Quantum Rotational Tunneling of Methyl Groups in Polymers

J. Colmenero,[1] R. Mukhopadhyay,[1,3] A. Alegría,[1] and B. Frick[2]

[1]*Departamento de Física de Materiales, Universidad del País Vasco, Apartado 1072, 20080 San Sebastián, Spain*
[2]*Institute Laue Langevin, B.P. 156X, F-38042 Grenoble, France*
[3]*On leave from Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai (Bombay) 400 085, India*
(Received 3 November 1997)

Quantum rotational tunneling of methyl groups has directly been observed for the first time in polymers by high resolution inelastic neutron scattering. The experimental results are readily explained and reproduced quantitatively, without any adjustable parameter, by considering the distribution of tunneling lines which is obtained from the distribution of energy barriers for classical hopping of methyl groups at high temperature.   [S0031-9007(98)05564-1]

PACS numbers: 61.41.+e, 61.12.Ex

The existence of quantum molecular motions in polymer systems, especially rotational tunneling of symmetric methyl groups, was expected for a long time, but has never been directly observed. Rotational tunneling of methyl groups is well established in crystalline low molecular weight systems, but not in amorphous solids like polymers. Tunnel splitting of different torsional levels has been detected in several molecular crystalline systems by nuclear magnetic resonance (NMR), specific heat measurements, inelastic neutron scattering (INS) techniques, etc. [1,2]. Among these techniques, INS has the advantage to observe the tunneling transitions directly. Moreover, the intensities of all spectral features can, in principle, be calculated quantitatively. The size of the observed tunnel splitting is very sensitive to the strength and shape of the rotational potential and thus to the structural disorder. For well ordered crystals sharp tunneling lines are observed by INS at low temperatures ($T < 50$ K), whereas for amorphous systems a wide distribution of local environments and, therefore, of tunnel splitting is expected. This fact may have prevented such an observation up to now. In the case of polymers, there exists a number of claims or predictions about quantum motions in the literature. In particular, NMR measurements by Hoch *et al.* [3] showed methyl group dynamics in poly(vinyl acetate), (PVAc), to be active down to a very low temperature. Rotational tunneling of methyl groups was also claimed to be present in poly(methyl methacrylate), which would account for the reported non-Arrhenius behavior of the mechanical relaxation time at very low temperatures [4]. At high temperatures, methyl group dynamics is usually described in terms of classical hopping processes over the rotational barrier, which can be observed by INS as a quasielastic broadening. In this case the width of the quasielastic line increases as the jumping rate increases with temperature. For several polymers the classical hopping process has recently been investigated and was described by a distribution of rotational energy barriers [5–7]. In this Letter we show that, besides the first direct observation of tunneling in amorphous polymers by INS, we can use the distribution of energy barriers, as determined from the classical regime, to describe, without any fitting parameter, the measured spectra at low temperatures.

The tunnel splitting of the different torsional levels can be calculated by solving a stationary Schrödinger equation which for a pure threefold potential $[V(\phi) = V_3(1 - \cos 3\phi)/2]$ takes the form of the well known Mathieu equation [1,2]. The solutions allow one to correlate the values of the potential parameter V_3 and the activation energy E (i.e., the energy difference between the top of the barrier and the ground state) with the corresponding value of the ground-state tunnel splitting. Activation energy barriers for methyl side-group rotation in polymers are generally higher than about 600 K [5–7] which should lead to very small values of the ground-state tunnel splitting. The observation of the corresponding tunneling lines by INS techniques would be very difficult. Our recent quasielastic neutron scattering investigation of methyl group rotation in PVAc, by means of time-of-flight (TOF) techniques, has shown that the activation energy barrier is widely distributed with an average value of about 450 K. It is noteworthy that this value is the lowest average barrier to methyl group rotation in any polymeric system reported so far [7]. For a pure threefold potential, this low average barrier yields a ground-state tunnel splitting of about 1.5 μeV, which should be observable by INS.

With these ideas in mind, we have carried out INS measurements on PVAc by means of a high resolution spectrometer. PVAc, $[\text{—CH}_2\text{-CH(OCO—CH}_3)\text{—}]$, is a well known glassy polymer with a glass transition temperature of about 315 K. A flat sample of thickness 0.07 mm was used to get a transmission higher than 90% allowing us to neglect multiple scattering effects. The measurements were carried out by means of the new backscattering spectrometer, IN16 at Institut Laue-Langevin (Grenoble) (ILL), which at an incident wavelength λ of 6.27 Å provides a resolution of nearly Gaussian shape with half width at half maximum of ≈ 0.45 μeV. The experimental spectra $S(Q, \omega)$, where Q and $\hbar\omega$ are the momentum transfer and energy transfer,

respectively, were recorded in the Q range from 0.2 to 1.9 Å^{-1} and in the temperature range from 2.4 to 300 K. The raw data were corrected for detector efficiency, sample container, and absorption using the standard programs available at the ILL.

Figure 1 shows, as an example, the measured $S(Q, \omega)$ at $Q = 1.75$ Å^{-1} and at three temperatures in comparison with the instrumental resolution function. No significant broadening was observed at $T > 150$ K [see Fig. 1(a)] which is in good agreement with our previous TOF results in this temperature range, where a very broad quasielastic (QE) component was observed in the TOF energy window (0.1–2 meV). This QE component would appear as a flat background in the IN16 window (0.5–10 μeV). At lower temperatures a clear QE component starts to develop as Fig. 1(b) shows for 70 K. Surprisingly this QE broadening was found to be present even at the lowest temperature investigated ($T = 2.4$ K). The broadening has been found to be more or less constant up to temperatures ~40 K [see Fig. 1(c)]. A similar temperature dependence was observed for other Q values in the range investigated (0.2 < Q < 1.9 Å^{-1}), although the quasielastic intensity becomes weaker as the Q value decreases. To follow the temperature dependence of the spectra in a more quantitative way and with better statistics, the measured $S(Q, \omega)$ were integrated in two different energy windows, $\pm(1.5$–5.6$)$ μeV and $\pm(5.6$–10$)$ μeV. The obtained integrated inelastic intensities for $Q = 1.75$ Å^{-1} are plotted versus temperature in Fig. 2(a). These intensi-

ties are very low at high temperatures (above 150 K) and then start to increase with decreasing temperature down to 70 K and, thereafter, remain more or less constant. The behavior above 70 K can be interpreted on the basis of a classical hopping motion (see below). However, below 70 K the intensities do not behave as expected from a thermally activated process, for which, at least at a very low temperature, the quasielastic broadening should disappear. These results strongly suggest the existence of quantum motions below 70 K.

The methyl group dynamics in the TOF energy window and in the temperature range from 100 to 240 K was well described [7] in the framework of the rotational rate distribution model (RRDM) previously proposed by us for methyl group hopping processes in polymers [5]. Thus, we can check whether the RRDM can also account for the experimental observations in the different energy range covered by the IN16 spectrometer. The RRDM is based on the fact that the structural disorder inherent to amorphous systems in general, should produce a distribution of potential barriers to methyl group rotation. In this framework, the scattering function $S(Q, \omega)$ is written as

$$S(Q, \omega) \approx e^{-2W}\left\{A(Q)\delta(\omega) + [1 - A(Q)]\sum_{i=1}^{N} g_i L_i(\omega)\right\}. \quad (1)$$

The first term in this equation is the pure elastic component where $A(Q)$ is the elastic incoherent structure factor. For PVAc, taking into account the proportion of the methyl group protons and assuming fixed main
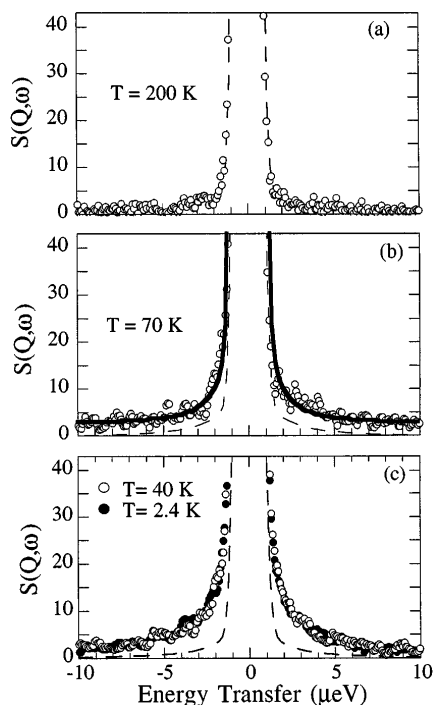

FIG. 1. $S(Q, \omega)$ of PVAc as obtained by IN16 at $Q = 1.75$ Å^{-1} and at the indicated temperatures. The dashed lines represent the instrumental resolution function. The solid line in (b) corresponds to the RRDM fit (see the text).
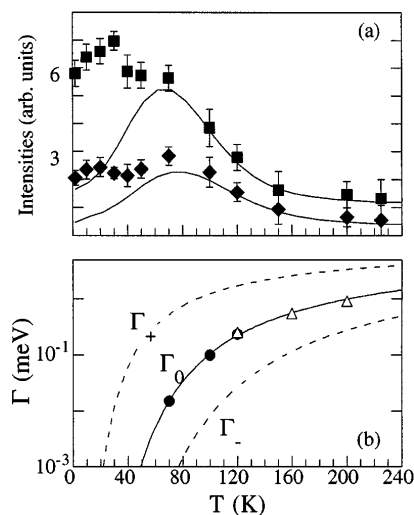

FIG. 2. (a) Measured integrated intensities in the energy ranges: $\pm(1.5 - 5.6)$ μeV (■) and $\pm(5.6 - 10)$ μeV (◆). The solid lines correspond to the RRDM description. (b) Temperature dependence of the jumping rate corresponding to the average energy barrier obtained by fitting the quasielastic spectra as measured by IN16 (●) and by TOF (△). The solid line corresponds to the Arrhenius behavior. The dashed lines represent the jumping rates corresponding to $E_0 \mp \sigma$.

chain atoms and a threefold potential, $A(Q) = 0.529 + 0.157\,[1 + 2j_0(Qr)]$, where $j_0(x)$ is the zeroth-order Bessel function and r is the proton-proton distance in the CH_3 group. The second term in Eq. (1) is the quasielastic part where $L_i(\omega)$ are Lorentzian functions of half width at half maximum Γ_i. The temperature dependence of Γ_i is expressed by an Arrhenius law $\Gamma_i = \Gamma_\infty \exp[-E_i/k_B T]$, where E_i are the activation energy barriers for rotation, k_B the Boltzman constant, and the prefactor Γ_∞ is related to the attempt frequency. A Gaussian distribution of activation energy barriers $g(E)$ given by

$$g(E) = \frac{1}{\sigma_E\sqrt{2\pi}}\exp\!\left[-\frac{(E-E_0)^2}{2\sigma_E^2}\right] \qquad (2)$$

is assumed. Here σ_E is the variance of the distribution function and E_0 the average energy barrier. The weight factors g_i of Eq. (1) are calculated by sampling $g(E)$ for 100 different E_i values equally spaced in the range $0 < E < E_0 + 3\sigma_E$. In Eq. (1) the term e^{-2W} is the Debye-Waller factor, with $W = Q^2\langle u^2\rangle/3$, where $\langle u^2\rangle$ is the mean-squared displacement. The spectra obtained by IN16 at temperatures $T \geq 70$ K and $0.6 < Q < 1.9$ Å^{-1} were analyzed in the framework of the RRDM. The values of the model parameters obtained by a joint analysis of all the Q and T values are $E_0 = 450 \pm 33$ K; $\sigma_E = 250 \pm 10$ K, and $\Gamma_\infty = 9.5 \pm 3.5$ meV. An example of the quality of the RRDM description is shown in Fig. 1(b). Figure 2(b) shows the temperature dependence of Γ_0, i.e., the jumping rate corresponding to the average energy barrier E_0, obtained from the fitting of both sets of data, TOF [7] and IN16. Figure 2(b) also shows the temperature dependence of the jumping rates Γ_+ and Γ_- defined as $\Gamma_\pm = \Gamma_\infty \exp[-(E_0 \pm \sigma_E)/k_B T]$ showing the effect of the energy distribution in the jumping rates. It is evident that the extrapolation to the low temperature range of Γ_0, Γ_+, and Γ_- cannot account for the low temperature results obtained by IN16, where the width of the apparent QE broadening observed was found to be unchanged below 40 K [see Fig. 1(c)]. This finding would imply an almost constant value of Γ_0, Γ_+, and Γ_- in this temperature range. The contribution from the classical hopping processes to the low temperature $S(Q,\omega)$ measured by IN16 can be evaluated by calculating the integrated inelastic intensities, $I(Q,T)$. In the framework of the RRDM, $I(Q,T)$ can be calculated as

$$I(Q,T) = \int_{\omega_1}^{\omega_2}\int_{-\infty}^{\infty} S(Q,\omega')R(Q,\omega-\omega')\,d\omega'\,d\omega\,, \qquad (3)$$

where $S(Q,\omega)$ is the RRDM scattering function [Eq. (1)], $R(Q,\omega)$ is the instrumental resolution function of IN16 spectrometer, and ω_1 and ω_2 define the inelastic window of interest. In the calculations the values of the parameters of the RRDM were fixed to those reported above and $\langle u^2\rangle = 3 \times 10^{-4}$ T was assumed [6]. The resulting behavior is shown in Fig. 2(a) as solid lines. As expected, the agreement found between the measured inelastic in-

tensities and the calculated ones above $\sim$70 K is quite good proving that the dynamics observed by IN16 in this temperature range is fully explained in terms of the methyl group hopping. However, Fig. 2(a) also shows that this classical description breaks down at temperatures below $\sim$70 K. The experimental behavior observed in this low temperature regime should be attributed to the methyl group rotational tunneling. To understand the experimental observations in the quantum regime ($T < 40$ K) in terms of methyl group rotational tunneling, two particular experimental features have to be taken into account. First, instead of well resolved tunneling lines, we have observed an apparent quasielastic behavior [see Fig. 1(c)] which suggests the possibility of a quasicontinuous distribution of tunneling lines. Second, the almost temperature independent behavior observed could indicate that this regime is mainly dominated by ground-state effects.

As mentioned before, the tabulated solutions of the Schrödinger equation [1] allow one to calculate the activation energy barrier and the ground-state tunnel splitting, $\hbar\omega_t$, for a given potential shape. Figure 3 shows the relationship between the values obtained when a pure threefold potential is assumed. In the range of the activation energy which is relevant here ($50 \leq E \leq 1000$ K) an approximated relationship can be established as

$$\hbar\omega_t = a\!\left(\frac{E}{b}\right)^{0.75}\exp\!\left[-\left(\frac{E}{b}\right)^{0.5}\right], \qquad (4)$$

with $a = 1.23$ meV and $b = 4.30$ K (solid line in Fig. 3). It is evident from Eq. (4) that the distribution of activation energies found in the classical regime for PVAc will give rise to a distribution of ground-state tunneling frequencies. This is schematically shown in Fig. 3 by the shaded area which extends in the activation energy range from $E_0 - \sigma_E$ to $E_0 + \sigma_E$. The corresponding distribution of ground-state tunneling frequencies $h(\hbar\omega_t)$ can formally be expressed as

$$h(\hbar\omega_t) = -g(E)\frac{dE}{d(\hbar\omega_t)}\,, \qquad (5)$$
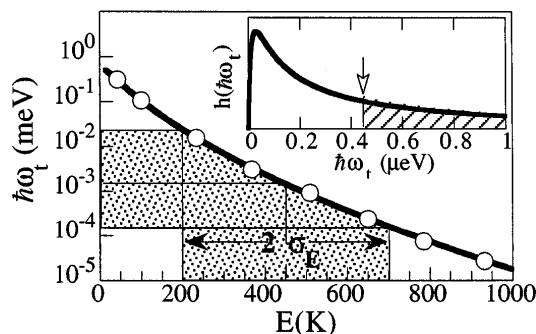

FIG. 3. Ground-state tunneling splitting as a function of the activation energy barrier for a pure threefold potential. The solid line corresponds to Eq. (4). The inset shows the obtained distribution function of tunneling lines. The arrow in the inset marks the IN16 resolution.

where $g(E)$ is the Gaussian distribution function of activation energies given by Eq. (2) and the term $dE/d(\hbar\omega_t)$ can be calculated using Eq. (4). The resulting $h(\hbar\omega_t)$ is shown in the inset of Fig. 3. The most relevant feature is that the symmetrical distribution of activation energies $g(E)$ transforms into a rather asymmetrical distribution of ground-state tunneling frequencies. This distribution does not show any maximum at the tunneling frequency ($\hbar\omega_t \sim 1.5$ μeV) corresponding to $E_0 = 450$ K where $g(E)$ has the maximum value. As can be seen in the inset of Fig. 3, the maximum of $h(\hbar\omega_t)$ is located at a very low value $\hbar\omega_t \sim 0.03$ μeV, which indeed is much lower than the resolution of the IN16 spectrometer (indicated by an arrow in the inset) and thereby could not be resolved from the instrumental resolution. This can explain why we do not observe any peak in the inelastic range of the measured $S(Q, \omega)$ [see Fig. 1(c)]. The apparent quasielastic broadening observed should be explained in terms of the high frequency tail of $h(\hbar\omega_t)$.

In the framework of the simple approach outlined above, the scattering function for quantum tunneling rotation of methyl group is constructed by generalizing the one proposed in Refs. [1] and [2] with a distribution of tunneling frequencies

$$S(Q, \omega) \propto \left\{ \left[\frac{5}{3} + \frac{4}{3} j_0(Qr) \right] \delta(\omega) + \frac{2}{3} [1 - j_0(Qr)] \right.$$
$$\left. \times \sum_{i=1}^{N} h_i [\delta(\omega + \omega_{t_i}) + \delta(\omega - \omega_{t_i})] \right\}. \tag{6}$$

In this equation, the weight factors $h_i \propto h(\hbar\omega_{ti})$ are calculated by means of Eqs. (4) and (5) for the same E_i values used in the classical description [Eqs. (1) and (2)]. Figure 4 shows the $S(Q, \omega)$ calculated using Eq. (6) for $Q = 1.75$ Å^{-1}, and properly convoluted with the IN16 instrumental resolution, in comparison with the measured spectra at 2.4 K. It is evident that the agreement is extremely good taking into account that there are no adjustable parameters. Similar results are obtained for other Q values (0.6 Å^{-1} < Q < 1.9 Å^{-1}) as well. Figure 4 also shows (thin solid lines) the inelastic contributions to $S(Q, \omega)$ given by Eq. (6) once convoluted with the instrumental resolution. It is clear that these inelastic peaks cannot be resolved from the IN16 resolution, and, therefore, an apparent quasielastic feature is observed in $S(Q, \omega)$. A similar behavior is expected for other polymers as well because, independent of the value of the activation energy E_0, the width of the activation energy distribution $g(E)$ is always of the same order [7]. Therefore, the quasi-elastic-like behavior seems to be a characteristic feature of methyl group tunneling in polymers and likely in amorphous systems in general.

In summary, we have reported a clear experimental evidence of quantum rotational tunneling of methyl groups in a polymer, PVAc, by means of INS. To the best of
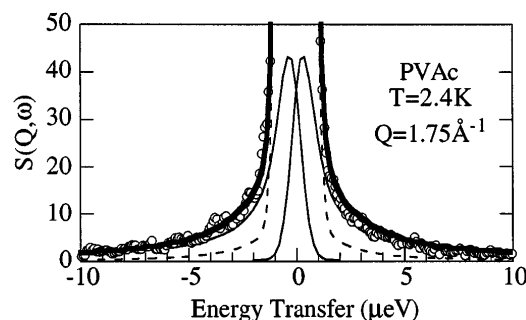

FIG. 4. $S(Q, \omega)$ of PVAc at 2.4 K and $Q = 1.75$ Å^{-1}. The dashed line represents the instrumental resolution. The thick solid line is the result of the calculation based on the model proposed in this work (see the text). The thin solid lines correspond to the inelastic contribution of the rotational tunneling processes.

our knowledge this is the first direct observation of quantum motions in a polymer or in a glassy system. The results obtained have been explained by a simple model which takes into account the distribution of tunneling frequencies deduced from the distribution of energy barriers describing the high temperature classical dynamics. This model can be regarded as an extension of the classical RRDM to the quantum regime. Thus, the methyl group dynamics in glassy polymers is consistently described by a distribution of the barriers for random hopping in the classical regime and by a distribution of the tunneling frequencies in the quantum regime, both having the same physical origin: the distribution of potentials associated with the disorder inherent to the amorphous state. Since the parameters of the model can be determined from the high temperature classical regime, this approach can be used to estimate the possibility of observation of quantum tunneling effects in polymers and glasses by INS. In particular, we "predict" that methyl group tunneling effects in poly(methyl methacrylate) would also be observable as an apparent quasielastic broadening by the IN16 spectrometer. Checking of these predictions is now in progress.

[1] M. Prager and A. Heidemann, "Rotational Tunneling and Neutron Spectroscopy: A Compilation," Chem. Rev. **97**, 2933 (1997).

[2] W. Press, *Single Particle Rotations in Molecular Crystals,* Springer Tracts in Modern Physics Vol. 92 (Springer, Berlin, 1981).

[3] M. J. R. Hoch et al., Macromolecules **4**, 712 (1971).

[4] J. Williams and A. Eisenberg, Macromolecules **11**, 700 (1978).

[5] A. Chahid, A. Alegría, and J. Colmenero, Macromolecules **27**, 3282 (1994).

[6] B. Frick and L. J. Fetters, Macromolecules **27**, 975 (1994).

[7] R. Mukhopadhyay, A. Alegría, J. Colmenero, and B. Frick, Macromolecules (to be published).