We plot the water vapor absorption profile versus frequency for different levels of humidity in Fig. 2. The concentration independent absorption profile was calculated using the formula $\alpha(\nu) = (-1/d)\log(I_t/I_0)$, where α is the power absorption, d is the terahertz path length in the sample, I_t is the transmitted terahertz power, and I_0 is the reference power. In Fig. 2, as humidity increases from 15% to 90%, the absorption intensity of most *para* transitions increases, while most *ortho* transitions increase and then decrease. Figure 3 shows how the absorption of *para* transitions and *ortho* transitions change with increasing humidity from the measured absorption profiles. The description for each rotational transition observed is given in Table I.

DISCUSSION

Water molecule, such as H_2, has two orientations for the hydrogen atom nuclear spins parallel (total spin $I=1$, an *ortho* molecule) or antiparallel ($I=0$, a *para* molecule). Correspondingly, it has two different types of rotational energy levels in Fig. 3. The difference in I brings in a nuclear spin statistical weight $2I+1$ of the *ortho* levels that is three times larger than that of the *para* levels. As a result, at high temperature (>50 K), the equilibrium OPR is 3:1. The two types of water molecules are readily separable due to the fact that the mutual conversion upon collision of molecules and radiative transitions between them is forbidden by quantum mechanics.[11] Only *para* water molecules can reach the ground rotational level with a zero-point rotational energy, which means that the molecule is not rotating. This makes the energy of interaction with solid surface maximal so that the molecule will be most likely adsorbed by the solid surfaces. While all *ortho* molecules have nonzero rotational energies, for them the energy of interaction with the surface is
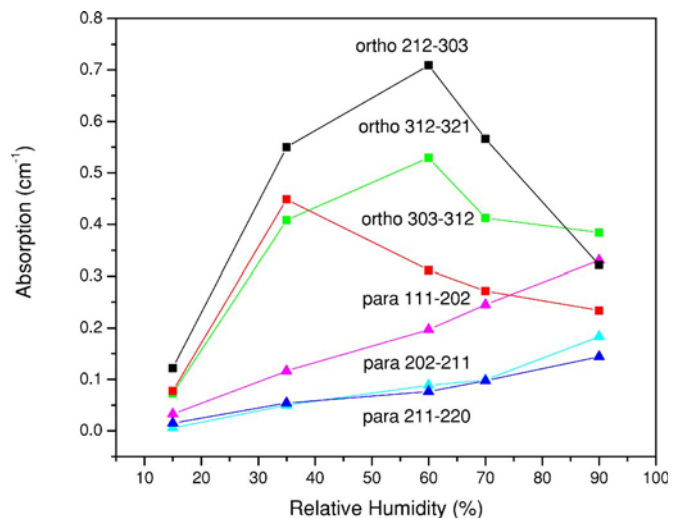

FIG. 3. (Color online) The peak intensity of three *para* (triangles) and three *ortho* (squares) rotational transitions for different humidities. While *para* transitions increase, *ortho* transitions increase and then decrease with increasing humidity.

TABLE I. Rotational transitions in H$_2$O vapor (Ref. [21]) from 0.2 to 2.4 THz (refer to Fig. [2]).

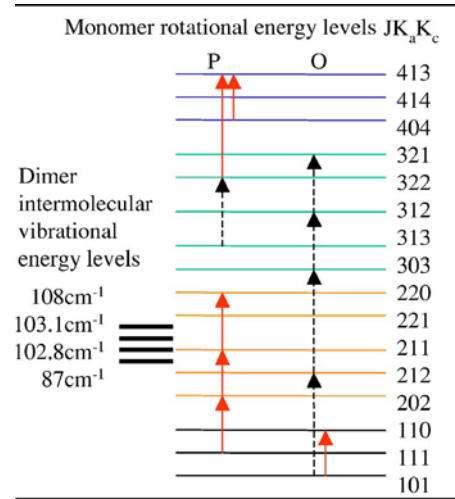| Number	Frequency (THz)	Low state	High state	E_L (cm^{-1})	Type of transition
1	0.557	101	110	23.794	*Ortho*
2	0.753	202	211	70.091	*Para*
3	0.989	111	202	37.137	*Para*
4	1.098	303	312	136.76	*Ortho*
5	1.164	312	321	173.365	*Ortho*
6	1.2264	211	220	95.176	*Para*
7	1.4116	514	523	399.457	*Ortho*
8	1.603	404	413	222.052	*Para*
9	1.67107	101	212	23.794	*Ortho*
10	1.718	212	303	79.496	*Ortho*
11	1.7984	725	734	782.410	*Ortho*
12	1.869	523	532	446.511	*Ortho*
13	1.9207	313	322	142.278	*Para*
14	2.0759	322	413	206.301	*Para*
15	2.2644	414	423	224.838	*Ortho*
16	2.3459	716	725	704.214	*Ortho*
17	2.3932	313	404	142.278	*Para*

FIG. 4. (Color online) Water monomer energy level diagram depicting both *ortho* and *para* transitions. Also shown are the water dimer intermolecular vibrational energy levels. Interactions between dimers and monomers as well as monomers themselves can change their populations among the energy levels. The solid lines represent that the absorption increases as humidity increases. The dashed lines represent that the absorption increases and then decreases as humidity increases.

averaged due to the fact that rotation and attraction may be much lower.[4,12] Because the ground state is nonrotational, the *para* molecules have the most chance to be trapped by the solid surfaces, e.g., aluminum surfaces of the mirrors we used in the setup. The result is that most of the molecules left in the pathway of the terahertz beam are *ortho* water molecules.

The monomers in the predominantly *ortho* vapor undergo interactions with themselves either as in collisions or formations of hydrogen bonds with neighboring molecules. Two water monomers can interact to form one dimer molecule by hydrogen bonding as a result of the polarity of each molecule; the positive regions in one water molecule will attract the negatively charged regions of the neighboring molecules. Dimer formation is generally governed by the following rate equation:[13]

$$M + M + M \underset{k_R}{\overset{k_F}{\rightleftarrows}} D + M, \qquad (1)$$

where M stands for monomers and D for dimers formed. The rate of reaction is given by the forward rate constant (k_F). As humidity increases at room temperature, we expect more dimers to form due to the close proximity among molecules.[14–16] The study of the thermal conductivity of water dimerization in water vapor shows that water dimer has binding energy of −5.2 kcal/mol.[17] The strength of this hydrogen bond is strong enough to withstand room temperature, allowing for significant concentration of water dimers to exist (e.g., 10^{16} dimers/cm^3 at 40 °C and 100% humidity) (Ref. [18]) and can contribute significantly to the absorption of sunlight and atmospheric reaction kinetics.[19] From these investigations we predict that the maximum concentration of water dimer in our measurements is around 2.5% of the total monomer concentration at 90% relative humidity. At room temperature we expect a majority of the molecules to lie in states with rotational quantum number $J < 4$ with respect to

the Boltzmann distribution. Near these energy levels, water dimers have well documented intermolecular vibrational modes,[20] which can be excited due to collisional energy exchanges between monomers in predominantly *ortho* levels. These levels are depicted in Fig. 4. Collisions between monomers can also redistribute populations among monomer energy levels. From Table [I], the majority of the *ortho* level transitions, which decrease in absorption intensity, are between consecutive levels. Collisions will in turn excite the population to move up the ladder, thereby causing a decrease in the observed absorption intensity for *ortho* level transitions.

Both collisions between dimers and monomers and monomers themselves as well as dimer formation rates are insufficient to explain the observed decrease in the *ortho* rotational absorption strengths. To model the absorption strength decrease as seen in our measurements we assumed a bimolecular interaction where the energy exchanges were governed by the *ortho* to *para* population ratio. Among *ortho* water molecules, over 40% of water monomers have to be involved in some sort of bimolecular interaction, such as dimer formation, far above the predicted concentration of 2.5% and much larger than can be expected assuming standard collision theories of molecules in a gas at room temperature.

For high water vapor concentrations condensation and nucleation can occur on all solid surfaces. In these highly saturated environments, the water molecules can form droplets surrounded by the vapor, whereby interactions between water molecules in the vapor and liquid states can lead to a decrease in the observed absorption profile of water vapor.[5] In these simulations the water molecules were classified into "liquid," "surface," or "vapor" with respect to the number of neighbor molecules. Thus most of the vapor absorption dominated by *ortho* transitions will dramatically decrease once liquid and surface molecules are formed in or around

the terahertz beam path. While bimolecular interactions are an important factor, we believe that interactions between water monomers in the vapor phase with neighboring molecules in the liquid and surface states is the primary effect for our observation on the decrease of *ortho* transitions with increasing humidity.

CONCLUSION

In summary, the water vapor absorption in 0.2–2.4 THz was measured at different humidities at room temperature by using time-domain terahertz spectroscopy. The experimental results show that water molecules that undergo *ortho* level rotational transitions increase then decrease in absorption strength with increasing humidity, while most *para* transitions simply increase as expected for higher concentrations in the terahertz beam path. In terms of nuclear spin statistics, the *ortho* levels possess populations three times larger than the *para* levels at room temperature due to the presence of two symmetric hydrogen nuclei. Furthermore, *para*-H_2O adsorbs onto aluminum and silica surfaces preferentially due to its nonrotational ground state. The condensation of *para* molecules results in an abundance of *ortho*-H_2O. At higher humidity levels, *ortho* molecules are involved in interactions between neighboring molecules more so than *para* molecules. These interactions can be explained by dimerization and energy-coupling processes between dimers and monomers, however, the dominant interaction that contributes to the decrease in absorption of *ortho* level transitions arises from interactions between molecules in the vapor phase which coalesce around liquid droplets either in the terahertz beam path or on the surfaces. Dimerization, energy coupling between dimers and monomers, collisional energy exchanges between consecutive energy levels of the same flavor, and most importantly, interactions between molecules in liquid

and vapor phases can all contribute to the observed decrease in the absorption intensity of *ortho* level transitions.

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