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Molecular Conformation of Butanenitrile in Gas, Liquid, Glass, and Crystalline States: In Relation to the Stability of the Glass State

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Molecular conformation of butanenitrile in gas, liquid, glass, and crystalline states was studied to clarify the cause of the stability of its glass state against crystallization. The crystal comprises *gauche* molecules. However, the *trans* and *gauche* conformations have energies very close to each other, with an in-between energy barrier that cannot be surmounted at low temperatures. The multiple conformation that exists in gas and liquid is frozen in the glass, keeping the glass of butanenitrile in the disordered state even at temperatures as high as 100 K.

We have studied by Raman scattering and X-ray diffraction the structure and structural relaxation of amorphous molecular systems made up of simple molecules such as benzene or naphthalene.[1—3)#] For preparing amorphous states with these molecules, we employed the method of vacuum deposition of the vapor on cold substrates. The samples were films with the thickness of about 10 μm, and their initial structures on deposition are considered to be highly disordered. It has been found that the amorphous films thus prepared undergo crystallization without manifesting the glass transition. The high enthalpy expected for the highly-disordered vapor-deposited amorphous state has been pointed out to allow the local molecular relaxation in the solid state, causing the crystallization.[4,5)]

Hikawa et al.[6)] found that butanenitrile (C_3H_7CN, conventionally called butyronitrile) is one of the novel examples of simple organic compounds that manifest the glass transition in the vapor-deposited sample. The melting point of butanenitrile is 161.3 K,[7)] and the glass-transition temperature T_g was reported to be 97 K.[6)] This T_g is comparable to the crystallization temperature T_{cryst} of amorphous monosubstituted benzenes, the molecular sizes of which are larger than that of butanenitrile. On the basis of the results of calorimetry, Hikawa et al. showed that a large enthalpy relaxation takes place before the glass transition. However, the glass does not undergo crystallization. It is therefore interesting to study the factor that stabilizes the glass of this compound at temperatures as high as 100 K.

Butanenitrile molecules take the *trans* or *gauche* conformations, the energies of which have been inferred to be close to each other.[8,9)] It has also been inferred from the infrared spectroscopy results that both the *trans* and *gauche* conformations exist in the glass state prepared at the liquid-nitrogen temperature, and that there exists only the *gauche* conformation in the crystal.[10,11)] However, the data accumulated hitherto on the properties of butanenitrile are fragmentary. We considered it important to make a collective interpretation of the stability of the glass state of butanenitrile, especially by establishing (1) the energetic relationship between the *trans* and *gauche* conformations of the molecule, (2) the molecular structure in the crystal, and (3) the molecular-structure evolution during the annealing of the glass.

We thus performed the molecular-orbital calculation of butanenitrile with several methods and the crystal-structure analysis by X-ray diffraction. We also performed careful Raman measurements on various states of butanenitrile, and recorded the spectral evolution due to the temperature change. In this paper, we summarize the results of these studies, and discuss the stability of the glass of butanenitrile.

Experimental

(i) Molecular Orbital Calculations. Molecular orbital calculations were carried out with several methods. The MOPAC[12)] program was used for examining the torsion-angle dependence of the enthalpy of formation. The GAUSSIAN 94[13)] program was used with several levels of basis sets for the calculation of the energies of the *trans* and *gauche* conformations.

(ii) X-Ray Analysis of Crystal Structure. Butanenitrile purchased from Tokyo Chemical Industry was distilled after dehydration with molecular sieves. A small amount of the sample thus treated was poured into a glass capillary with the diameter of 0.7 mm, and was mounted on the diffractometer. The sample was cooled down with cold nitrogen gas until polycrystals appeared. The polycrystalline sample was warmed up at the rate of 10 K $\min^{-1}$ to the melting point, and then was cooled down at 3 K h^{-1} to the

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In this paper, the term "amorphous" means structurally non-crystalline in general, and "glass" means a non-crystalline material for which the thermodynamical glass transition has been observed.

temperature lower by 20 K below the melting point. After several cycles of the heating-up and cooling-down processes, a cylindrical single crystal was obtained in the glass capillary.

The non-screen Weissenberg measurement[14] was performed at 123 K. The crystal data and the experimental details are summarized in Table 1. The structure was solved with the program SHELXS-86,[15] and refined by the full-matrix least-squares with the program SHELXL-93.[16] Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located on a difference-Fourier synthesis and refined with appropriate isotropic temperature factors. The atomic scattering factors were taken from International Table for Crystallography.[17] The final atomic parameters are given in Table 2. Lists of the observed and calculated structure factors and the anisotropic temperature factors for non-hydrogen atoms are deposited as Document No. 70034 at the Office of the Editor of Bull Chem. Soc. Jpn.

(iii) Raman Spectra Measurements. The optical system for Raman measurements was essentially the same as in our previous studies.[1] The 514.5 nm radiation from an Ar^+-ion laser was used for the excitation.

Raman spectra in the liquid and polycrystalline states were measured for the sample sealed in a glass tube. The sample temperature was controlled using a cryostat (Oxford, DN1704) in which the sample tube was held in a nitrogen atmosphere cooled with liquid nitrogen. The laser light was introduced through the glass wall of the tube, and the Raman light was detected at a right angle. The spectra were recorded in a sequence from the room-temperature liquid to the low-temperature crystal state by lowering the temper-

Table 1. Crystal Data and Experimental Details

Chemical formula	C_4H_7N
Chemical formula weight	69.11
Crystal system	Monclinic
Space group	$P2_1/a$
a/Å	8.5443(3)
b/Å	6.5446(5)
c/Å	8.7946(6)
$\beta/°$	114.136(5)
V/Å^3	448.79(5)
Z	4
D_X/Mg m^{-3}	1.023
$F(000)$	152
Radiation type	Mo $K\alpha$
Wavelength/Å	0.71069
μ/mm^{-1}	0.062
Temperature/K	123
Crystal form	Cylindrical
Crystal color	Transparent
Diffractometer	Rigaku R-AXIS-II-CS
Data collection method	Weissenberg
Absorption correction	None
No. of measured reflections	3481
No. of independent reflections	1012
No. of observed reflections	930
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.0513
$\theta_{\max}/°$	27.55
Range of h,k,l	$-10 \rightarrow 10$ $-8 \rightarrow 8$ $-11 \rightarrow 11$
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0435
$wR(F^2)$	0.1127
S	1.104
No. of reflections used in refinement	3481
No. of parameters used	68
Weighting scheme	$w = 1/[\sigma^2(F^2)+(0.0579P)^2+0.0556P]$, where $P = (F_o^2+2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.001
$\Delta\rho_{\max}$/e Å^{-3}	0.243
$\Delta\rho_{\min}$/e Å^{-3}	−0.184
Extinction correction	SHELXL-93
Extinction coefficient	1.4672(961)

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2)

Atom	x	y	z	U_{eq}[a] or U_{iso}
N1	0.5633(1)	0.2019(1)	0.1758(1)	0.0471
C1	0.5647(1)	−0.2749(2)	0.4112(1)	0.0425
C2	0.4284(1)	−0.2821(1)	0.2341(1)	0.0336
C3	0.3430(1)	−0.0755(2)	0.1724(1)	0.0363
C4	0.4656(1)	0.0814(1)	0.1734(1)	0.0353
HC1A	0.614(2)	−0.412(2)	0.446(2)	0.064
HC1B	0.514(2)	−0.232(2)	0.491(2)	0.064
HC1C	0.656(2)	−0.175(2)	0.421(2)	0.064
HC2A	0.479(2)	−0.331(2)	0.158(1)	0.040
HC2B	0.338(2)	−0.381(2)	0.226(1)	0.040
HC3A	0.255(2)	−0.085(2)	0.059(2)	0.044
HC3B	0.287(1)	−0.023(2)	0.244(1)	0.044

a) $U_{eq}=(1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

ature.

The temperature evolution of Raman spectra of vapor-deposited samples was recorded using the cryostat designed by us for compounds that are liquid at room temperature.[1)] The cold finger in the cryostat was cooled with the flow of cold helium or nitrogen gas. The substrate temperature was controlled with a Lake Shore 805 temperature controller, and measured with a chromel–gold/iron (0.07%) thermocouple. The film thickness was estimated by monitoring the interference of the laser light in the film during the sample deposition. Spectra were recorded for the samples prepared under different conditions. The sample-deposition temperature was set around 15 or 80 K. The film thickness was made about 5, 10, or 20 μm. Each spectrum was measured at a constant temperature by raising the temperature stepwise during the annealing process of the sample.

Results and Discussion

(i) Molecular Orbital Calculations and Stability of *Trans* and *Gauche* Conformations. The torsion-angle dependence of the enthalpy of formation $\Delta_f H$ of the butanenitrile molecule was calculated with MOPAC. The calculated $\Delta_f H$ had the minimum value 54.9 kJ mol^{-1} at the torsion angle $\phi=180°$ and a second minimum around $\phi=70°$. The former conformation corresponds to the *trans* and the latter conformation corresponds to the *gauche*. Thus, according to the MOPAC results, the *trans* was the most stable conformation. The difference of $\Delta_f H$ between the *trans* and *gauche* was 2.0 kJ mol^{-1}, and the barrier in-between was 6.6 kJ mol^{-1}. These results gave us a rough idea of the molecular structure. It should be noted, however, that the calculated minimum value of $\Delta_f H$ is larger by 21.3 kJ mol^{-1} than the experimentally obtained $\Delta_f H$ value of the gaseous state, 33.6 kJ mol^{-1}.[18)]

The results obtained by the ab initio calculations with different levels of the calculation method are summarized in Table 3. By the method of the Hartree–Fock level with the STO-3G or 6-31G* basis sets, we obtained the result that the *trans* is slightly stable than the *gauche* by about 0.5 kJ mol^{-1}. However, by the MP2/6-31G* method in which the electron correlation is taken into account to improve the approximation, the *gauche* was found to be more stable than *trans* by 1.7 kJ mol^{-1}. By the same method, the torsion angle of the most-stable conformation was calculated to be 60.8°.

Table 3. Results of ab initio Calculation by GAUSSIAN 94

Calculation method	Energy difference between the two conformations ($E_{gauche}-E_{trans}$)/kJ mol^{-1}
STO-3G	0.53
6-31G*	0.48
MP2/6-31G*	−1.65

It has been pointed out by Hirota[8)] that butanenitrile molecules exist in two conformations, i.e. the *trans* and *gauche* conformations. On the basis of the microwave absorption intensity, he inferred that the energy difference between the two conformations was less than 4 kJ mol^{-1}. Later, also on the basis of the microwave measurements, Wlodarczak et al.[9)] reported that *trans* was more stable than *gauche* by 1.1 kJ mol^{-1}. Our results of the molecular orbital calculations essentially coincide with these experimental results in the sense that the energies of the two conformations are very close to each other. However the calculated relative stability between the *trans* and *gauche* depended on the choice of the calculation methods and/or the basis sets.

The tendency of molecules with electronegative substituents to prefer the *gauche* conformation is referred to as the "*gauche* effect".[19)] Compounds such as 1,2-dicyanoethane[20)] tend in fact to have the *gauche* structure. In the case of butanenitrile, this rule contradicts the experimental result so far obtained from the microwave measurements, although the MP2/6-31G* ab initio calculation gave us a delicate result on this issue. Thus we have not yet reached a conclusion about the most stable conformation of the free butanenitrile molecule.

(ii) Crystal Structure. The crystal structure at 123 K viewed along the *b* axis and the ORTEP drawing[21)] of the molecular structure in the crystal are shown in Figs. 1 and 2, respectively. Figure 2 also displays the numbering of the atoms that is referred to hereafter when the structure is discussed. In Fig. 1, the molecules seem to make pairs, coupling through the dipole–dipole interaction between the CN groups. The CN groups in neighboring molecules orient antiparallel to each other, and the intermolecular N1···C4 distance is 3.509 Å. In addition, the CN group directs toward C3 of another neighboring molecule, and the intermolecular N1···C3 distance and C4–N1···C3 angle are 3.428 Å and 177.66°, respectively. Layers are formed in parallel to the *ab* plane, owing to the interaction between the antiparallel CN groups and the N1···C3 interaction. The crystal seems to be constructed further by closely stacking the layers along the *c* axis.

The selected bond distances and bond angles are listed in Table 4 together with the results of geometry optimization by the ab initio calculation at the MP2/6-31G* level. The molecule takes a *gauche* conformation with the C–C–C–C torsion angle of 60.0° in the crystal. The geometric param-

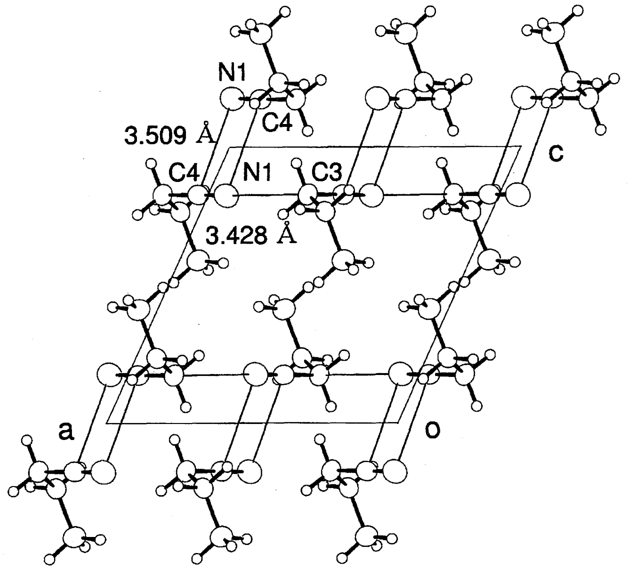

Fig. 1. Crystal structure at 123 K viewed along the *b* axis. Interactions between the CN groups in the neighboring molecules are indicated by narrow lines. The thermal ellipsoids of non hydrogen atoms are drawn at 50% probability level and the circles of hydrogen atoms are taken in an arbitrary scale.

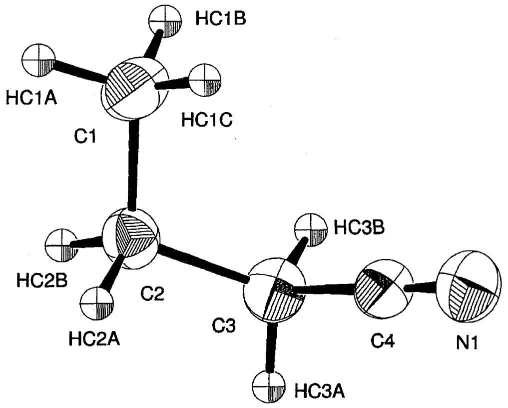

Fig. 2. Molecular structure showing 50% probability displacement ellipsoids and the numbering of the atoms.

Table 4. Selected Bond Distances (Å), Bond Angles (°) and Torsion Angle (°) with the Calculated Values

Distance or angle	Observed	Calculated[a]
N1–C4	1.143(1)	1.181
C1–C2	1.517(1)	1.525
C2–C3	1.527(1)	1.535
C3–C4	1.464(1)	1.467
C1–C2–C3	113.11(8)	112.7
C4–C3–C2	112.47(7)	111.9
N1–C4–C3	178.9(1)	178.7
C1–C2–C3–C4	60.0(1)	60.8

a) MP2/6-31G*.

eters are in good agreement with the values calculated at the MP2/6-31G* level. The *gauche* structure confirms the inference so far made by the vibrational spectroscopy.[10,11] However, as described above, the energies of the *trans* and *gauche* conformations have been estimated to be very close to each other. It is well known that molecules in crystals sometimes do not take the most stable conformation if the molecular packing is not favorable for that conformation.[22] Thus, the *gauche* conformation of butanenitrile is inferred to be favorable for the packing in the crystal.

(iii) Raman Spectra of Liquid and Crystal. Raman spectra of the liquid and crystal were measured for comparing with those of the films. The wide-range spectra of the liquid at room temperature and the crystal at 88 K are displayed in Fig. 3. The spectral quality was greatly improved compared with the previously reported results.[10,11] The major differences between the liquid and crystal spectra were confirmed to be attributable to the difference in the molecular conformation in these states, if we take the previously reported assignments of the vibrational bands.[11]

We recorded the spectral evolution of the liquid by lowering the temperature to temperatures below the melting points. Some spectral features are summarized in Figs. 4 and 5. In the same figures, we also summarize the data obtained for the deposited film; such results will be discussed later. The ordinate of Fig. 4 indecates the ratio of the 529 $\mathrm{cm^{-1}}$ band intensity against the sum of the intensities of the 529 and 558 $\mathrm{cm^{-1}}$ bands (see also Fig. 3). Here, we refer to the integrated intensities. The 529 and 558 $\mathrm{cm^{-1}}$ bands have been attributed to the deformation modes of the *trans* and *gauche* molecules, respectively.[10,11] Thus the ordinate is qualitatively related to the fraction of the molecules with the *trans* conformation.

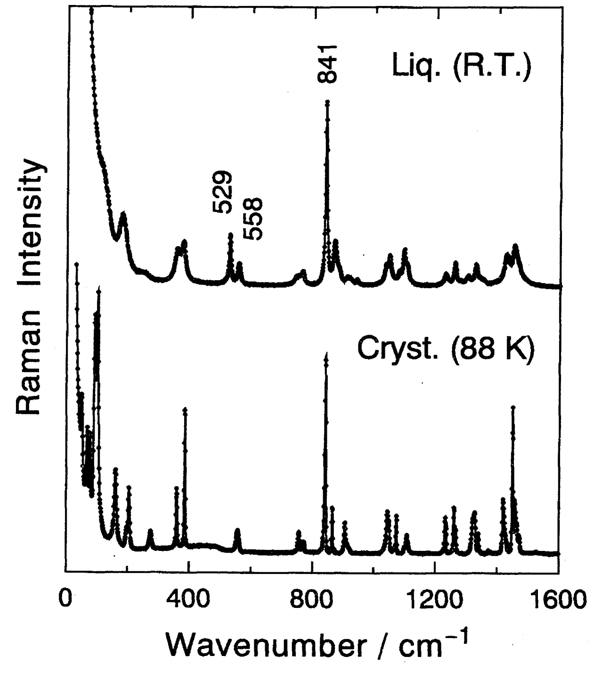

Fig. 3. Raman spectra of the room-temperature liquid and the polycrystalline state at 88 K.

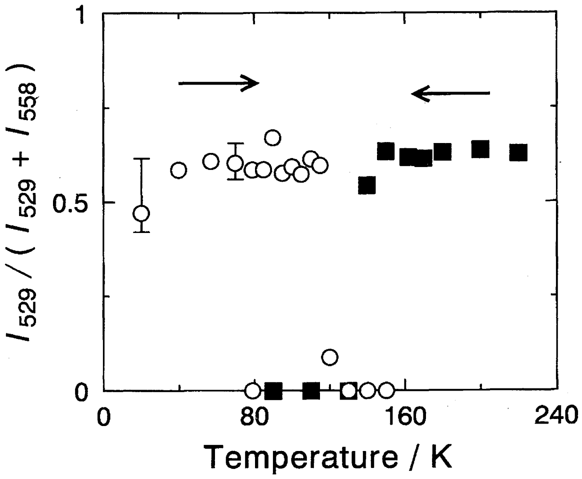

Fig. 4. Change of integrated intensity of the 529 cm^{-1} Raman band of the liquid sealed in a glass tube (closed squares, lowering the temperature) and of the film deposited at 20 K (open circles, raising the temperature). The intensity is normalized by the sum of the 529 and 558 cm^{-1} band intensities.

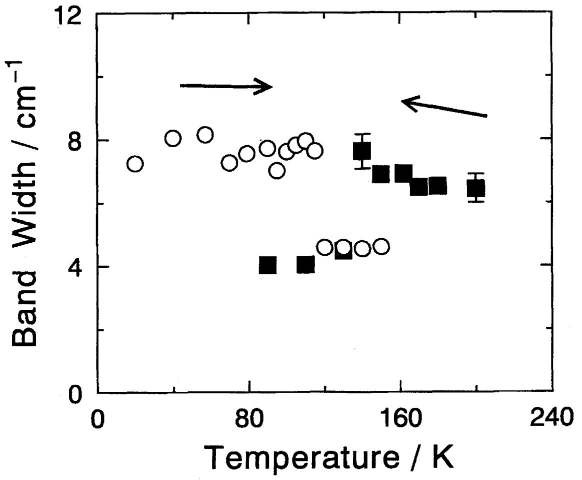

Fig. 5. Change of band width of the 841 cm^{-1} Raman band of the liquid sealed in a glass tube (closed squares, lowering the temperature) and of the film deposited at 20 K (open circles, raising the temperature). The width is not corrected for the spectral slit width of the monochromator of about 3.6 cm^{-1}.

From the result in Fig. 4, the fraction of the *trans* molecules in the liquid seems almost independent of the temperature. If this fraction reflects the equilibrium distribution between the *trans* and *gauche*, the energy difference between these conformations in the liquid is inferred to be smaller than 1 kJ mol^{-1}.

The widths of many bands of the liquid are larger than those of corresponding bands of the crystal. This indicates that the degree of distribution of the molecular conformation is larger in the liquid, and/or that the vibrational and orientational relaxations are faster in the liquid. The width of the 841 cm^{-1} band, the nature of which will be described later, is plotted in Fig. 5. Here, the plotted width has not been corrected for the spectral slit width of about 3.6 cm^{-1}. The fact that this width of the liquid increases a little on lowering the temperature implies that the primary cause of the band broadening is not the fast relaxation but the large degree of distribution of the molecular conformation in the liquid.

(iv) Raman-Spectral Evolution of Vacuum-Deposited Films. The films deposited around 80 K were transparent, while those deposited at temperatures as low as 20 K were slightly opaque. However, all the samples showed spectra similar to those of the liquid, although the details of band-shapes or band-intensities seemed dependent on the temperature of the sample deposition. The above spectral similarity is a type of the evidence of the amorphousness of the films deposited at low temperatures. The amorphousness of the vacuum-deposited films was also confirmed by X-ray diffraction.[23] That is, the films deposited at low temperatures below 80 K showed a very weak and broad diffraction peak centered around $2\theta = 20°$, and such a diffraction pattern suddenly changed to crystal-like one around 120—130 K. Thus, the films prepared below 80 K are considered amorphous on deposition. It is interesting that the fraction of the *trans* and the 841 cm^{-1} band width of the glass are almost the same as those of the liquid, respectively (see the following descriptions and Figs. 4 and 5). This implies that the distribution of the molecular conformation in the glass resembles that in the liquid, although the distribution may be static in the glass and may be dynamic in the liquid.

The spectral evolution of a sample deposited at 20 K, during the annealing process by the stepwise elevation of temperature, is displayed in Fig. 6. A slight change in the spectrum was observed in the small-wavenumber spectrum shown in Fig. 6a when the temperature was raised from 100 to 105 K. That is, a weak and broad band appeared in the region around 190 cm^{-1} (see the arrow in Fig. 6a). This band then disappeared when the temperature was raised from 115 to 120 K; at 120 K, the spectrum was almost the same as that of the crystal, with definite bands below 100 cm^{-1} which may be attributed primarily to lattice vibrations.

A corresponding change in the spectrum was observed in the region 510—590 cm^{-1} (Fig. 6b). Until 100 K, the bands around 530 and 560 cm^{-1} which are related to the *trans* and *gauche* molecules respectively were observed very weakly. When the temperature was raised to 105 K, the Raman intensity increased, although the intensity ratio between the *trans* and *gauche* bands was almost unchanged. We consider that this particular sample underwent the glass transition between 100 and 105 K as will be discussed later. By the further temperature elevation from 115 to 120 K, the *trans* band decreased in intensity very much, while the *gauche* band increased. On the basis of the crystal-structure analysis described already, we consider that this sample started to crystallize between 115 and 120 K. The spectrum at 130 K was in fact almost the same as that of the crystal.

The intensity evolution of the 530 cm^{-1} band which is related to the *trans* molecules is plotted in Fig. 4. A large decrease of the *trans* was observed when the temperature of the film was raised from 115 to 120 K. In the same figure, the corresponding evolution observed for the liquid

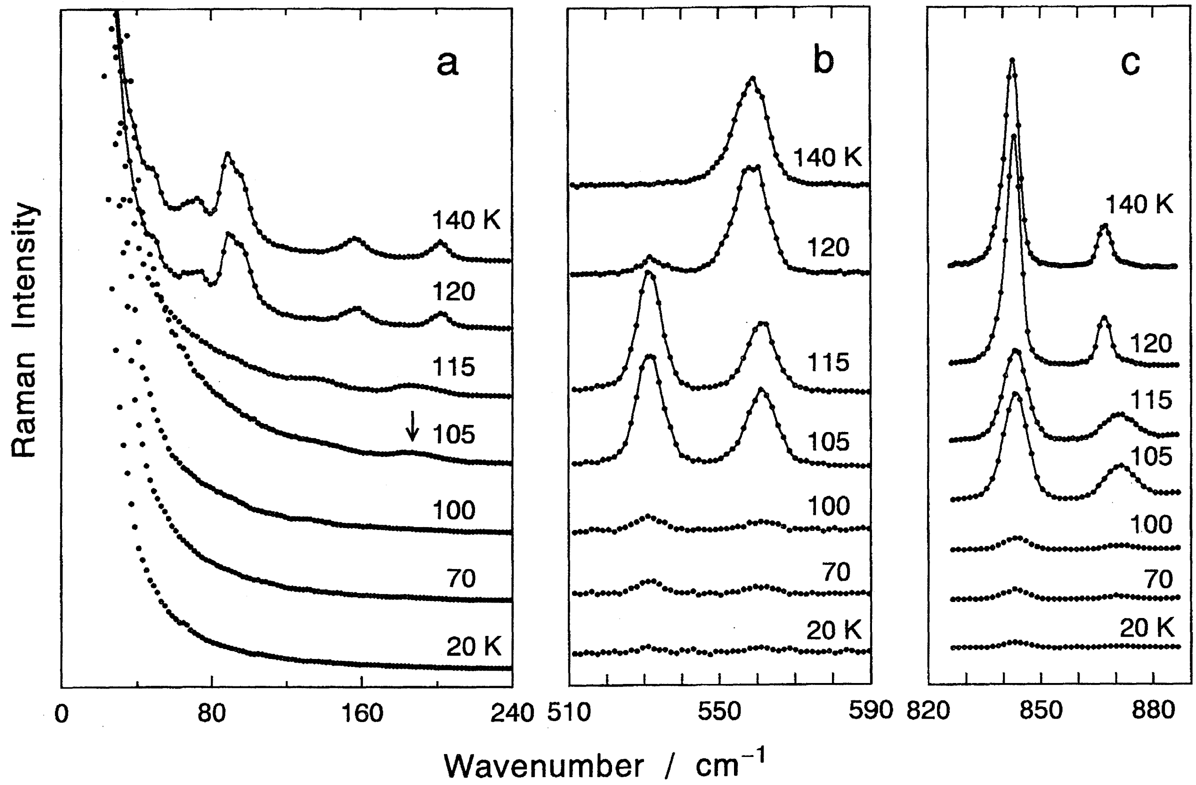

Fig. 6. Evolution of Raman spectra of a film deposited at 20 K during the annealing by the stepwise elevation of temperature.

is plotted as described already. In this case, decrease of the *trans* was observed when the temperature was lowered from 140 to 130 K. These data imply that the film on the gold substrate crystallized around 120 K and the liquid in a glass tube crystallized around 130 K.

The spectral evolution displayed in Fig. 6c reflects the same structural change of the film. The band around 841 cm^{-1} arises mainly from the C–C stretching mode of both the *trans* and *gauche* molecules, while the band around 869 cm^{-1} arises mainly from the CH_2 rocking mode of those molecules.[10,11] We paid attention to the width of the 841 cm^{-1} band. The evolution of this width is plotted in Fig. 5 for the annealing process of the film deposited at 20 K. When the temperature of the film was raised to 120 K, the width decreased to the value of the crystal. On the contrary, the width of the liquid increased a little, as described previously, by lowering the temperature from room temperature, and it suddenly decreased to the value of the crystal at 130 K. These behaviors of the 841 cm^{-1} band width of the film and liquid are considered to correspond to the changes observed for the bands in the region 510—590 cm^{-1}.

Now we summarize the spectral evolution of the deposited films. When the temperature was raised, large spectral changes took place in two steps. The first step took place around 105 K, where an increase of Raman intensity was observed in the whole range of the spectrum, although the magnitude of this increase seemed dependent on the sample. In the same temperature region, a slight spectral change was observed in the small-wavenumber region shown in Fig. 6a. There appeared weak bands around 130 and 190 cm^{-1} which correspond very well to those observed for the liquid. This first step is therefore considered to be related to the glass transition, T_g of which has been reported to be 97 K.[6] In fact, after the above changes, the slightly opaque appearance of the original film on deposition changed to be transparent. Raman bands around 130 and 190 cm^{-1} may be related respectively to those observed for the crystal around 160 and 205 cm^{-1} (Fig. 6a). Such small-wavenumber bands are considered to arise from the vibrational modes of deformation of the whole molecule and to be affected by the intermolecular interaction. Thus the broadness of the bands observed above the glass transition is naturally understood, since molecules in the liquid may exist with various conformations under various intermolecular circumstances.

As the cause of the increase of the Raman intensity at the glass transition, two possibilities are considered. One is the change of the thickness of the laser-irradiated region of the sample. This is plausible, since the sample material after the glass transition was able to flow with the inclined geometry of the sample substrate in our experiment. Another possibility is the change of the Raman polarizability of the sample.[3] Namely, Raman intensity of amorphous solids might be suppressed by the space fluctuation of the Raman polarizability of the sample. This fluctuation may arise from the unhomogeneity of the number density of the molecule in amorphous solids. If this is the case, the suppression may be released in the liquid above T_g. We are planning now further experiments to study this issue of Raman intensity.

The second step of the spectral changes took place in the region around 120 K. All the features of these changes are attributed to the crystallization of the super-cooled liquid. It is interesting that the fraction of the *trans* (Fig. 4) and the 841 $\mathrm{cm^{-1}}$ band width (Fig. 5) of the film after the second step show good agreements respectively with those observed for the state attained by cooling the liquid from room temperature. This suggest that the crystal, which appeared in the film after the glass transition, is the same as that obtained by the cooling of the room-temperature liquid.

(v) Stability of Glass State of Butanenitrile against Crystallization. As we mentioned in the introduction, amorphous films made by the low-temperature vacuum deposition of molecules such as benzene tend to undergo crystallization before the expected glass transition. This is considered primarily due to the small intermolecular force between simple molecules. Amorphous solids are considered to have microscopic free space in them to some extent. In amorphous states made of simple molecules, the local motion of the molecule is considered to become allowed in such space at temperatures a little below the expected T_g, and the structural relaxation may take place even in the solid, leading to the nucleation of the crystal.

In contrast to the instability of amorphous states of molecules such as benzene against the crystallization, the glass of butanenitrile is stable up to the temperature where the system undergoes the glass transition. This is unexpected if we considered only the following facts. Namely, the molecular size of butanenitrile is smaller than that of benzene, and its vapor pressure[7)] is comparable to those of fluorobenzene or chlorobenzene, the amorphous states of which undergo crystallization around 90 and 105 K, respectively.[2)]

The structural feature that is special of butanenitrile molecules is the multiple conformation involving the *trans* and *gauche* structures. As has been found by the present Raman studies, these structures coexist even in the super-cooled liquid state. The fraction of the *trans* in the glass is almost the same as in the liquid (Fig. 4). The molecular-orbital calculations indicated that the energy barrier intervening between the *trans* and *gauche* conformations cannot be surmounted at low temperatures. Therefore, it is considered difficult to grow a periodic arrangement of butanenitrile molecules in the glass, even if some local relaxation in the position and/or orientation of the molecules was allowed. This may be the cause of the stability of the butanenitrile glass against the crystallization. Thus this compound shows the glass transition in spite of its small molecular size.

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