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Incoherent thermally activated proton hopping process in calix[4]arene observed by anelastic spectroscopy

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The anelastic spectrum of calix[4]arene was measured at two different vibrational frequencies. Three thermally activated peaks were detected. The lowest temperature peak can be described considering a continous distribution function of activation energies for the relaxation. This anelastic peak can be ascribed to a thermally activated hopping process of H atoms of the OH groups, corresponding to a flip-flop of the OH bond. The results of the present study indicate that anelastic spectroscopy is a good experimental technique to study atomic motion inside molecules at a mesoscopic (few molecules) level.

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I. INTRODUCTION

Calix[n]arenes are cuplike [1_n] metacyclophanes which derive from the condensation of phenols and formaldehyde in different conditions.[1] The bracketed number indicates the number of phenol units (the atoms inside the rectangle in Fig. 1) and hence defines the size of the macrocycle. The tetramer is named calix[4]arene (see Fig. 1) The number of the phenolic units can vary from 3 to 14 and different substituents can be attached to the aromatic ring in the *para* position (position 2 in Fig. 1) and at the phenolic oxygen. During the last decades calix[n]arene have been extensively utilized as molecular platforms for the synthesis of potent receptors for neutral and charged species and for their ability to form endocavity inclusion complexes with guests of complementary size.[2,3] On the other hand, the discovery of quantum tunneling processes involving the hydrogen atoms of the OH groups was recently reported.[4,5] Both the design of molecules with an internal cavity able to recognize metal cations and/or neutral molecules[2,3] and the study of the transfer of protons involved in hydrogen bonding, which is fundamental to many chemical and biological processes,[6,7] are important subjects; however, many questions remain unsolved and, especially concerning the second item, very few studies have been reported for the condensed state.

Quite recently, NMR relaxometry measurements indicated that hydrogen atoms in calix[4]arene and *p*-tert-butyl-calix[4]arene might move both by means of a thermally activated hopping process and by a coordinated quantum tunneling process by which the four H atoms of the O-H groups move in a coordinated fashion giving rise to an interconversion between the two tautomers of the molecule.[4,5] In *p*-tert-butyl-calix[4]arene the coordinated proton transfer (relaxation) rate τ_c has been directly determined and it was found to be independent of temperature between 15 and 19 K, clearly demonstrating that the dynamical behavior of the system is non-Arrhenius in character.[4] In the calix[4]arene molecule, in addition, a thermally activated proton hopping process was found, with a classical Arrhenius behavior described by a relaxation time $\tau_c = 1.2\times 10^{-12}\cdot e^{(900\ K)/T}$ s, which has been ascribed to rotational flips of the single O-H group (jump of the H atom between state 1 and 1′ in Fig. 1).[5]

In the following we will report anelastic spectroscopy measurements on calix[4]arene containing four phenolic units (Fig. 1). All the carbon and oxygen bonds are saturated by hydrogen atoms. We will show that a peak in the anelastic spectrum can be possibly ascribed to the same hopping process detected by NMR measurements and we will discuss in detail a quantitative analysis of this peak. NMR relaxometry is a well-established experimental technique for the study of molecular dynamics. From the present study we can deduce that anelastic spectroscopy has great potentialities to study the movements of atoms in molecules at a mesoscopic (several-molecule) level.

II. EXPERIMENTAL AND RESULTS

Calix[4]arene is produced as a powder sample. In order to measure its elastic properties, the powder was mixed with a pure KBr powder and was pressed at high pressure in order to obtain a bar of $7\times 38\times 2.0\ \mathrm{mm}^3$. A pure KBr bar was prepared in the same way and its anelastic spectrum was also measured for comparison.

The complex Young's modulus $E(\omega)=E'+iE''$, whose reciprocal is the elastic compliance $s=E^{-1}$, was measured as a function of temperature by electrostatically exciting the lowest odd flexural mode. The vibration amplitude was detected by a frequency modulation technique. The vibration frequency, $\omega/2\pi$, is proportional to $\sqrt{E'}$, while the elastic

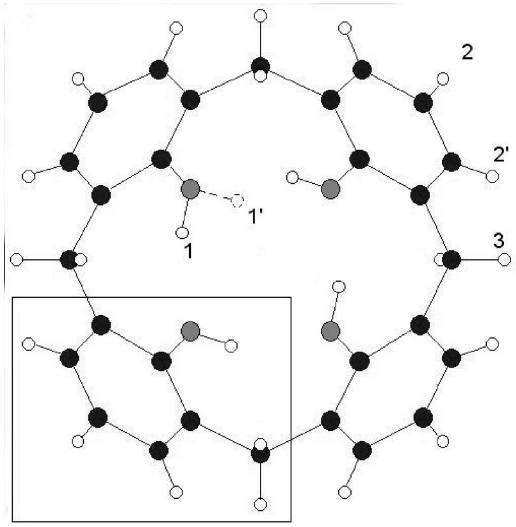

FIG. 1. Schematic representation of the calix[4]arene molecule. Black, grey, and white circles represent C, O, and H atoms, respectively.

energy loss coefficient (or reciprocal of the mechanical Q) is given by[8] $Q^{-1}(\omega,T)=E''/E'=s''/s'$, and was measured by the decay of the free oscillations or the width of the resonance peak. The imaginary part of the dynamic susceptibility s'' is related to the spectral density $J_\varepsilon(\omega,T)=\int dt\, e^{i\omega t}\langle\varepsilon(t)\varepsilon(0)\rangle$ of the macroscopic strain ε through the fluctuation-dissipation theorem, $s''\propto(\omega/2k_\mathrm{B}T)J_\varepsilon$.

In order to study the presence of thermally activated peaks in the anelastic spectrum of calix[4]arene the measurements are carried out at different vibration frequencies. Higher-order flexural modes could not be excited on the sample presently used; however, as the flexural mode frequency, $\omega/2\pi$, is directly proportional to the height of the sample, h, the specimen thickness was reduced with sand paper changing h from 2.2 to 1.1 mm and consequently $\omega/2\pi$ changed by almost a factor 2.

The anelastic spectra of the pure KBr and the mixed KBr-calix[4]arene bar are reported in Fig. 2. In the temperature range from 1.1 to 400 K the KBr sample presents just a featureless background which increases slightly between 1 and 300 K and more significantly above room temperature. Instead, the calix[4]arene sample exhibits three well developed peaks around 60 (peak P1), 150 (P2), and 270 K (P3). As they are not present in the KBr specimen, they can be attributed to intrinsic anelastic processes inside the calixarene molecule.

An analysis of the three peaks is presented in the next section, where it will be shown that the peak at the lowest temperature can be identified with the same thermally activated hopping process of H atoms detected by NMR measurements, giving rise to rotational flip of the OH bond.[5]

III. DISCUSSION

In order to obtain useful information from the three peaks present in the spectrum of calix[4]arene a quantitative analysis of them is needed. The most common model describing relaxation processes (anelastic, dielectric, etc.) is due to Debye. The contribution of a relaxation process to the dynamic Young's modulus is[8]

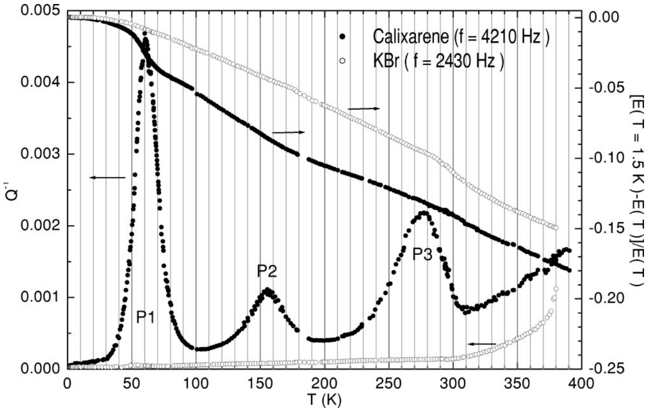

FIG. 2. The Q^{-1} spectrum and the relative variation of the real part of the Young's modulus as a function of temperature for the pure KBr and the mixed KBr-Calix[4]arene bars.

$$\begin{bmatrix} Q^{-1} \\ \delta E'/E' \end{bmatrix} = E v_0 c(\lambda_1-\lambda_2)^2\cdot\frac{f_1 f_2}{T}\,\frac{1}{1+(\omega\tau)^{2\alpha}}\begin{bmatrix}(\omega\tau)^\alpha \\ -1\end{bmatrix}, \tag{1}$$

where c is the molar concentration of relaxing units; f_1 and f_2 are the equilibrium fractions in the two possible configurations 1 and 2 between which the relaxation can occur with a characteristic time $\tau(T)$ which classically follows an Arrhenius law, $\tau=\tau_0\exp(E_a/kT)$; λ_i is the elastic dipole of the state i, i.e., the average macroscopic strain which the sample would have if each cell (molecule) contained one relaxing unit in the state i; v_0 is the cell (molecule) volume and $\alpha\equiv1$. The contribution of a relaxation process to the absorption is a peak whose maximum is centered at the temperature at which $\omega\tau=1$. Since τ decreases as T increases, the peak shifts to higher temperature if measured at higher ω. Around the same temperature, the real part of the Young's modulus presents a negative step whose amplitude, from theoretical models, is twice the peak height.

The Debye formula describes a relaxation process between two possible states which occurs with a single activation energy E_a and a single characteristic time τ. Often real processes are broader than Debye peaks; in those cases a correction factor α is introduced in Eq. (1) (Fuoss-Kirkwood model[8]). Physically this means that the relaxation process has a distribution of activation energies and relaxation times which become broader as α decreases.

A first quantitative analysis of the Q^{-1} spectrum of calix[4]arene was obtained after the subtraction of a smooth background, adding a Debye contribution for peak P2, a Debye contribution for peak P3 and a Fouss-Kirkwood peak for P1. The experimental data and the theoretical curves at the two measured frequencies are reported in Fig. 3. The parameters of the three peaks are reported in Table I.

P2 and P3 can be described by the Debye process characterized by a single relaxation time, with the assumption that the $\tau(T)$ follows an Arrhenius law, $\tau=\tau_0\exp(E_a/kT)$. For

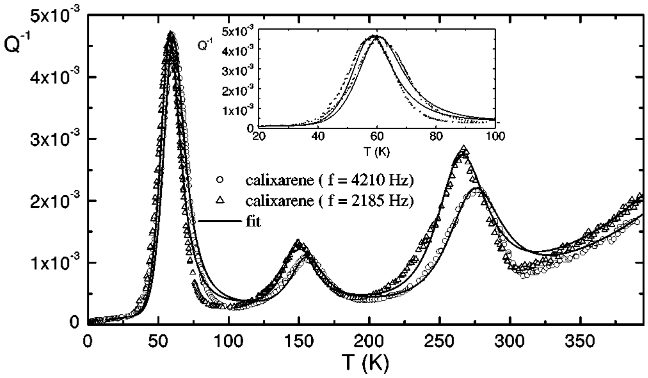

FIG. 3. The Q^{-1} spectrum of calix[4]arene measured at two different frequencies (symbols) and the best-fit curves (continous lines) obtained adding two Debye contributions for the higher temperature processes and a Fuoss-Kirkwood relaxation with $\alpha = 0.48$ for the lower temperature process. In the inset the region around 60 K is reported in more detail.

peak P3 the fit is less satisfactory and this may be due to an imperfect substraction of the background, which in that range of T starts to increase very fast. However, P3 does not seem to be larger than a pure Debye relaxation with the given parameters. For a Debye process, the height of the peak decreases as the frequency increases almost as $1/T$, unless the atom or the defect relaxes between the states of an asymmetric potential well. In the present case for both higher temperature peaks the $1/T$ law is not valid and a multiplicative factor was introduced in Eq. (1) to account for the different height of the peaks at the two different frequencies. The intensity of the relaxation peaks is also proportional to the concentration of the relaxing units. We are not sure that the distribution of calixarene molecules in our sample is really uniform. After the mechanical process used to decrease the thickness of the sample we could have retained a part of the specimen with a different concentration of calixarene, thus affecting the absolute height of the relaxation peaks. The incertainty regarding this point prevents us from a quantitative analysis of the dependence of the peaks' height on frequency.

All the peaks are certainly due to some atomic motion inside the calix[4]arene molecule as they are not present in the pure KBr specimen. Usually in solids relaxations of different types of defects (i.e., point, line, plane defect) give τ_0 values which differ by orders of magnitude. From Table I one can notice that the τ_0 values for the three peaks do not change more than a factor 25. In the following it will be shown that peak P1 can be ascribed to the reorientation of the OH bond of calix[4]arene, so that it corresponds to the motion of a single atom within the molecule. The similarity among the characteristic times of the three peaks of calix[4]arene may suggest that also the higher temperature relaxation involves the motion of single atoms or a small number of them. Peak P3 is not present in the anelastic spectrum of *p*-tert-butyl-calix[4]arene, while a peak similar to P2 is present also in the last compound.[9] Considering the similarities of the structure of the calixarene and *p*-tert-butyl-calixarene molecules, it seems that peak P2 may be due to the reorientation of the H atoms at positions 2 and 2′ in Fig. 1.[9] However, more experimental studies are needed to ascribe peak P2 and P3 to some physical processes. We want to point out that the activation energy and the relaxation time obtained from the fit procedure are not affected by the possible uncertainty on the peak height.

TABLE I. The best-fit parameters of the three anelastic peaks of calix[4]arene.

Peak	T_{max} (K)	τ_0 (s)	E_a (K)	α
P1	60	0.8×10^{-12}	1120	0.48
P2	150	2.0×10^{-11}	2370	1
P3	270	3.0×10^{-12}	4720	1

In the following we will deal with peak P1. It can be quite satisfactorily described by a Fuoss-Kirkwood model with $\alpha = 0.48$; it means that the characteristic time and activation energy have a continuous distribution function around the values $\tau_0 = 0.8\times10^{-12}$ s and $E_a = 1120$ K. These values are quite similar to the parameters of the thermally activated proton hopping process, with a classical Arrhenius behavior measured by NMR relaxometry, which gave $\tau_0 = 1.2\times10^{-12}$ s and $E_a = 900$ K.[5] This close similarity indicates that the NMR and anelastic relaxation processes may be originated by the same physical process, that is, the rotational flips of the O-H groups of the calix[4]arene molecules.[5]

In order to gain insight and to have more information about the distribution functions of τ and E_a, we tried a different approach based on a direct evaluation of the distribution of activation energies; at this step we fixed τ_0 to the single value obtained for the Fuoss-Kirkwood peak, both for simplicity of calculation and considering that we are dealing with a single relaxation process which corresponds to a well defined reorientation. This approach is very useful in describing a similar peak found in *p*-tert-butyl-calix[4]arene, which cannot be modeled by a Debye or by a Fouss-Kirkwood relaxation or even by the sum of a big number of them.[9] The expression for the elastic energy-loss coefficient used for the fit procedure was

$$Q^{-1} = a\int_0^{\infty}\frac{f_1 f_2}{T}\cdot\frac{\omega\tau(E_a)}{1+[\omega\tau(E_a)]^2}\,g(E_a)\,dE_a, \tag{2}$$

where a is a constant and $g(E_a)$ is a normalized distribution function of the activation energy E_a. Both a Lorentzian and a Gaussian distribution function have been tested. The Gaussian distribution is able to better reproduce the experimental data than a Lorentzian curve. The best fit curves using a Gaussian distribution function are reported in Fig. 4. The best fit parameters are: $\tau_0 = 0.8\times10^{-12}$ s, $E_a = 1070$ K, $\sigma(E_a) = 130$ K, where $\sigma(E_a)$ is the standard deviation of the Gaussian distribution.

The existence of a distribution of activation energies more than a single E_a can be explained considering that each H atom of the OH groups in a calixarene molecule moves in an environment (potential well) which can vary as the others three H atoms of the OH groups in the same molecule

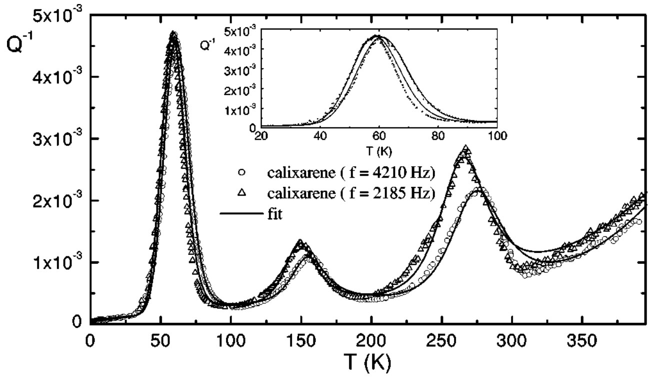

FIG. 4. The Q^{-1} spectrum of calix[4]arene measured at two different frequencies (symbols) and the best-fit curves (continous lines) obtained adding two Debye contributions for the higher temperature processes and a relaxation with the distribution of activation energies as discussed in the text for the lower temperature process. In the inset the region around 60 K is reported in more detail.

change their position. Moreover the potential energy of the H atom can be at least partially influenced by the surrounding calix[4]arene molecules.

A distribution of activation energies for a relaxation process measured by NMR relaxometry has been discussed also in the case of 1,3-di-*t*-butylbenzene, which was a very interesting case for the study of H dynamics in organic molecules in the condensed state.[10] The experimental data were described by a non-Bloembergen-Purcell-Pound (BPP) spectral density. In the case of anelastic relaxation, the BPP spectral density has its exact counterpart in the Debye model with an Arrhenius-like dependence of τ on T and E_a. Beckmann *et al.* pointed out that the non-BPP behavior can also be interpreted in terms of a distribution of exponential correlation function (leading to the Arrhenius law), with the distribution at least partially characterized by a correlation time τ which could either be a cutoff correlation time or a mean correlation time, depending on the model. Correspondingly there is a distribution of activation energies. However, the relation between the two distribution functions cannot be determined until the dependance of τ on E_a is modeled. In the present case τ_0, which has been fixed to the best-fit value, can be interpreted as a mean correlation (relaxation) time. Moreover, the Arrhenius dependence of τ on T and E_a has been explicitly used. However, the Gaussian distribution function of the activation energies has not been derived from a model, but has been found to describe quite well the experimental data.

Finally in the temperature range above 1.3 K we could not observe any feature which can be ascribed to a quantum tunneling process as that detected by NMR relaxometry.[4,5] One can argue that as our measuring frequency is of the order of 1 kHz, the condition $\omega\tau = 1$ in order to have a peak in the elastic energy-loss coefficient is not fullfilled, at least considering the τ values obtained in the temperature range 15–19 K in *p*-tert-butyl-calix[4]arene.[4] However, we cannot procede further in the interpretation of the apparent lack of this process in the anelastic spectrum of calix[4]arene.

IV. CONCLUSION

We measured the anelastic spectrum of a bar of KBr containing a few percent of calix[4]arene powder. We observed three thermally activated peaks. The lowest temperature peak can be described both by a Fuoss-Kirkwood model and by a model considering a Gaussian distribution of activation energies, leaving the correlation time τ_0 fixed. Due to the similarity between the physical parameters of this peak and of a relaxation found in the NMR spectrum of the same compound, the anelastic peak can be ascribed to hopping of H atoms of the OH groups, which corresponds to a flip-flop of the OH bond. From the results of the present study, anelastic spectroscopy appears as a good tool for studying atomic motion inside molecules at a mesoscopic (few molecules) level.

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