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Time-domain terahertz spectroscopy of spin state transition in $[Fe(NH_2 - trz)_3]^{2+}$ spin crossover compounds

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We have measured the evolution of the THz spectrum of iron(II) spin crossover compounds within the low-spin/high-spin thermal hysteresis loop in the 0.6–6 THz frequency range. This study enabled to follow both the variations of the refractive optical index and absorption during the spin state transition. Marked absorptions centered ~2–3 THz and ~5 THz shifting with the spin state are revealed. Our work provides a means to store optically information and to read it out in the THz domain and also offers indications about the structural evolution occurring during the spin state transition. © *2011 American Institute of Physics*. [doi:10.1063/1.3624600]

Spin crossover (SCO) molecular compounds are very promising materials that exhibit a change in their physical properties when stimulated by light, temperature, or pressure. Since their discovery in the 1960's, these materials raised huge interest and have many potential applications, such as data storage devices or molecular switches. While SCO compounds have already been widely studied in many ways,[1–6] their characterization in the far infrared region (<150 cm^{-1}) is still incomplete and deserves further experimental studies. Indeed, the spin state transition should affect the lattice vibration of the compounds, vibrations that lay below 150 cm^{-1} (<4.5 THz). The time-domain terahertz spectroscopy (THz-TDS) is a powerful tool to provide useful information in this particular spectral region. In a previous study, we used this technique to characterize the dielectric of such materials in the 0.1–0.6 THz frequency range[7] and we have demonstrated the use of SCO compounds for the design of tunable THz filters.[8] This present work is made to characterize two $[Fe(NH_2 - trz)_3]^{2+}$ different SCO polymers. It led us to reveal marked absorption bands that are shifted during the spin state transition. While the overall absorption is similar for both compounds, this results in absorption and index modulation that can be as high as ~50% and ~22%, respectively at ~5 THz. We also demonstrate that the used counter-ions impacts the absorption, the dispersion of the refractive index, and their evolutions during the spin transition (ST).

Among the existent SCO compounds, the iron (II) polymeric complexes $[Fe(NH_2 - trz)_3]^{2+}$ are of interest. They present an octahedral geometry: the iron metallic ion Fe^{2+} lies in the center of the octahedron and is bonded to the $NH_2 - trz$ (1,2,4-aminotriazole) ligands. Such materials exhibit a well-known spin state transition, from a diamagnetic low-spin (LS) state (S = 0) to a paramagnetic high-spin (HS) state (S = 2). Depending on the nature of the triazole derivative and of the anion, a wide hysteresis can be observed near room temperature.[9] These compounds hardly crystallize but details about their structures have been obtained using extented x-ray absorption fine structure (EXAFS)[10] and wide x-ray scattering experiments (WAXS).[11] We studied two kinds of compounds with different counter-ions, $[Fe(NH_2 - trz)_3]Br_2$ and $[Fe(NH_2 - trz)_3](NO_3)_2$. The synthesis has been described elsewhere.[12,13] The samples are in powder form and have been pressed into pellets, avoiding any air-cell or cell-sample interfaces. It also simplifies the extraction of dielectric properties of the sample. Our pellets (~200 μm-thick) are placed into an oven that controls the sample temperature.

Our experimental set-up is the following: a THz beam consisting in a single-cycle THz wave, spanning in the 0.3–7 THz frequency range, is generated by four-wave mixing of the fundamental and the second harmonic of 50 fs pulses at 800 nm in ionized air. After transmission through the sample, this wave is measured by electro-optical (EO) sampling in a 200 μm-thick ⟨110⟩ GaP crystal.[14] Fig. 1 presents the waveforms $E_s(t)$ of different THz pulses measured after propagation in the studied samples in their HS and LS states. The reference field $E_r(t)$ corresponds to the THz wave recorded without any sample. In this figure, we have also reported the thermal hysteresis loop deduced from the evolution of the sample reflectivity at ~550 nm vs the temperature.

The first motivation of our study is to compare the THz spectra in both spin states. Fig. 2 displays transmitted THz spectra measured for samples in the LS and HS states. With

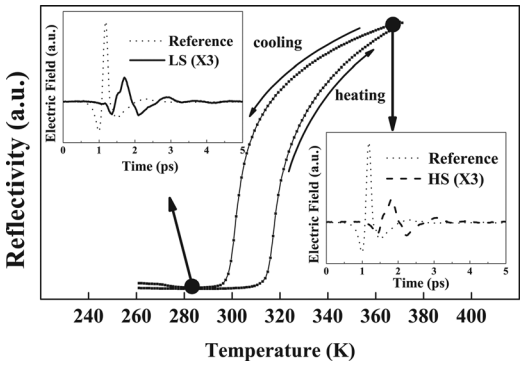

FIG. 1. Thermal hysteresis loop of the $[Fe(NH_2 - trz)_3]Br_2$ compound. The two insets show the measured temporal waveforms of THz pulses with and without the sample in both spin states.

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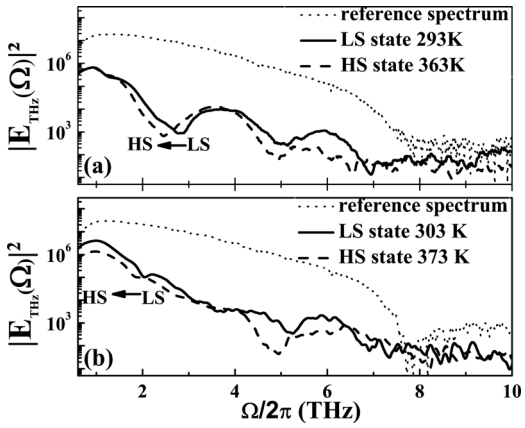

FIG. 2. Spectra of the reference and of the waveforms transmitted by the sample in the LS and the HS states for: (a) $[Fe(NH_2-trz)_3]Br_2$ and (b) $[Fe(NH_2-trz)_3](NO_3)_2$.

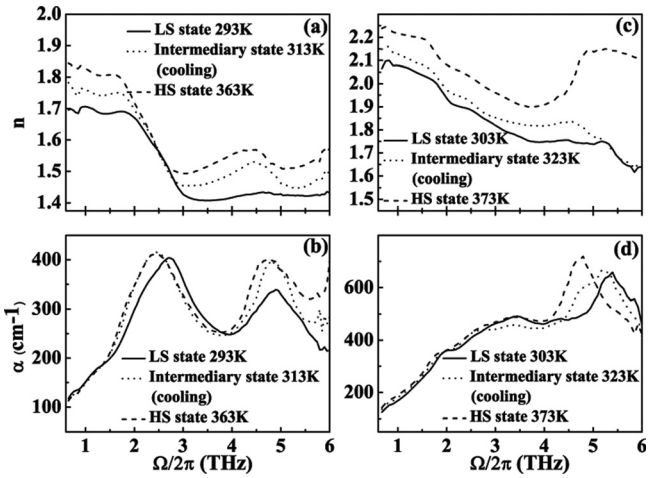

FIG. 3. Refractive index n and absorption coefficient α of $[Fe(NH_2-trz)_3]Br_2$ compound (a) and (b) and $[Fe(NH_2-trz)_3](NO_3)_2$ compound (c) and (d).

respect to the reference spectrum, we observe marked absorption bands that shift during the ST. In both cases, the spectra are clearly different depending on the spin state. For the $[Fe(NH_2-trz)_3]Br_2$ compound (Fig. 2(a)), the LS state exhibits a marked absorption around 2.8 THz and 5 THz. After the ST, these absorption bands experience a slightly shift of a few hundred GHz towards lower frequencies. For the $[Fe(NH_2-trz)_3](NO_3)_2$ compound (Fig. 2(b)), the absorption bands of the LS state are also around 2 and 5 THz and also exhibit a slight shift towards lower frequencies in the HS state. These measurements clearly evidence the THz fingerprints of the spin state of these compounds. It is interesting to notice that a change in the counter-ion strongly affects the THz absorption in both spin states. The spin crossover phenomenon is also known to result in an increase of the metal-ligand bond lengths.[17] This latter should lead to a decrease of the stiffness of the compounds that agrees with the shift of absorption towards lower frequencies during the ST. This result is interesting since it provides a means to read out information in the THz domain.

Thanks to Kramers-Kronig relations, the change of the absorption is accompanied by the refractive index. Fortunately, THz-TDS technique makes it possible to extract both the real and imaginary parts of the dielectric constant in THz frequency range as well as their evolutions within the hysteresis loop. As explained previously, we use a numerical method to recover the frequency-dependent complex refractive index of our samples. To this end, we consider the complex transmission function $T(\Omega)=E_s(\Omega)/E_r(\Omega)$, where $E_s(\Omega)$ and $E_r(\Omega)$ are, respectively, the Fourier transform of $E_s(t)$ and $E_r(t)$. An initial value of the absorption is computed at the frequency where the sample transmits the most. Different methods can be used to extract the refractive index n and the extinction coefficient κ from $T(\Omega)$.[16] The extraction of the refractive index requires knowing precisely the sample thickness, which in our case is measured thanks to a caliper rule with a one micrometer precision. Fig. 3 shows the computed absorption coefficients $\alpha=\Omega\kappa/c$ and optical indices n for our two compounds in the LS state, the HS state and also in an intermediary state (i.e., inside the hysteresis loop). In this latter case, the sample was warmed or cooled and brought along the ascending or descending branch of the hysteresis loop. In this case, the sample state is a mixture of both the HS and LS state. Hence, the absorption can be considered as a linear combination of the absorption of the LS and HS states. It makes it possible to follow the variations that occur during the ST. Looking at the evolution of the optical index in Figures 3, we observe a strong dependence with the frequency. The maximum index modulation is ~14% for $[Fe(NH_2-trz)_3]Br_2$ and ~23% for $[Fe(NH_2-trz)_3](NO_3)_2$. Similarly, the maximum absorption modulation is ~18% for $[Fe(NH_2-trz)_3]Br_2$ and ~50% for $[Fe(NH_2-trz)_3](NO_3)_2$.

From n and κ, one can compute the dielectric function $\tilde{\varepsilon}(\Omega)=\varepsilon'+i\varepsilon''$, with $\varepsilon'=n^2-\kappa^2$ and $\varepsilon''=2\,n\kappa$. We have fitted this function considering it results from a sum of Lorentzian oscillators,[15] i.e.,

$$\tilde{\varepsilon}(\Omega)=\varepsilon'(\Omega)+i\varepsilon''(\Omega)=\varepsilon_\infty+\sum_k\frac{F_k}{\Omega_k^2-\Omega^2-i\Gamma_k\Omega}. \quad (1)$$

In Eq. (1), Ω_k is the frequency of the resonance, F_k its oscillator strength, and Γ_k its linewidth; ε_∞ is the high-frequency dielectric constant. Fig. 4 displays the results of this fit for one compound and illustrates the procedure we used to perform our fits. The number of lorentzian and their initial

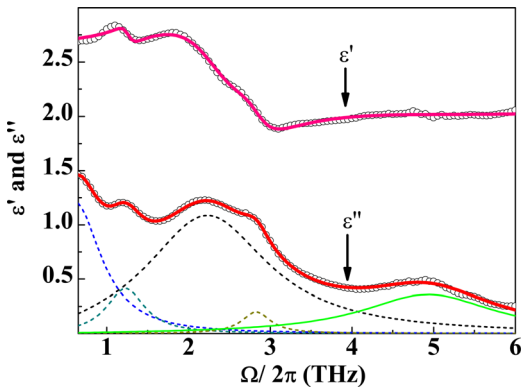

FIG. 4. (Color online) $\varepsilon'(\Omega)$ and $\varepsilon''(\Omega)$ for the $[Fe(NH_2-trz)_3]Br_2$ compound in the LS state. The circles are the experimental data and the solid lines are the fits to the data using Eq. (1). The position, width, and amplitude of the five Lorentzians used to fit these data are displayed in dashed lines.

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TABLE I. Parameters of the fits: Ω_k in THz, Γ_k in THz, and strength (w:weak or S:strong). IS stands for the intermediate state.

Counterion	LS	IS	HS
Br_2	0.72, 0.79, w	0.67, 0.61, w	0.67, 0.62, w
	1.26, 0.57, w	1.21, 0.60, w	1.19, 0.73, w
	2.40, 1.84, S	2.33, 1.52, S	1.87, 0.40, S
	2.84, 0.42, S	2.63, 11.39, S	2.40, 1.72, S
	5.03, 1.98, S	4.86, 1.16, S	4.75, 1.24, S
	—	6.02, 0.54, w	6.05, 1.45, w
NO_3	0.86, 1.23, w	0.86, 0.66, w	0.86, 1.33, w
	1.57, 1.06, w	—	—
	2.01, 0.61, S	1.87, 0.49, S	1.81, 0.74, S
	2.71, 1.08, w	2.63, 0.33, w	2.85, 1.72, w
	3.63, 1.87, S	3.29, 5.50, S	3.45, 1.96, S
	—	4.83, 0.54, S	4.83, 0.63, S
	5.25, 1.73, S	5.25, 0.63, S	—

central frequency is fixed by the number and the position of the peaks one can clearly evidenced in the imaginary part of the dielectric function. In this figure, the different lorentzians used to perform the best fit are displayed in dashed lines. There widths are adjusted to improve the fit, the real part of the dielectric function. The fits obtained using this procedure are in good agreements with our experimental data. The parameters extracted from these fits are summarized on Table I. Attempt to assign the measured absorption bands to specific vibrational modes via discrete Fourier transform (DFT) calculations is currently under progress. Let-us stress that the computations in this latter case are rather difficult since the determination of the position of the different atoms of the complexes by x-ray diffraction is still the object of active researches.

In conclusion, we have demonstrated the existence of strong absorption bands in the THz range of SCO compounds. These latter are shifted by the spin state transition. They result in a strong modulation of the absorption and the refractive index. This THz-TDS technique can be easily extended to the study of other SCO compounds. Moreover, our results indicate that the optical pump-THz probe experiments can also be performed to study the kinetics of photo-induced spin-state transitions.

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