Observation of an incoherent thermally activated proton hopping process in calix-[4]-arene by means of 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 continuous 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. From the results of the present study, it seems that anelastic spectroscopy is a good experimental technique to study atomic motion inside molecules at a mesoscopic (few molecules) level.
I. INTRODUCTION

Calix[n]arenes are cup-like [l_n] metacyclophanes which derive from the condensation of phenols and formaldehyde in different conditions. The bracketed number indicates the number of phenolic 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) and hence defines the size of the endo-cavity inclusion complexes with guests of complementary size. On the other hand the discovery of quantum tunnelling processes involving the hydrogen atoms of the OH groups was recently reported. Both the design of molecules with an internal cavity are to recognize metal cations and/or neutral molecules and the study of the transfer of protons involved in hydrogen bonding, which is fundamental to many chemical and biological processes, 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. In p-tert-butyl-calix[4]arene the coordinated proton transfer (relaxation) rate, \( \tau_c \), 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. 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 \( \tau_c = 1.2 \times 10^{-12} \) sec. 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).

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 7x38x2.0 mm³. 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 energy loss coefficient (or reciprocal of the mechanical \( Q \)) is given by \( Q^{-1}(\omega,T) = E'/E'' = s''/s' \), 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 \( J_e(\omega,T) = \int dt e^{i\omega t} \langle \varepsilon(t) \varepsilon(0) \rangle \) of the macroscopic strain \( \varepsilon \) through the fluctuation-dissipation theorem, \( s'' \propto \langle \omega/2k_B T \rangle J_e \).

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 exited 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.

III. DISCUSSION

In order to obtain useful information from the three peaks present in the spectrum of calix[4]arene a quantita-
The Debye formula describes a relaxation process between two possible states which occur with a single activation energy, $E_a$, and a single characteristic time, $\tau$. Often real processes are broader than Debye peaks; in those cases a correction factor, $\alpha$, is introduced in (1) (Fuoss-Kirkwood model). Physically this means that the relaxation process has a distribution of activation energies and relaxation times which become broader as $\alpha$ 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 P1, a Debye contribution for peak P2 and a Fouss-Kirkwood peak for peak P3. 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.

P1 and P2 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 peak P3 the fit is less satisfactory and this may be due to an imperfect subtraction of the background, which in that range of $T$ starts to increase very fastly. 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 (1) to account for the different height of the peaks at the two different frequencies. In the following we will not analyze the dependence of the peak heights on frequency, as the mechanical process used to obtain a second vibrational frequency could have affected the distribution of calixarene powders.

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. From Table I one can notice that the $\tau_0$ values for the three peaks are the same within one order of magnitude. Peak P1 can be ascribed to a relaxation process involving the reorientation of a single bond or equivalently to the motion of a single atom. The similarity among the three characteristic times 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, whilst a peak similar to P2 is present also in the last compound. 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. 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.

In the following we will deal with peak P1. It can be quite satisfactorily described by a Fouss-Kirkwood model with $\alpha = 0.48$; it means that the characteristic time and activation energy have a continuous distribution function around the values $\tau_0 = 0.8 \cdot 10^{-12} \text{ s}$ and $E_a = 1120 \text{ K}$. 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 $\tau_0 = 1.2 \cdot 10^{-12} \text{ s}$ and $E_a = 900 \text{ K}$. 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.

In order to gain insight and to have more information about the distribution functions of $\tau$ and $E_a$, we tried a different approach based on a direct evaluation of the distribution of activation energies; at this step we fixed $\tau_0$ to the single value obtained for the Fouss-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 modelled by a Debye or by a Fouss-Kirkwood relaxation or even by the sum of a big number of them. The expression for the elastic energy loss coefficient used for the fit procedure was:

$$Q^{-1} = a \int_0^\infty \frac{f_1 f_2}{T}.$$
where \( a \) is a constant, \( g(E_a) \) 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: \( \tau_0 = 0.8 \cdot 10^{-12} \text{ s}, E_a = 1070 \text{ K}, \sigma(E_a) = 130 \text{ K} \), where \( \sigma(E_a) \) is the variance 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 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-butylibenzenes, which was a very interesting case for the study of H dynamics in organic molecules in the condensed state.\(^8\) 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 \( \tau \) on \( T \) and \( E_a \). Beckmann et al.\(^9\) 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 \( \tau \) 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 dependence of \( \tau \) on \( E_a \) is modeled. In the present case \( \tau_0 \), which has been fixed to the best fit value, can be interpreted as a mean correlation (relaxation) time. Moreover the Arrhenius dependence of \( \tau \) 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.

A last consideration regards the lack of any quantum tunneling process in the anelastic spectrum of calix[4]arene, as that detected by NMR relaxometry.\(^3\) One possible explanation for this, is that we perform measurements of the dynamical Young’s modulus as a function of temperature, measured with a practically fixed frequency. If the correlation time \( \tau \) in the tunnelling process becomes temperature independent, like in the case of p-tert-butyl-calix[4]arene, the condition \( \omega \tau = 1 \) in order to have a peak in the elastic energy loss coefficient could be never fulfilled.

### 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 \( \tau_0 \) 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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**FIG. 1.** Schematic representation of the calix[4]arene molecule. Black, grey and white circles represent C, O and H atoms, respectively.

**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.
FIG. 3. The $Q^{-1}$ spectrum of calix[4]arene measured at two different frequencies (symbols) and the best fit curves (continuous 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.

FIG. 4. The $Q^{-1}$ spectrum of calix[4]arene measured at two different frequencies (symbols) and the best fit curves (continuous 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.

| peak | $T_{max}$ (K) | $\tau_0$ (s) | $E_a$ (K) | $\alpha$ |
|------|---------------|---------------|-----------|----------|
| $P1$ | 60            | $8 \cdot 10^{-12}$ | 1120      | 0.48     |
| $P2$ | 150           | $2 \cdot 10^{-11}$ | 2370      | 1        |
| $P3$ | 270           | $3 \cdot 10^{-12}$ | 4720      | 1        |

TABLE I. The best fit parameters of the three anelastic peaks of calix[4]arene.
Calixarene ($f = 2430$)

KBr ($f = 2430$)
calixarene (f = 4210 Hz)
calixarene (f = 2185 Hz)
fit