

Inelastic neutron scattering study of low energy excitations in glassy 1butene

Osamu Yamamuro, Takasuke Matsuo, Kiyoshi Takeda, Toshiji Kanaya, Tatsuya Kawaguchi, and Keisuke Kaji

Citation: *The Journal of Chemical Physics* **105**, 732 (1996); doi: 10.1063/1.471928

View online: <http://dx.doi.org/10.1063/1.471928>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/105/2?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Inelastic neutron scattering study of low-energy excitations in vapor-deposited glassy propylene](#)

J. Chem. Phys. **106**, 2997 (1997); 10.1063/1.473045

[Microscopic view of glass transition dynamics: A quasielastic neutron scattering study on trans-1,4 polychloroprene](#)

J. Chem. Phys. **105**, 4342 (1996); 10.1063/1.472250

[Impulsive stimulated thermal scattering study of \$\alpha\$ relaxation dynamics and the Debye–Waller factor anomaly in \$\text{Ca}_{0.4}\text{K}_{0.6}\(\text{NO}_3\)_{1.4}\$](#)

J. Chem. Phys. **104**, 5429 (1996); 10.1063/1.471782

[Fast process of amorphous polystyrene below and above the glass transition temperature \$T_g\$ as studied by quasielastic neutron scattering](#)

J. Chem. Phys. **104**, 3841 (1996); 10.1063/1.471037

[Structure and dynamics of undercooled and glassy aqueous ionic solutions by NMR, X-ray and neutron scattering](#)

AIP Conf. Proc. **256**, 89 (1992); 10.1063/1.42462



Inelastic neutron scattering study of low energy excitations in glassy 1-butene

Osamu Yamamuro and Takasuke Matsuo^{a)}

Department of Chemistry and Microcalorimetry Research Center, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

Kiyoshi Takeda

Department of Chemistry, Naruto University of Education, Naruto, Tokushima 772, Japan

Toshiji Kanaya, Tatsuya Kawaguchi, and Keisuke Kaji

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

(Received 6 June 1995; accepted 1 April 1996)

Glassy 1-butene ($\text{CH}_2=\text{CHCH}_2\text{CH}_3$) was studied by incoherent inelastic neutron scattering below 10 meV in the temperature range $18 \leq T \leq 80$ K covering the glass transition temperature ($T_g = 60$ K). A broad excitation peak due to the *low-energy excitation* was found at 3–4 meV. The spectra corrected for the Bose factor could be scaled to a unique curve for temperatures below T_g . The absolute density of vibrational states was derived from the spectrum at 18 K and the previously measured heat capacity data. The number of vibrational states associated with the low energy excitation was 1.4 per molecule. This is much larger than those for SiO_2 and other amorphous materials studied so far. The density of vibrational states was well reproduced by the soft potential model originally conceived for network glasses. © 1996 American Institute of Physics. [S0021-9606(96)50126-1]

I. INTRODUCTION

Low energy excitation in amorphous materials is one of the current topics in condensed matter physics.^{1–4} It is observed as non-Debye excess heat capacities and anomalous thermal conductivities in the temperature range 10–30 K^{5–11} and as a boson peak in the energy range 1–3 meV in inelastic neutron and Raman spectra.^{12–34} Various types of amorphous materials (e.g., network glasses,^{12–21} amorphous metals,²² molecular glasses,^{23–27} glassy polymers^{28–33}) have been studied and several models^{34–44} have been proposed to reproduce their results. However, the origin and the microscopic mechanism of the low energy excitation have not been explained successfully. Empirically, it has been claimed that the intensity of the low energy excitations in the strong glasses (mostly network glasses like SiO_2) is larger than those of the fragile glasses (molecular liquids like *o*-terphenyl).⁴⁵

We performed incoherent inelastic neutron scattering (INS) experiments on glassy 1-butene ($\text{CH}_2=\text{CHCH}_2\text{CH}_3$). The molecular glasses which have been studied in relation to the low-energy excitation have large molecular weights, e.g., *o*-terphenyl ($M=230$)²⁶ and 1,3,5-tri- α -naphthylbenzene ($M=457$),³ or form intermolecular hydrogen bonds, e.g., methanol^{4,25,27} and glycerol.⁴⁵ 1-Butene ($M=56$) has the lowest molecular weight among the molecular liquids which can be vitrified by normal liquid quenching, and being a hydrocarbon, condenses by weak van der Waals interaction. It is of interest to compare the low energy excitation of 1-butene with those of other amorphous materials studied so far.

Our heat capacity study⁴⁶ has shown that 1-butene is vitrified easily by cooling the liquid and also crystallized by annealing the undercooled liquid at around 70 K for 1–2 d. The glass transition and fusion temperatures are 60 and 87.8 K, respectively. The heat capacity of the glassy 1-butene is much larger than that of the crystal at low temperatures around 10 K. This suggests a strong contribution from the low energy excitation in the glassy state even though 1-butene may be a fragile liquid. It is the aim of the present study to analyze the heat capacity data combining with the density of vibrational states derived from the INS experiment. This allows us to determine quantitatively the excess density of states.

II. EXPERIMENT

A. Sample

The commercial reagent of 1-butene (98%, Tokyo Kasei Kogyo Co. Ltd.) was purified by vacuum distillation at 200 K. The liquified 1-butene ($T_b=268$ K) was confined in the concentric double-cylinder aluminum can (115 mm in height, 14.5 mm in the outer diameter of the outer cylinder, 13.5 mm in the outer diameter of the inner cylinder, 0.25 mm in thickness of both cylinders) using an indium gasket. The mass and thickness of the sample were 0.39 g and 0.25 mm, respectively.

B. Neutron scattering measurement

The inelastic neutron scattering (INS) experiment was performed with the inverted geometry time-of-flight (TOF) spectrometer LAM-40⁴⁷ installed at the pulsed spallation cold neutron source in the National Laboratory for High Energy Physics (KEK) in Tsukuba, Japan. The energy resolu-

^{a)} Author to whom correspondence should be addressed.

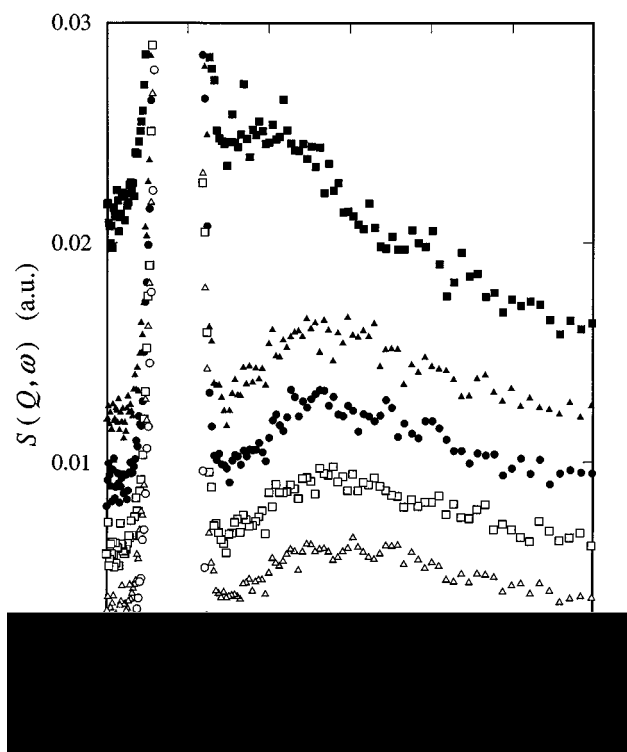


FIG. 1. $S(Q, \omega)$ of 1-butene observed by LAM-40 below and above the glass transition temperature ($=60$ K). The spectra were obtained by summing up six spectra at scattering angles of 24° , 40° , 56° , 72° , 88° , and 104° . The mean Q value is 1.54 \AA^{-1} . The data were corrected using the Debye–Waller factor and symmetrized using the Bose factor. Each spectrum is shifted upward by 0.002 for the sake of clarity. \circ : 18 K, \triangle : 38 K, \square : 45 K, \bullet : 54 K, \blacktriangle : 63 K, \blacksquare : 80 K.

tion was 0.2 meV and the energy window extended to 10 meV . The magnitude of the scattering vector Q at the elastic position ranges from 0.2 to 2.4 \AA^{-1} . The measurement was carried out at 18 , 38 , 45 , 54 , 63 , and 80 K covering the glass transition temperature $T_g = 60 \text{ K}$.

In the present measurement of 1-butene, the observed neutron cross section was dominated by incoherent scattering from hydrogen atoms. This is because 1-butene contains only H and C atoms, and the incoherent atomic cross section of hydrogen is much larger than the incoherent and coherent atomic cross section of carbon and the coherent cross section of hydrogen.⁴⁸

III. RESULTS AND DISCUSSION

A. Boson peak

The LAM-40 spectrometer collects the scattered intensity at six scattering angles 24° , 40° , 56° , 72° , 88° , and 104° corresponding to different scattering vectors. The shape of spectra, including the position of the peak due to the low energy excitation described later, did not depend on the scattering angles within the experimental precision. Therefore, they were added together to produce the Q -independent INS spectrum. The mean Q value was 1.54 \AA^{-1} . Figure 1 shows the incoherent inelastic scattering functions $S(Q, \omega)$ of 1-butene from the INS spectra for different temperatures.

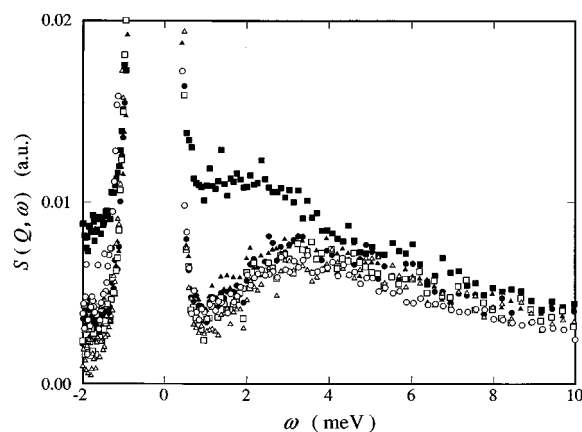


FIG. 2. $S(Q, \omega)$ spectra of 1-butene reduced to the values at 60 K ($= T_g$) by using the Bose factor. \circ : 18 K, \triangle : 38 K, \square : 45 K, \bullet : 54 K, \blacktriangle : 63 K, \blacksquare : 80 K.

The data were corrected using the Debye–Waller factor and symmetrized using the Bose factor. Each spectrum was shifted upward by 0.01 for the sake of clarity. One recognizes a peak attributed to the total low energy excitation at around 3 meV . At 80 K where the sample was a supercooled liquid; a quasielastic scattering (due to the fast β process) contributed significantly near the elastic peak.

In order to compare the spectra collected at different temperatures, they were adjusted to 60 K ($\approx T_g$) by multiplication of appropriate Bose factors and plotted in Fig. 2. The positions of the low energy excitation peaks did not depend on the temperature and the intensity of every peak except that at 80 K could be well scaled by the Bose factor.

It has been claimed that the larger the fragility is, the weaker is the boson peak.⁴⁵ The ratio I_{\min}/I_{\max} at T_g , where I_{\min} is the minimum value of the scattered intensity close to the elastic peak and I_{\max} the maximum value of the inelastic peak, was used as a measure of the relative contribution of the boson peak to the fast β relaxation.⁴⁵ This ratio was 0.55 for 1-butene. This value is comparable with the value (0.50) of SiO_2 of a typical strong glass and much smaller than the value (1.00) of o -terphenyl of a typical fragile glass.

Since the fragility of 1-butene is not known, we estimated it from the temperature dependence of the structural relaxation times τ in the Adam–Gibbs form

$$\tau = \tau_0 \exp(A/TS_c), \quad (1)$$

where A is a constant related to the activation energy and τ_0 is a frequency factor. The temperature dependence of the configurational entropy S_c was calculated from the calorimetric data.⁴⁶ The constant A was evaluated to be 47.3 kJ mol^{-1} by substituting $\tau_0 = 10^{-13} \text{ s}$ and the appropriate values for S_c ($=21.4 \text{ J K}^{-1} \text{ mol}^{-1}$) and τ ($=10^3 \text{ s}$) at T_g into Eq. (1). The calculated $\log(\tau/s)$ were plotted as a function of T_g/T in Fig. 3 (Angell plot^{49,50}). The fragility m defined by

$$m \equiv \left. \frac{d \log \tau}{d(T_g/T)} \right|_{T=T_g} \quad (2)$$

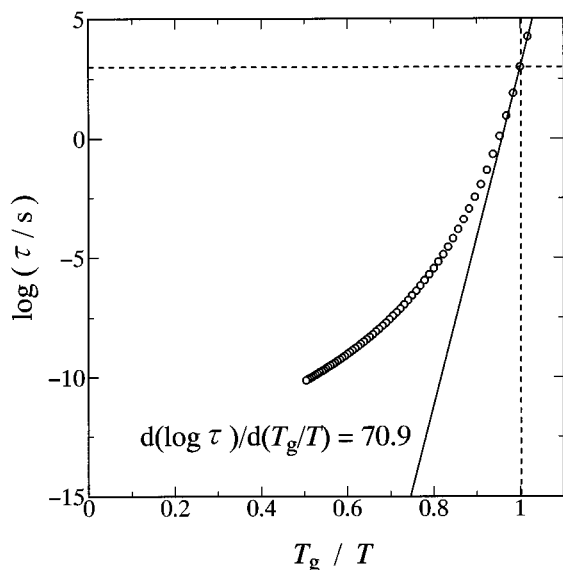


FIG. 3. Angell plot ($\log(\tau/s)$ vs T_g/T) of 1-butene. The plotted data were calculated from the calorimetric data and Adam–Gibbs relation (see the text for the details). The solid line represents the slope at T_g , corresponding to the fragility of 71.

was calculated to be 71 from the slope of the curve at T_g in Fig. 3. 1-Butene was thus confirmed to be quite a fragile liquid as expected from the intermolecular-bond nature; cf. *o*-terphenyl ($m=81$) and SiO_2 ($m=20$).⁵¹ We have thus an intense boson peak on the one hand and a high fragility on the other. These have previously been believed incompatible in a compound. The different behaviors can be attributed to the difference in molecular weight and structure between 1-butene and *o*-terphenyl; i.e., the unit constituting a molecule is methyl and methylene groups for 1-butene ($M=56$) and phenyl group for *o*-terphenyl ($M=230$). The number of flexible modes per atom in 1-butene, including the overall rotation, is larger than that in *o*-terphenyl. The previously believed empirical relation may hold for a limited group of substances to which 1-butene does not belong.

B. Density of vibrational states

The incoherent inelastic scattering function $S(Q, \omega)$ at 18 K was converted to a relative density of vibrational states, $G_a(\omega)$. Magnitude of the correction for the Debye Waller factor was less than 3% of $G_a(\omega)$ at 3 meV where the Boson peak occurred. The absolute value of the density of vibrational states per molecule of 1-butene, $G(\omega)$, is related to the relative density of states by

$$G(\omega) = bG_a(\omega). \quad (3)$$

The normalization factor b was determined from the low temperature heat capacity data⁴⁶ by the following method.

In the low energy region relevant to the present problem, $G(\omega)$ is assumed to consist of the terms representing the low energy excitation $G_{\text{LEE}}(\omega)$ and the Debye vibration $G_{\text{Debye}}(\omega)$,^{30–32,40,41}

$$G(\omega) = G_{\text{LEE}}(\omega) + G_{\text{Debye}}(\omega). \quad (4)$$

$G_{\text{Debye}}(\omega)$ is given by

$$G_{\text{Debye}}(\omega) = a\omega^2 \quad (\omega \leq \omega_D) \\ = 0 \quad (\omega > \omega_D), \quad (5)$$

where a is a constant and ω_D is the Debye frequency. These are related by the normalization condition

$$\omega_D = (9/a)^{1/3}. \quad (6)$$

ω_D was assumed to be 11.2 meV (130 K), which is the value for crystalline 1-butene calculated from the heat capacity data.⁴⁶ The difference in ω_D between the glassy and crystalline states is usually less than 5% and neglected in the following analysis. The parameter a was determined to be $6.41 \times 10^{-3} \text{ meV}^{-3}$ from Eq. (6).

The molar heat capacity C_p is related to the density of vibrational states by

$$C_p/R = \int_0^\infty E(\omega)G(\omega)d\omega \quad (7) \\ = \int_0^\infty E(\omega)G_{\text{LEE}}(\omega)d\omega + \int_0^{\omega_D} E(\omega)G_{\text{Debye}}(\omega)d\omega, \quad (8)$$

where $E(\omega)$ is the Einstein function. From Eqs. (3)–(5), $G_{\text{LEE}}(\omega)$ is given by

$$G_{\text{LEE}}(\omega) = bG_a(\omega) - a\omega^2. \quad (9)$$

In order to perform integration of $G_{\text{LEE}}(\omega)$ over ω including the region below 0.7 meV and above 10 meV, it was necessary to fit $G_{\text{LEE}}(\omega)$ by a closed-form function of ω . Functional representation also helps in reducing the effect of random errors in the $G_a(\omega)$ data. The function need not have a physical interpretation and may involve as many parameters as are appropriate. We used a flexible function

$$G_{\text{LEE}}(\omega) = \frac{n}{(\omega_0^2/\omega^2 + 1)} \exp[-(\omega - \mu)^2/2\sigma_L] \quad (\omega \leq \mu), \\ = \frac{n}{(\omega_0^2/\omega^2 + 1)} \exp[-(\omega - \mu)^2/2\sigma_H] \quad (\omega > \mu). \quad (10)$$

This is a modified Gaussian function in which n is a scale factor, μ the energy of the peak top, σ_L and σ_H the half-widths at half maximum on the lower and higher sides of the peak top, respectively. The pre-exponential factor $1/(\omega_0^2/\omega^2 + 1)$ was introduced to make the function approach the Debye function [$G_{\text{LEE}}(\omega) \propto \omega^2$] near $\omega=0$.

The unknown parameters in Eqs. (9)–(10) were determined by the least-squares fitting as follows. Equation (10) was first fitted to the $G_{\text{LEE}}(\omega)$ calculated by Eq. (9) for an arbitrarily chosen b value using n , σ_L , σ_H , and ω_0 as adjustable parameters and then the heat capacities calculated by Eq. (8) was compared with the experimental heat capacities in the temperature range between 5 and 25 K. This procedure was repeated for various b values to find the best fit for both $G(\omega)$ and C_p data. The best fit parameters were as follows:

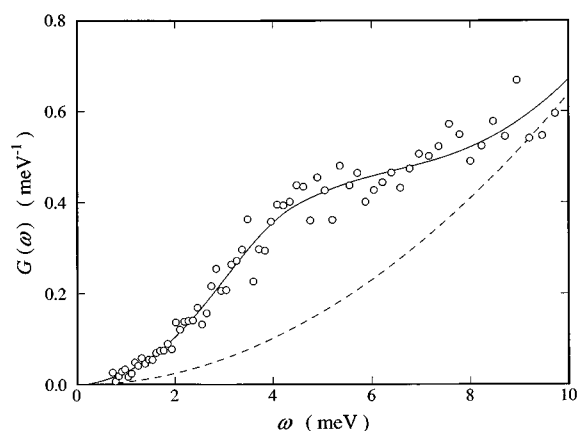


FIG. 4. Density of vibrational states of 1-butene obtained from $S(Q, \omega)$ spectrum at 18 K and the low temperature heat capacity. The solid line represents the result of the fitting and the dashed line the Debye part (see the text for the details).

$b=0.032 \text{ meV}^{-1}$, $n=0.270 \text{ meV}^{-1}$, $\mu=4.49 \text{ meV}$, $\sigma_L=1.63 \text{ meV}$, $\sigma_H=4.49 \text{ meV}$, and $\omega_0=0.48 \text{ meV}$. There are six adjustable parameters in this fitting, and may give an impression that they are difficult to determine accurately. Actually it is not so, because μ , σ_L , and σ_H were quite independent of each other and independent of the other three parameters, and b is only slightly correlated to n . Only the correlation between n and ω_0 was substantial but their standard deviations are still less than 10% of their values.

Figure 4 shows the plot of $G(\omega) [= bG_a(\omega)]$ thus obtained. The solid and dashed lines represent the calculated value of $G(\omega)$ and $G_{\text{Debye}}(\omega)$, respectively, showing a satisfactory result of the fitting. Figure 5 shows the experimental molar heat capacities of glassy (open circles) and crystalline (closed circles) 1-butene.⁴⁶ The solid line represents the result of the fitting described above. The agreement between the experiment and theory is satisfactory up to ca. 20 K. The deviation becomes larger in the high temperature region.

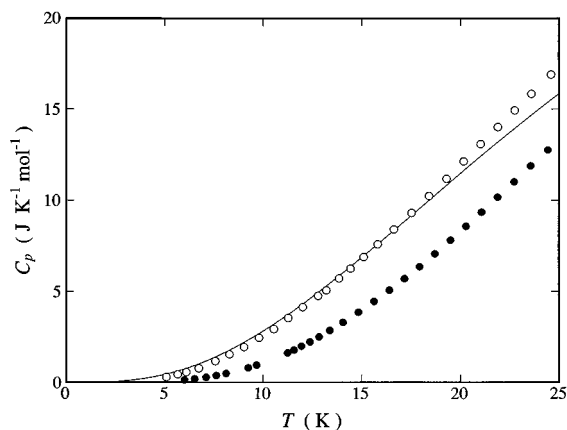


FIG. 5. Low temperature heat capacities of 1-butene (Ref. 46). Open circles represent the heat capacities of the glassy state and the closed circles those of the crystalline state. The solid line represents the result of the fitting corresponding to the solid line in Fig. 4.

This is not because Eq. (10) is inadequate but because the contribution from the vibrational modes which appear above 10 meV (116 K) was not included in this calculation and may become significant at higher temperatures.

The number of the extra modes N_{LEE} for a 1-butene molecule is given by

$$N_{\text{LEE}} = \int_0^{\infty} G_{\text{LEE}}(\omega) d\omega \quad (11)$$

and equal to 1.40/molecule, corresponding to 0.35/carbon atom and 0.12/atom. This value is considerably larger than the corresponding value for SiO_2 and Se glasses (ca. 0.02/atom).⁴¹

In the analysis presented above, it has been assumed that the normal vibrational density of states is represented by the Debye model and that the extra states are simply added to it. The assumption of the Debye model is acceptable for long wave vibrations since macroscopic elastic properties of crystalline and glassy states of a substance do not differ much. However, this assumption may not hold at shorter wavelengths where the dispersion curve approaches the zone boundaries or meets rotational modes coming down from the high frequency range. Nevertheless, we assume the Debye spectrum for the entire frequency region in order to extract the excess part due to the low energy excitation and to facilitate the analysis with the soft potential model described below. Note, however, that the number of states below ω_D ($=11.2 \text{ meV}$) is 4.40, which is significantly larger than 3, independently of the validity of the Debye model and the additivity between the normal acoustic vibration and the excess low energy excitation. Some vibrational mode other than the translational one should be involved in $G(\omega)$ below ω_D .

C. Soft potential model

At present, the best model to describe various anomalous physical properties due to the low energy excitation is the soft potential model developed by Buchenau *et al.*³⁹⁻⁴¹ This model, though phenomenological, can reproduce the anomalies in density of vibrational states, heat capacity, and thermal conductivity of network glasses in the low energy (temperature) region. The potential of the soft mode is given by

$$V(x) = W(D_1 x + D_2 x^2 + x^4), \quad (12)$$

where x is the displacement and W the constant energy characterizing the system. D_2 characterizes the small positive or negative restoring force and D_1 describes the asymmetry of the potential. Assuming that different values of D_1 and D_2 are distributed in the glasses, one obtains a broad distribution of soft modes ranging from tunneling to vibrational states. The distribution function $P(D_1, D_2)$ is independent of D_2 and Gaussian in D_1 with the center at zero

$$P(D_1, D_2) = P_s \exp(-AD_1^2), \quad (13)$$

where A can be related to the thermal strain which occurs below glass transition temperature T_g .⁵² Based on these as-

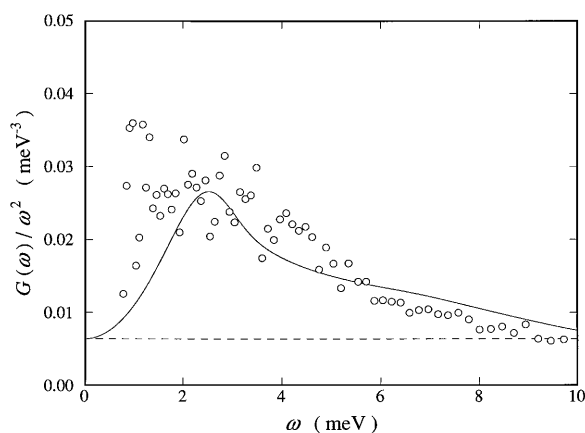


FIG. 6. Density of vibrational states divided by ω^2 . The solid line represents the result of the fitting in terms of the soft potential model and the dashed line the Debye part determined by the fitting shown in Fig. 4.

sumptions, Ramos *et al.*⁴¹ have derived a simple form of the density of vibrational state $G_{\text{LEE}}(\omega)$ of the soft modes in the following form:

$$G_{\text{LEE}}(\omega)/\omega^2 = \frac{1}{8}(P_s/W^5)\omega^2 \times \int_0^1 \exp[-5.41(\omega/\omega_{\text{max}})^6 t^2(1-t^2)^2] dt. \quad (14)$$

Here, the unit of ω is meV and $G_{\text{LEE}}(\omega)$ is given as the number of states per particle and per meV.

With ω_{max} and P_s/W^5 as adjustable parameters, Eq. (14) was fitted to the experimentally obtained $G_{\text{LEE}}(\omega)/\omega^2$. Figure 6 shows the result of the fitting; the solid and dashed lines represent the calculated values of $G_{\text{LEE}}(\omega)/\omega^2$ and $G_{\text{Debye}}(\omega)/\omega^2$, respectively. The fitted curve reproduces the general energy dependence of the low energy excitation; i.e., a peak with a long tail on the high energy side. The best fit parameters are as follows: $\omega_{\text{max}} = 2.53$ meV and $P_s/W^5 = 3.67 \times 10^{-2}$ meV⁻⁵. For glasses at low temperatures, a minimum and a maximum ($T_{\text{min}} < T_{\text{max}}$) appears in the plot of C_p/T^3 corresponding to the effects of the tunneling and excess vibrational states due to the soft modes, respectively. In the soft potential model, T_{max} is related to ω_{max} by the relation

$$k_B T_{\text{max}} = 2.20 \times 10^{-4} \omega_{\text{max}}, \quad (15)$$

where k_B is the Boltzmann constant (8.61×10^{-5} eV K⁻¹). The T_{max} calculated from ω_{max} was 6.5 K, which is close to the experimental value of 8.0 K.⁴⁶ Since T_{min} of 1-butene was lower than the lowest temperature of the C_p measurement (5 K), it was calculated from the empirical relation⁴⁵

$$T_{\text{min}} = 0.914 T_g^{-1/3} T_{\text{max}}^{4/3} \quad (16)$$

to be 3.74 K using $T_g = 60$ K and $T_{\text{max}} = 8.0$ K. On substitution of this value into

$$W = 1.8 k_B T_{\text{min}} \quad (17)$$

in the soft potential model, W was found to be 0.58 meV, giving $P_s = 2.41 \times 10^{-3}$. The corresponding quantities of SiO₂ glass are $W = 0.33$ meV and $P_s = 1.5 \times 10^{-6}$ (Ref. 41). W is approximately the same but P_s of 1-butene is much larger than that of SiO₂ glass, in agreement with the large excess density of states obtained in the previous section. It is interesting that the low energy excitation of 1-butene is roughly reproduced by the soft potential model originally conceived for network glasses.

D. Origin of the low energy excitations

One may ask where the extra 1.40 modes per molecule in glassy 1-butene come from. We propose that the origin of the low energy excitation is the softening of the rigid-body rotational mode of molecule, whose frequency is around 10–30 meV in simple molecular crystals. The softening may be caused by frozen density fluctuations and local strain fields in the amorphous structure. It is also possible that the methylene rotation, though their frequencies are usually higher than that of the overall rotation, is involved in the low energy excitation. Other internal degrees of freedom (methyl rotation, C–H stretching, C–C stretching and bending modes) are at higher energies and thus cannot take part in the low energy excitation. In the crystalline state, the rigid body rotations and internal rotations are localized motions with little wavelength dependence. The present conjecture for the mechanism of the low energy excitation assumes that the energy of some of these modes is as small as 3 meV. An alternative model, in which one may attribute the low energy excitation entirely to the translational mode, is not acceptable because the number of states below ω_D (4.40) is much larger than 3.

It was demonstrated that 10–100 atoms move together in a single soft mode in the molecular dynamics simulations for glassy methanol,⁵³ selenium,⁵⁴ and even for simple soft-sphere glass.^{55,56} In 1-butene, however, this picture is not acceptable considering the fact that the number of the states associated with the low energy excitation is as large as 1.4 per molecule. The intermolecular interaction in molecular glasses is weaker and more isotropic than those of the network glasses, and so it is inconceivable that such a large-scale group motion sustain itself in molecular glasses. Actually any collective motion or domainlike structure of more than ten molecules has not been observed in molecular glasses. We suppose that the soft mode in molecular glasses is associated with the motion of a single molecule or at most a few molecules.

The INS experiment in the energy range higher than 10 meV is desirable because it will allow investigation of the density of states for the rotational modes of the molecule and critically test the validity of our model. It is also desirable to investigate other molecular glasses homologous to the present one and others containing phenyl and hydroxyl groups.

ACKNOWLEDGMENT

Contribution No. 120 from the Microcalorimetry Research Center.

- ¹ *Amorphous Solids—Low-temperature Properties*, edited by W. A. Phillips (Springer, Berlin, 1981).
- ² W. A. Phillips, *Rep. Prog. Phys.* **50**, 1657 (1987).
- ³ U. Buchenau, in *Dynamics of Disorder Materials*, edited by D. Richter, A. J. Dianoux, W. Petry, and J. Teixeira (Springer, Berlin, 1989).
- ⁴ U. Buchenau, in *Phase Transitions and Relaxation in Systems with Competing Energy Scales*, edited by T. Riste and D. Sherrington (Kluwer, Dordrecht, 1993).
- ⁵ R. C. Zeller and R. O. Pohl, *Phys. Rev. B* **4**, 2029 (1971).
- ⁶ R. O. Pohl and E. T. Swartz, *J. Non-Cryst. Solids* **76**, 117 (1985).
- ⁷ R. B. Stephens, *Phys. Rev. B* **8**, 2896 (1973).
- ⁸ R. B. Stephens, *Phys. Rev. B* **13**, 852 (1976).
- ⁹ D. P. Jones and W. A. Phillips, *Phys. Rev. B* **27**, 3891 (1983).
- ¹⁰ J. J. Freeman and A. C. Anderson, *Phys. Rev. B* **34**, 5684 (1986).
- ¹¹ M. García-Hernández, R. Burriel, F. J. Bermejo, C. Piqué, and J. L. Martínez, *J. Phys. Condens. Matter* **4**, 9581 (1992).
- ¹² U. Buchenau, N. Nücker, and A. J. Dianoux, *Phys. Rev. Lett.* **53**, 2316 (1984).
- ¹³ A. J. Dianoux, U. Buchenau, M. Prager, and N. Nücker, *Physica B* **138**, 264 (1986).
- ¹⁴ U. Buchenau, M. Prager, N. Nücker, A. J. Dianoux, N. Ahmad, and W. A. Phillips, *Phys. Rev. B* **34**, 5665 (1986).
- ¹⁵ U. Buchenau, H. M. Zhou, N. Nücker, K. S. Gilroy, and W. A. Phillips, *Phys. Rev. Lett.* **60**, 1318 (1988).
- ¹⁶ U. Buchenau, M. Prager, W. A. Kamitakahara, H. R. Shanks, and N. Nücker, *Europhys. Lett.* **6**, 695 (1988).
- ¹⁷ W. A. Phillips, U. Buchenau, N. Nücker, A. J. Dianoux, and W. Petry, *Phys. Rev. Lett.* **63**, 2381 (1989).
- ¹⁸ V. K. Malinovsky, V. N. Novikov, P. P. Parshin, A. P. Sokolov, and M. G. Zemlyanov, *Europhys. Lett.* **11**, 43 (1990).
- ¹⁹ U. Buchenau, *Physica B* **174**, 131 (1991).
- ²⁰ M. García-Hernández, F. J. Bermejo, B. Fåk, J. L. Martínez, E. Enciso, N. G. Almarza, and A. Criado, *Phys. Rev. B* **48**, 149 (1993).
- ²¹ A. P. Sokolov, A. Kisliuk, and D. Quitmann, *Phys. Rev. B* **48**, 7692 (1993).
- ²² J.-B. Suck, H. Rudin, H.-J. Güntherodt, and H. Beck, *Phys. Rev. Lett.* **50**, 49 (1983).
- ²³ A. J. Dianoux, J. N. Page, and H. M. Rosenberg, *Phys. Rev. Lett.* **58**, 886 (1987).
- ²⁴ F. J. Bermejo, J. L. Martínez, M. García-Hernández, D. Martín, F. J. Mompeán, J. Alonso, and W. S. Howells, *Europhys. Lett.* **15**, 509 (1991).
- ²⁵ F. J. Bermejo, J. Alonso, A. Criado, F. J. Mompeán, J. L. Martínez, M. García-Hernández, A. Chahid, *Phys. Rev. B* **46**, 6173 (1992).
- ²⁶ J. Wuttke, M. Kiebel, E. Bartsch, F. Fajara, W. Petry, and H. Sillescu, *Z. Phys. B* **91**, 357 (1993).
- ²⁷ F. J. Bermejo, A. Criado, M. García-Hernández, J. Alonso, C. Prieto, and J. L. Martínez, *J. Phys. Condens. Matter* **6**, 405 (1994).
- ²⁸ H. M. Rosenberg, *Phys. Rev. Lett.* **54**, 704 (1985).
- ²⁹ T. Kanaya, K. Kaji, S. Ikeda, and K. Inoue, *Chem. Phys. Lett.* **150**, 334 (1988).
- ³⁰ K. Inoue, T. Kanaya, S. Ikeda, K. Kaji, K. Shibata, M. Misawa, and Y. Kiyonagi, *J. Chem. Phys.* **95**, 5332 (1991).
- ³¹ T. Kanaya, K. Kaji, and K. Inoue, *Physica B* **180 & 181**, 814 (1992).
- ³² T. Kanaya, T. Kawaguchi, and K. Kaji, *J. Chem. Phys.* **98**, 8262 (1993).
- ³³ U. Buchenau, C. Schönefeld, D. Richter, T. Kanaya, K. Kaji, and R. Wehrmann, *Phys. Rev. Lett.* **73**, 2344 (1994).
- ³⁴ E. Rössler, A. P. Sokolov, A. Kisliuk, and D. Quitmann, *Phys. Rev. B* **49**, 14967 (1994).
- ³⁵ U. Buchenau, *Solid State Commun.* **56**, 889 (1985).
- ³⁶ A. J. Sievers and S. Takeno, *Phys. Rev. B* **39**, 3374 (1989).
- ³⁷ U. Buchenau, Yu. M. Galperin, V. L. Gurevich, and H. R. Schober, *Phys. Rev. B* **43**, 5039 (1991).
- ³⁸ J. P. Sethna, E. R. Grannan, and M. Randeria, *Physica B* **169**, 316 (1991).
- ³⁹ U. Buchenau, Yu. M. Galperin, V. L. Gurevich, D. A. Parshin, M. A. Ramos, and H. R. Schober, *Phys. Rev. B* **46**, 2798 (1992).
- ⁴⁰ L. Gil, M. A. Ramos, A. Bringer, and U. Buchenau, *Phys. Rev. Lett.* **70**, 182 (1993).
- ⁴¹ M. A. Ramos, L. Gil, A. Bringer, and U. Buchenau, *Phys. Stat. Sol. A* **135**, 477 (1993).
- ⁴² D. A. Parshin, X. Liu, O. Brand, and H. V. Löhneysen, *Z. Phys. B* **93**, 57 (1993).
- ⁴³ F. J. Bermejo, A. Criado, and J. L. Martínez, *Phys. Lett. A* **195**, 236 (1994).
- ⁴⁴ V. N. Novikov, E. Duval, A. Kisliuk, and A. P. Sokolov, *J. Chem. Phys.* **102**, 4691 (1995).
- ⁴⁵ A. P. Sokolov, E. Rössler, A. Kisliuk, and D. Quitmann, *Phys. Rev. Lett.* **71**, 2062 (1993).
- ⁴⁶ K. Takeda, O. Yamamuro, and H. Suga, *J. Phys. Chem Solids* **52**, 607 (1991).
- ⁴⁷ K. Inoue, Y. Ishikawa, N. Watanabe, K. Kaji, Y. Kiyonagi, H. Iwasa, and M. Kohgi, *Nucl. Instrum. Method A* **238**, 401 (1984).
- ⁴⁸ G. E. Bacon, *Neutron Diffraction* (Clarendon, Oxford, 1975).
- ⁴⁹ C. A. Angell, *J. Non-Cryst. Solids* **102**, 205 (1988).
- ⁵⁰ C. A. Angell, in *Relaxations in Complex Systems*, edited by K. L. Ngai and G. B. Wright (Naval Research Laboratory, Washington, 1984).
- ⁵¹ R. Böhmer, K. L. Ngai, C. A. Angell, and D. J. Plazek, *J. Chem. Phys.* **99**, 4201 (1993).
- ⁵² L. Ferrari, W. A. Phillips, and G. Russo, *Europhys. Lett.* **3**, 611 (1987).
- ⁵³ J. Alonso, F. J. Bermejo, M. García-Hernández, J. L. Martínez, W. S. Howells, and A. Criado, *J. Chem. Phys.* **96**, 7696 (1992).
- ⁵⁴ F. J. Bermejo, E. Enciso, A. Criado, J. L. Martínez, and M. García-Hernández, *Phys. Rev. B* **49**, 8689 (1994).
- ⁵⁵ B. B. Laird and H. R. Schober, *Phys. Rev. Lett.* **66**, 636 (1991).
- ⁵⁶ H. R. Schober and B. B. Laird, *Phys. Rev. B* **44**, 6746 (1991).