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THz and IR spectroscopy of endofullerene H₂O@C₆₀

Alexander Melentev¹, Sergey Zhukov¹, Vasileios Balos², Gabriela Hoffman³, Shamim Alom³, Mikhail Belyanchikov¹, Elena Zhukova¹, Martin Dressel^{1,4}, George Bacanu³, Pavel Abramov¹, Malcolm Levitt³, Richard Whitby³, Boris Gorshunov^{1*}, Mohsen Sajadi^{2,5}

*zs1978@mail.ru

¹Moscow Institute of Physics and Technology, Moscow, Russia

²Fritz-Haber-Institut der MPG, Berlin, Germany

³School of Chemistry, University of Southampton, Southampton, United Kingdom

⁴1. Physikalisches Institut, Universität Stuttgart, Stuttgart, Germany

⁵Department of Chemistry, University of Paderborn, Paderborn, Germany

Abstract. Terahertz time-domain and infrared Fourier-transform spectroscopy techniques are used to investigate the properties of H₂O@C₆₀ endofullerene in 6 K – 300 K temperature interval. A number of absorption lines associated with rotational transitions of water molecule entrapped inside C₆₀ cages are observed and assigned. Fitting the resonances with Lorentzian lineshapes allowed us to obtain temperature dependencies of absorption lines parameters – frequency, strength and damping.

1. Introduction

Endofullerenes represent a unique opportunity to study the dynamics of isolated atoms and small molecules (He, Ne, H₂O, H₂, HF, etc.). In case of H₂O@C₆₀ individual water molecules are free from intermolecular hydrogen bonds making it possible to study the quantum dynamics of the “isolated” water molecules, the collective effects in the system of dipole-dipole-coupled H₂O molecules and also gain insight into ortho-to-para spin conversion mechanism of water.

2. Experimental details

High quality H₂O@C₆₀ powder (filling factor 5%) was prepared by the method known as “molecular surgery” [1] and pressed into a pellet with a thickness of d=254 μm. Measurements of transmission coefficient spectra of the pellet were carried out in a wide temperature range of 6 K – 300 K using time-domain terahertz spectrometer TeraView TPS Spectra 3000 and infrared Fourier-transform spectrometer Bruker Vertex v80. To capture the process of ortho-para-conversion of water molecules, the sample was kept at temperature T= 20 K for about an hour and then quickly cooled down to 6 K in a span of ≈5 minutes. This method delivers the sample in an ortho-isomer enriched state, because characteristic conversion time for water at 20 K is on the order of tens of minutes [2]. The real and imaginary parts of permittivity of H₂O@C₆₀ were directly calculated from the complex transmissivity spectra. All observed absorption resonances were fitted with the corresponding Lorentzian expression for complex dielectric



permittivity $\varepsilon(\omega) = \sum_n \frac{f_{osc} n}{\omega_{0n}^2 - \omega^2 - i\gamma_n \omega}$, where f_{osc} is the oscillator strength, ω_0 – the peak frequency position and γ – the damping factor. This way, temperature and time dependences of these parameters were obtained.

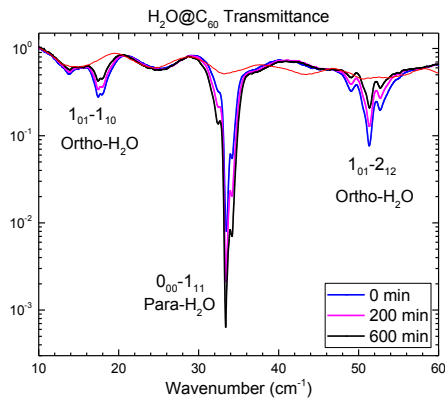


Figure 1. Time-dependent transmittance spectra of a $\text{H}_2\text{O}@C_{60}$ pellet (254 μm thick) measured at 6 K (solid lines). Minima in the spectra correspond to dipolar transitions between split rotational energy levels of ortho and para water molecules. The intensity of transitions changes over time due to ortho-para-conversion. Red solid line corresponds to the spectrum measured at 70 K when no absorption lines were observed; oscillations in the spectra are due to Fabry-Perot effect – interference of radiation within plane-parallel pellet.

3. Results

Absorption peaks seen as minima in the transmissivity spectra (Fig. 1) were previously identified as pure rotational transitions of encapsulated water molecule [3]. We associated groups of minima at 13–18, 32–35 and 49–53 cm^{-1} with transitions $1_{01}-1_{10}$, $0_{00}-1_{11}$ and $1_{01}-2_{12}$, respectively. Multiple structures around mentioned frequencies indicate splitting of corresponding energy levels (Fig. 2). Previous neutron scattering study [4] reported splitting of triply degenerate level 1_{01} into a lower energy non-degenerate level and a doubly degenerate higher energy level. The predicted splitting magnitude of $\sim 4 \text{ cm}^{-1}$ coincides with the distance between the peaks detected here at 13 cm^{-1} and 17 cm^{-1} .

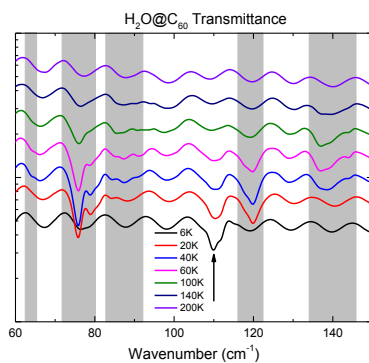


Fig. 2. Far-infrared transmission coefficient spectra of $\text{H}_2\text{O}@C_{60}$ pellet measured at different temperatures in the interval 6–200 K. Spectra are vertically shifted for clarity. The grey areas indicate yet unidentified absorption peaks. The arrow marks pure translational transition of water molecule within C_{60} cage.

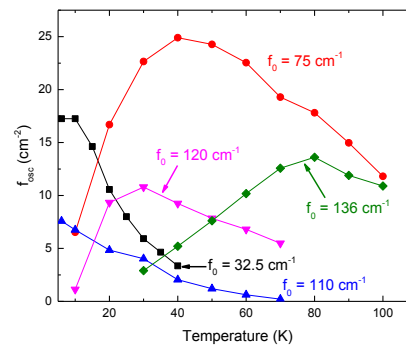


Figure 3. Temperature dependence of oscillator strength of the absorption peaks observed at different frequencies as indicated.

The origin of most peaks observed in the infrared part of the spectra (Fig. 2) are not yet identified, except for the peak at 110 cm^{-1} . To characterize the intensity of the peaks we use the oscillator strength that is defined as $f_{osc} = \Delta\varepsilon\omega_0^2$ with $\Delta\varepsilon$ the transition dielectric strength. This value is proportional to the squared plasma frequency of the peak or to corresponding area in the optical conductivity spectrum (see, e.g., [5]), i.e. proportional to the concentration of molecules involved in the transition. The oscillator

strength of the peak at 110 cm^{-1} grows monotonically as the temperature decreases (Fig. 3), therefore the initial state of the corresponding transition must be one of the lowest energy levels of water molecule. Since there are no rotational transitions whose frequency position is close to 110 cm^{-1} , this peak is assigned to the translational motion of the entrapped water molecules inside C_{60} cages [6].

The analysis of the obtained temperature dependent oscillator strengths of the 75 , 120 and 136 cm^{-1} peaks (Fig. 3) indicates that the corresponding transitions reach maximal intensity at 40 , 30 and 80 K , respectively. We discuss the origin of all the observed transitions and the mechanisms of their temperature and time evolution.

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