Infrared and Raman Spectra of Polyethylene and Polyethylene-d_4 in He Temperature Region (5−300 K)

Yasuhiro Takahashi

Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

Received April 23, 2001; Revised Manuscript Received July 31, 2001

ABSTRACT: Infrared and Raman spectra of polyethylene and polyethylene-d_4 in the temperature region 5−300 K were measured. Low temperature brings about the sharpening and the shifting of the bands. Furthermore, new fundamental bands were observed. In particular, all the lattice modes can be observed. The wavenumber shifts of the bands, especially those of the lattice modes, tend to slow as the temperature decreases. This tendency is consistent with the dependence of the unit cell parameters a and b. As the lattice parameters a and b decrease, the intermolecular forces become stronger. The stronger intermolecular forces bring about the sharpening and the shift of the bands. The temperature dependence of the width of the splitting of the bending and rocking modes is not so large that these might not be a measure of the intermolecular force.

Introduction

In the previous paper,[1] the crystal structure analysis of deuterated polyethylene was carried out in the He temperature region 10−300 K by neutron diffraction method. It was clarified that the unit cell parameters decrease as temperature decreases but the azimuthal angle φ between the molecular plane and the b axis is 45°, independent of the temperature. In other words, the crystal structure of polyethylene does not change, and only the intermolecular distance decreases as temperature decreases.

On the other hand, the infrared and Raman spectra of polyethylene and deuterated polyethylene are well characterized.[2−5] It is interested in what change can be observed on the infrared and Raman spectra of polyethylene and deuterated polyethylene in the He temperature region. The rocking modes[6] and lattice mode[7] on the infrared spectra of polyethylene were observed at low temperatures, 4 and 100 K, respectively, under rather low resolution. At low temperature (2 K), the 108 cm^{-1} band was observed in the far-infrared region of polyethylene and was assigned to the lattice mode (B_{2u}).[8] Furthermore, Frank et al.[9] measured the infrared spectra of polyethylene in the temperature region 14−412 K, and they found that the frequencies of lattice modes and rocking modes is linearly related to the lattice parameter a. Schlotter and Rabolt reported the far infrared and Raman spectra of polyethylene with chain-extended morphology at 10 K.[10] In the present study, the infrared and Raman spectra of polyethylene and deuterated polyethylene were measured in the temperature regions 5−300 and 6−300 K, respectively. As a result, the many fundamentals were newly observed, especially, all the lattice modes were observed. Temperature dependence of the band frequencies is very similar to the dependence of the lattice constants, which corresponds well to the observation for the infrared spectra of polyethylene by Frank et al.[9]

Experimental Section

For the polyethylene sample, Metal Box Grade X40 film was used for infrared and Raman spectra measurements. For deuterated polyethylene samples (Aldrich and Cambridge Isotope Laboratory: high-density polyethylene), film and powder were used for infrared spectra and Raman scattering measurements, respectively. For far-infrared spectra measurements, wedge-type films were made in order to avoid interference.

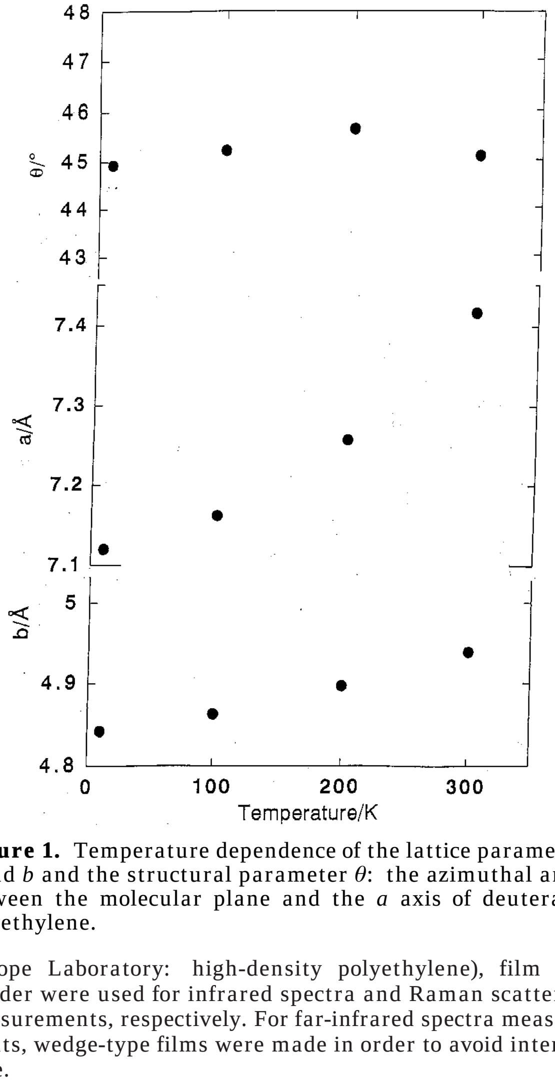

Figure 1. Temperature dependence of the lattice parameters a and b and the structural parameter θ: the azimuthal angle between the molecular plane and the a axis of deuterated polyethylene.

Infrared and far-infrared spectra were measured by the spectrometers JASCO WS/IR-8300 and BIO−RAD FTS-40V, respectively. Raman scattering measurements were made by the spectrometer JASCO NR-1800. The samples were cooled by liquid He by using a cryostat (Oxford). Infrared spectra were

10.1021/ma0107004 CCC: $20.00

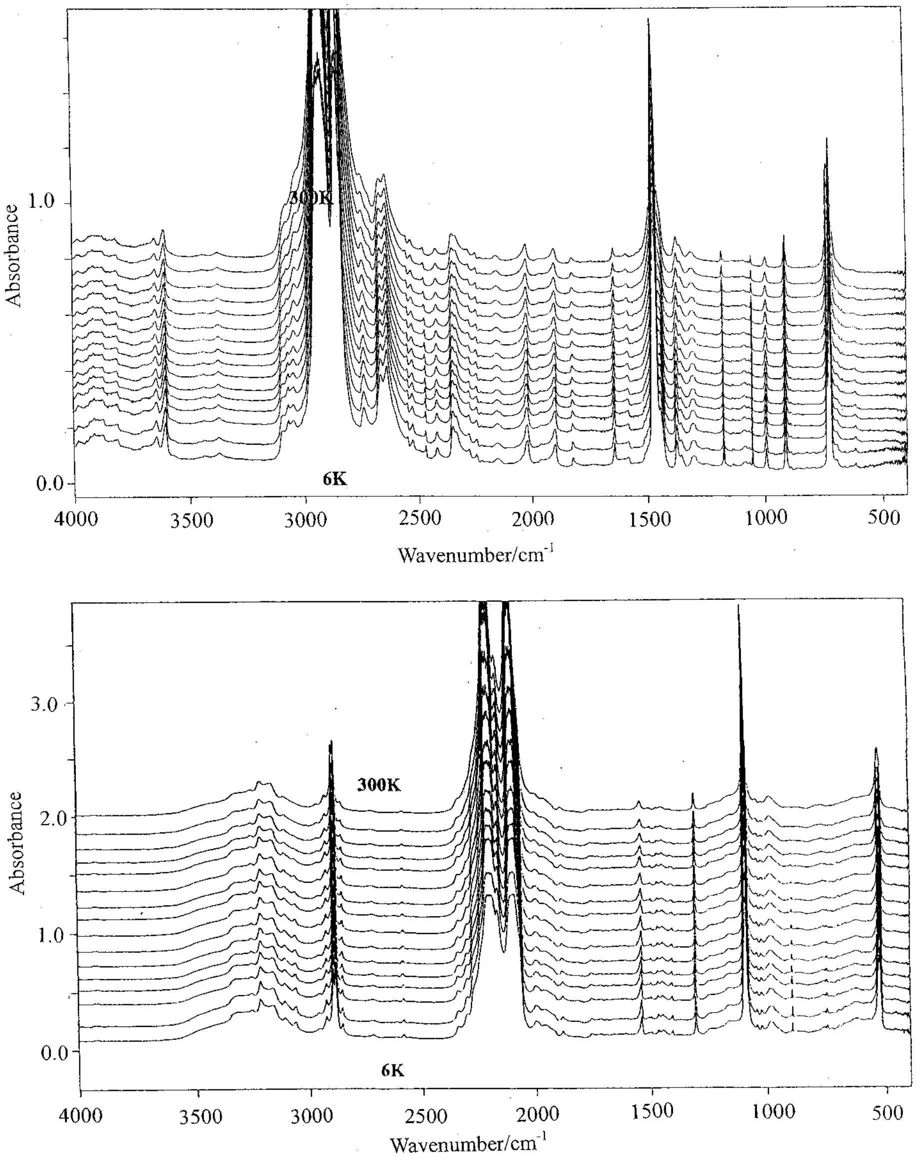

Figure 2. Infrared spectra of (a) polyethylene and (b) deuterated polyethylene in the temperature region 6−300 K.

measured at 6, 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220, 240, 260, 280, and 300 K, and Raman spectra were measured at 5, 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220, 240, 260, 280, and 300 K. Far-infrared spectra were measured in temperature region of 5−300 K.

Results and Discussion

In Figure 1, the cell parameters, *a* and *b*, and the azimuthal angle between the molecular plane and the *a* axis of deuterated polyethylene were shown. These structural parameters are considered to be almost the same as in the case of polyethylene, because the difference between hydrogen and deuterium is not considered to influence on these parameters. This figure shows that the intermolecular distances decreases, i.e., intermolecular forces increase as temperature decreases and this tendency becomes slower as temperature decreases.

In Figure 2, the infrared spectra of polyethylene and deuterated polyethylene measured in the temperature range 6−300 K are shown. All the bands are sharpened as the temperature decreases. This may be attributed to the fact that the effects of anharmonicity decrease,

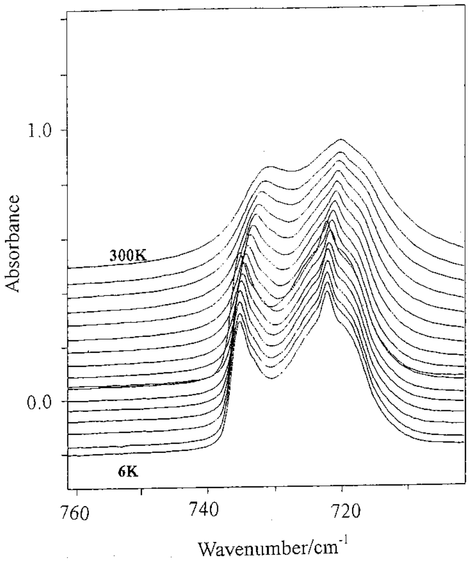

Figure 3. Temperature dependence of the rocking modes on the infrared spectra of polyethylene.

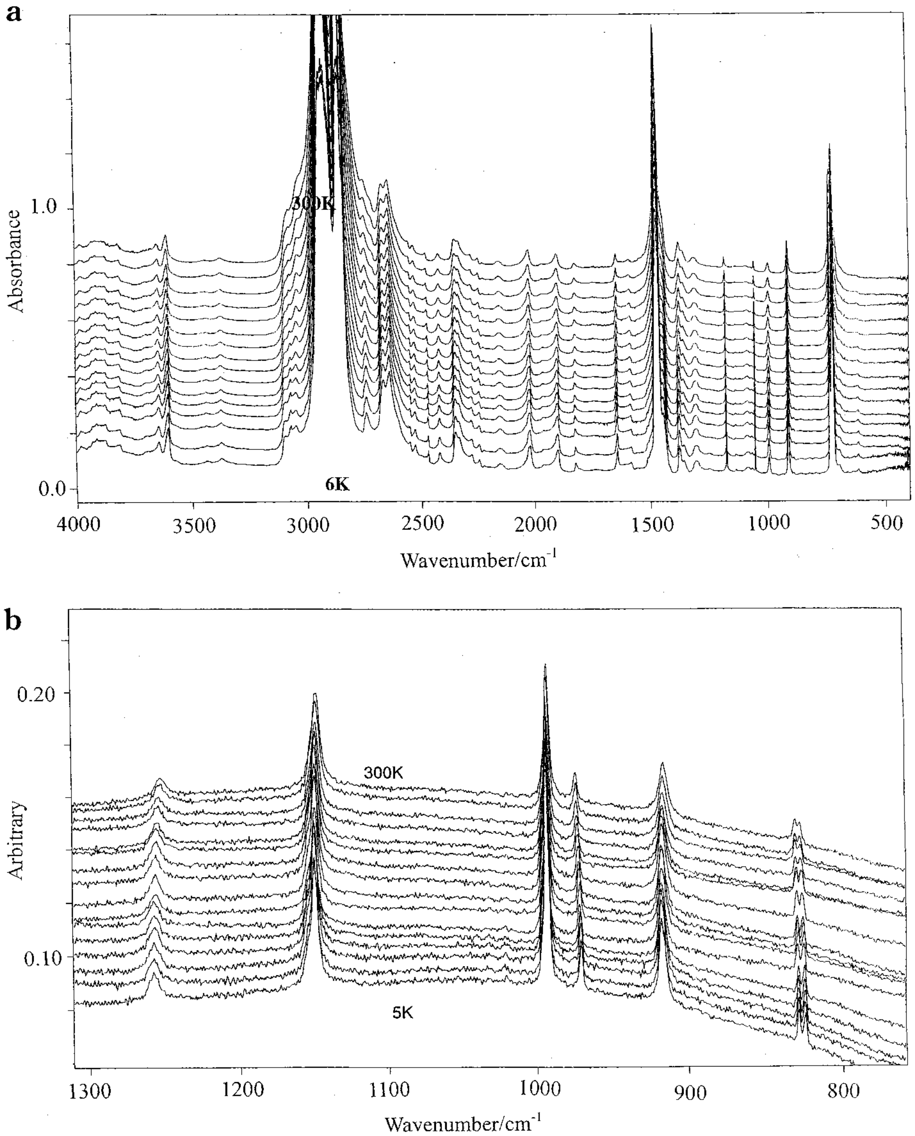

Figure 4. Raman spectra of (a) polyethylene and (b) deuterated polyethylene in the temperature region 5−300 K.

as intermolecular forces are strengthened and harmonicity increases. Furthermore, all the bands shift to high wavenumber, which may be brought about by the increase of intermolecular forces. These tendencies can be typically observed on the rocking modes of polyethylene (Figure 3). The effects of anharmonicity decrease and the fundamentals retain their intensity and become stronger as the temperature decreases. Both the rocking bands shift to the high wavenumber, but the tendency becomes slower at lower temperature. Here, it should be noted that the width of splitting of two rocking modes seems to be constant although the width is frequently used as a measure of intermolecular force. This corresponds well to the observation by Frank et al.[9] Both of 720 and 730 cm^{-1} bands are composed of sharp fundamental and broad band. The broad bands may be attributed to the disorder in the crystalline region, because the sample used in the present study has almost 100% crystallinity. In Figure 4, the Raman spectra of polyethylene and deuterated polyethylene measured in temperature range 5−300 K are shown. All the bands except for 1412 cm^{-1} band of polyethylene and 970, 828, and 824 cm^{-1} band of deuterated polyethylene show the same tendency as in the infrared spectra. These bands shift to low wavenumber as temperature decreases. The temperature dependence of Fermi resonance region[11,12] in Raman spectra of polyethylene is shown in Figure 5, which is composed of two

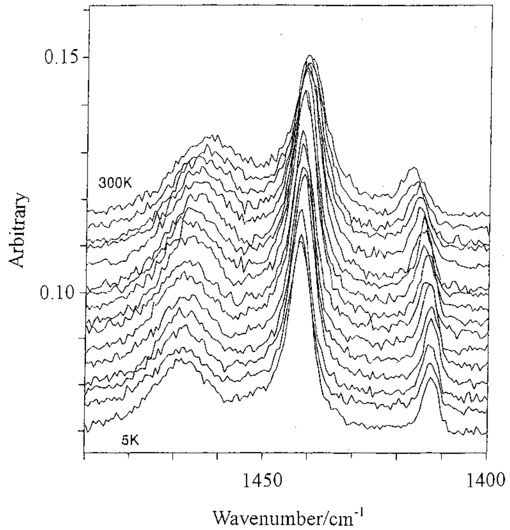

Figure 5. Temperature dependence of the 1412 cm^{-1} Raman band.

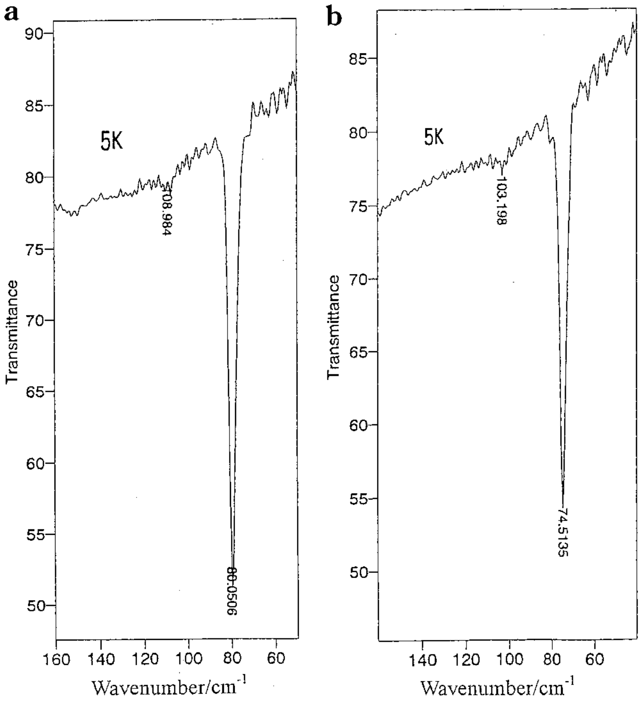

Figure 6. Far-infrared spectra of (a) polyethylene and (b) deuterated polyethylene at 5 K.

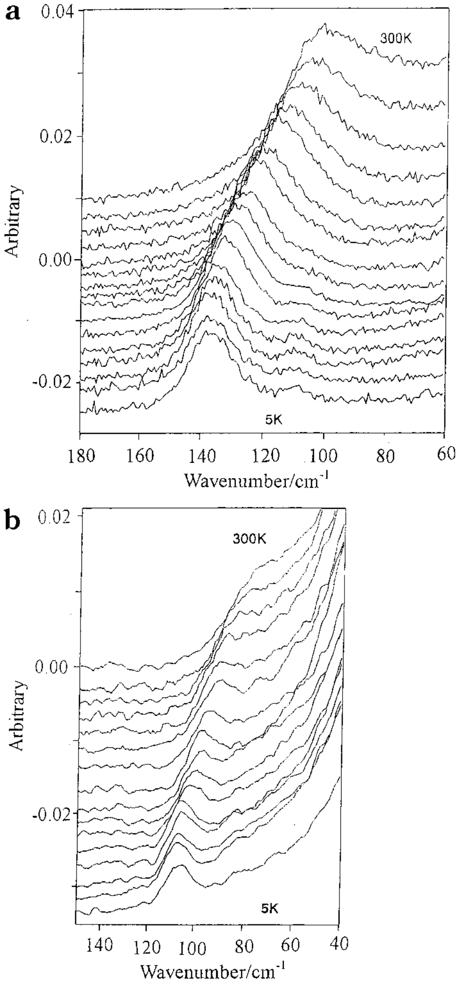

Figure 7. Low wavenumber region of Raman spectra of (a) polyethylene and (b) deuterated polyethylene in temperature region 5−300 K.

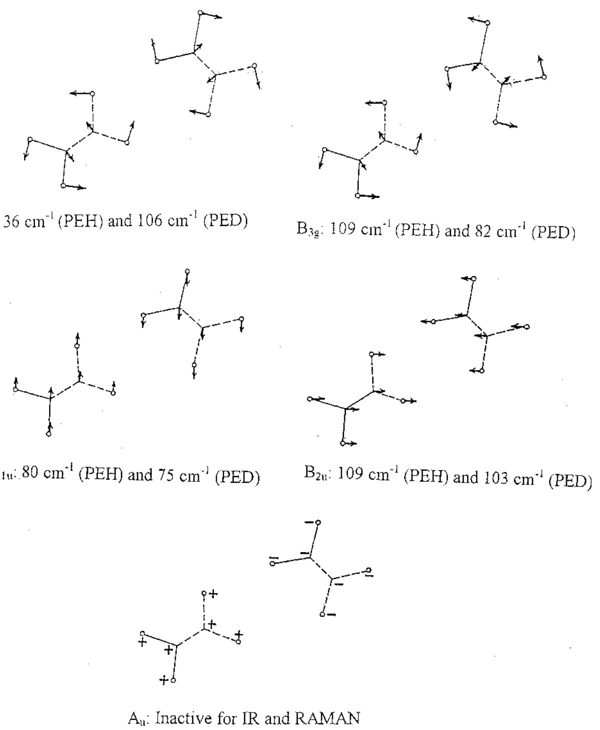

Figure 8. Schematical representation of the lattice modes of polyethylene (PEH) and deuterated polyethylene (PED).

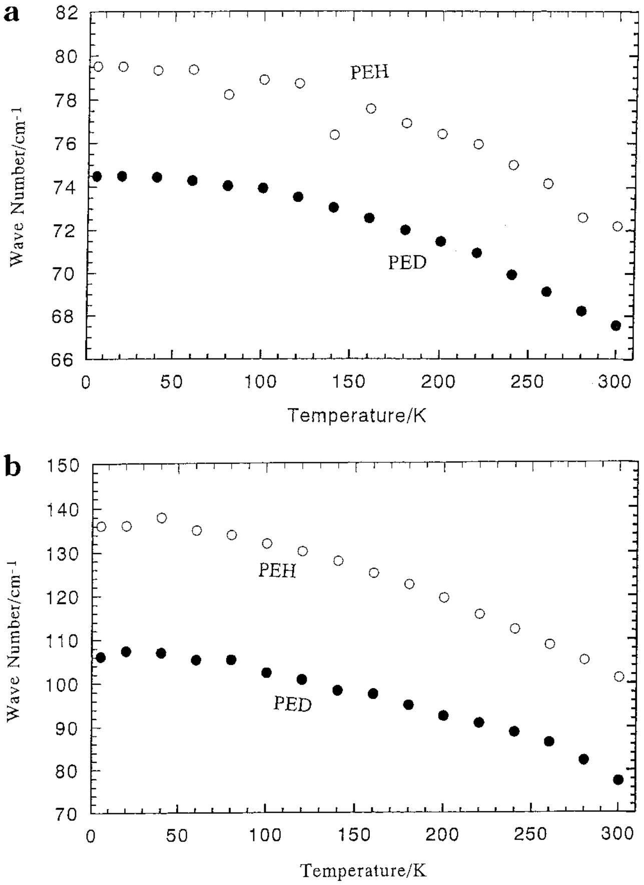

Figure 9. Temperature depdendence of wavenumbers of lattice modes on (a) the infrared and (b) Raman spectra of polyethylene and deuterated polyethylene.

bending modes and the overtone of rocking mode. The band 1412 cm^{-1} shifts to low wavenumber as temper-

Table 1. Observed and Calculated Frequencies of Polyethylene

mode	species	obsd	calcd[a]
$\nu_1^{a}(0)$	A_g	2846	2845
$\nu_1^{b}(0)$	B_{3g}		2838
$\nu_1^{a}(\pi)$	B_{1u}	2850	2874
$\nu_1^{b}(\pi)$	B_{2u}		2877
$\nu_2^{a}(0)$	A_g	1442	1437
$\nu_2^{b}(0)$	B_{3g}	1468	1445
$\nu_2^{a}(\pi)$	B_{1u}	1475	1489
$\nu_2^{b}(\pi)$	B_{2u}	1468	1479
$\nu_3^{a}(0)$	B_{3u}	1173	1175
$\nu_3^{b}(0)$	A_u	...	1184
$\nu_3^{a}(\pi)$	B_{2g}	1412	1413
$\nu_3^{b}(\pi)$	B_{1g}		1408
$\nu_4^{a}(0)$	A_g	1134	1127
$\nu_4^{b}(0)$	B_{3g}		1127
$\nu_4^{a}(\pi)$	B_{2g}	1062	1056
$\nu_4^{b}(\pi)$	B_{3g}		1051
$\nu_5^{a}(0)$	A_g	136	171
$\nu_5^{b}(0)$	B_{3g}	109	138
$\nu_5^{a}(\pi)$	B_{1u}	80	76
$\nu_5^{b}(\pi)$	B_{2u}	109	138
$\nu_6^{a}(0)$	A_g	2881	2899
$\nu_6^{b}(0)$	B_{3g}		2904
$\nu_6^{a}(\pi)$	B_{1u}	2920	2919
$\nu_6^{b}(\pi)$	B_{2u}		2917
$\nu_7^{a}(0)$	A_g	1172	1164
$\nu_7^{b}(0)$	B_{2g}		1164
$\nu_7^{a}(\pi)$	B_{2g}	1295	1303
$\nu_7^{b}(\pi)$	B_{1g}		1308
$\nu_8^{a}(0)$	B_{3u}	1050	1059
$\nu_8^{b}(0)$	A_u	...	1053
$\nu_8^{a}(\pi)$	B_{1u}	735	749
$\nu_8^{b}(\pi)$	B_{2u}	722	737
$\nu_9^{a}(0)$	B_{3u}	...	0
$\nu_9^{b}(0)$	A_u	...	59
$\nu_9^{a}(\pi)$	B_{1u}	...	0
$\nu_9^{b}(\pi)$	B_{2u}	...	0

[a] See ref 2.

Table 2. Observed and Calculated Frequencies of Deuterated Polyethylene

mode	species	obsd	calcd[a]
$\nu_1^{a}(0)$	A_g	2103	2050
$\nu_1^{b}(0)$	B_{3g}		2046
$\nu_1^{a}(\pi)$	B_{1u}	2095	2091
$\nu_1^{b}(\pi)$	B_{2u}		2094
$\nu_2^{a}(0)$	A_g	970	974
$\nu_2^{b}(0)$	B_{3g}		984
$\nu_2^{a}(\pi)$	B_{1u}	1094	1094
$\nu_2^{b}(\pi)$	B_{2u}	1088	1086
$\nu_3^{a}(0)$	B_{3u}	890	889
$\nu_3^{b}(0)$	A_u	...	894
$\nu_3^{a}(\pi)$	B_{2g}	1257	1270
$\nu_3^{b}(\pi)$	B_{1g}		1269
$\nu_4^{a}(0)$	A_g	1149	1154
$\nu_4^{b}(0)$	B_{3g}		1156
$\nu_4^{a}(\pi)$	B_{2g}	828	831
$\nu_4^{b}(\pi)$	B_{1g}	824	825
$\nu_5^{a}(0)$	A_g	106	134
$\nu_5^{b}(0)$	B_{3g}	82	109
$\nu_5^{a}(\pi)$	B_{1u}	75	71
$\nu_5^{b}(\pi)$	B_{2u}	103	99
$\nu_6^{a}(0)$	A_g	2200	2146
$\nu_6^{b}(0)$	B_{3g}		2149
$\nu_6^{a}(\pi)$	B_{1u}	2194	2160
$\nu_6^{b}(\pi)$	B_{2u}		2159
$\nu_7^{a}(0)$	A_g	992	999
$\nu_7^{b}(0)$	B_{3g}		1001
$\nu_7^{a}(\pi)$	B_{2g}	917	922
$\nu_7^{b}(\pi)$	B_{1g}		926
$\nu_8^{a}(0)$	B_{3u}	746	749
$\nu_8^{b}(0)$	A_u	...	745
$\nu_8^{a}(\pi)$	B_{1u}	529	540
$\nu_8^{b}(\pi)$	B_{2u}	522	531
$\nu_9^{a}(0)$	B_{3u}	...	0
$\nu_9^{b}(0)$	A_u	...	55
$\nu_9^{a}(\pi)$	B_{1u}	...	0
$\nu_9^{b}(\pi)$	B_{2u}	...	0

[a] See ref 2.

ature decreases. This shows that the stronger intermolecular interaction does not necessarily bring about the shift to high wavenumber as temperature decreases. This may be attributed to the fact that the stronger intermolecular interaction brings about the different ratio of the coupling of modes.

In Figure 6, the far-infrared spectra of polyethylene and deuterated polyethylene at 5 K are shown. Two bands, 109 and 80 cm^{-1} and 103 and 75 cm^{-1} are observed for polyethylene and deuterated polyethylene, respectively. These two bands are assigned to the lattice modes of B_{1u} and B_{2u} which are translational modes parallel to the *a* and *b* axes, respectively. In Figure 7, the low wavenumber region of Raman spectra of polyethylene and deuterated polyethylene in the region 5−300 K are shown. Two bands can be observed at low-temperature region: at 5 K, 136 and 109 cm^{-1} for polyethylene, and at 6 K, 106 and 82 cm^{-1} for deuterated polyethylene. These two bands can be assigned to the librational lattice modes of A_g and B_{3g}. In Figure 8, all the lattice modes are schematically shown. Temperature dependences of lattice modes are plotted in Figure 9. The tempearture dependences are very similar to those of the lattice constants (Figure 1). The temperature dependence of the lattice modes are strongly related to the intermolecular interactions. This corresponds well to the observation in the infrared spectra of polyethylene that the frequency shift is linearly related to the thermal expansion of the lattice parameter a.[9] The assignment of all the bands of infrared (5 K) and Raman (6 K) are given in Tables 1 and 2 in comparison with the calculated values reported by Tasumi and Shimanouchi.[2]

Tasumi and Shimanouchi[2] calculated the normal coordinates by taking only the few short-range hydrogen−hydrogen interactions into account and discussed the shape of the intermolecular hydrogen−hydrogen potential function. At low temperature, longer range hydrogen−hydrogen interactions should be taken into consideration in addition to the hydrogen−carbon and carbon−carbon interactions.

Acknowledgment. The author expresses his thanks to Mr. M. Ohama of this department for the measurements of infrared and Raman spectra.

References and Notes

(1) Takahashi, Y. *Macromolecules* **1998**, *31*, 3868.
(2) Tasumi, M.; Shimanouchi, T. *J. Chem. Phys.* **1965**, *43*, 1245.
(3) Tasumi, M.; Krimm, S. *J. Chem. Phys.* **1967**, *46*, 755.
(4) Krimm, S.; Liang, C. Y.; Sutherland, G. B. B. M. *J. Chem. Phys.* **1956**, *25*, 549.
(5) Ellinghorst, G. Thesis, University of Cologne, Cologne, 1968.
(6) King, G. W.; Hainer, R. M.; McMahon, H. O. *J. Appl. Phys.* **1949**, *20*, 559.
(7) Bertie, J. E.; Whalley, E. *J. Chem. Phys.* **1964**, *41*, 575.
(8) Dean, G. D.; Martin, D. H. *Chem. Phys. Lett.* **1967**, *1*, 415.
(9) Frank, W.; Schmidt, H.; Wulf, W. *J. Polym. Sci. Polym. Symp.* **1977**, *61*, 317.
(10) Schlotter, N. E.; Rabolt, J. F. *Macromolecules* **1984**, *17*, 1581.
(11) Snyder, R. G.; Hsu, S. L.; Krimm, S. *Spectrochim. Acta* **1978**, *34A*, 395.
(12) Abbate, S.; Zerbi, G.; Wunder, S. L. *J. Phys. Chem.* **1982**, *86*, 3140.

MA0107004