The Vibrational Assignments of Propyl Bromide and Its Two Asymmetrically-Deuterated Species

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(Received November 30, 1972)

The vibrational assignments of the observed spectra of propyl bromide and its two asymmetrically-deuterated species have been worked out. Since the two *gauche* isomers come not to be equivalent for the asymmetrically-deuterated species, the infrared bands of the *gauche* isomer can be expected to be split into doublets, while the bands of the *trans* isomer remain singlets. The observed infrared bands for the *gauche* isomer were actually the doublets for the C–Br stretching and two CH_2 rocking modes. The C–D stretching and deformation modes of the β-deuterated species were also in the expected spectral patterns. In order to confirm the vibrational assignments, the normal vibration calculation was carried out using a modified Urey-Bradley force field for the parent and two asymmetrically-deuterated species.

Brown and Sheppard[1] studied the rotational isomerism of propyl bromide using the infrared spectra in the liquid and crystalline states.

Komaki *et al.*[2] also studied the infrared and Raman spectra of this substance in relation to the rotational isomerism. They concluded that the *trans* and *gauche* isomers co-exist in the gaseous and liquid states, while only the *trans* isomer persists in the crystalline state. The conclusion as to the molecular forms of the isomers by Komaki *et al.* had been drawn on the basis of the normal vibration calculation and the vibrational product rule of the skeletal vibrations between isomers.

The molecular forms of the isomers have also been confirmed by Sarachman by means of microwave spectroscopy.[3]

McDevitt *et al.*[4] studied the far-infrared spectra of this substance. As for the vibrational assignments, they worked them out for only the skeletal and some CH_2 rocking vibrations.

Recently, Tanabe and Saëki[5] have worked out the vibrational assignments of propyl bromide and chloride on the basis of absorption intensity measurements. They have also carried out the normal vibration calculation in the local-symmetry force field.

In this paper, we will deal with vibrational assignments of propyl bromide based on a comparison of the spectra with those of its two asymmetrically-deuterated species and on the results of the normal vibration calculation. Our assignments of the spectra are almost the same as those by Tanabe and Saëki except for several points which will be discussed in the future.

For the determination of the molecular forms of the rotational isomers, the asymmetrically-deuterated species of the original molecule usually gives useful information as Neu and Gwinn,[6] de Hemptinne,[7] and Bernstein *et al.*[8] have shown for the case of 1,2-dibromoethane.

For propyl bromide, since the two *gauche* isomers come not to be equivalent for asymmetrically-deuterated species, such as the CH_3CHDCH_2Br and CH_3CH_2CHDBr species, the infrared bands of the *gauche* isomer are expected to be split into doublets, while the bands of the *trans* isomer remain singlets.

In order to find the molecular forms for a molecule with a structure similar to propyl bromide, such as propyl mercaptan, it is useful to find which asymmetrically-deuterated species gives better splitting patterns of the spectra, thus making possible an easier discrimination of the results. This is the second purpose of the present investigation of propyl bromide and its asymmetrically-deuterated species.

Experimental

The sample of the parent propyl bromide used in the measurements was a commercial product purified by redistillation. The α-deuterated species, CH_3CH_2CHDBr, was prepared by a method similar to that used in the preparation of α-deuterated butyl alcohol;[9] that is, propionaldehyde was reduced to α-deuterated propyl alcohol by $LiAlD_4$ in ethyl ether, and the resultant alcohol was brominated by PBr_3. The β-deuterated species, CH_3CHDCH_2Br, was prepared by the addition of propylene and DBr, with benzoylperoxide as the catalyst.[10] The purities of the deuterated species were found to be better than 90% by both gas chromatography and a study of the infrared spectra.

The infrared spectra in the region from 200 to 4000 cm^{-1} were recorded with a Perkin-Elmer instrument (model 621). For the measurements in the crystalline state, the vapor of the sample was directly condensed on a CsI plate in a cell cooled with liquid nitrogen in a vacuum and was then annealed several times in order to keep the sample from reaching the supercooled liquid state.

Vibrational Assignment

As is shown in Fig. 1, for the parent species there are equivalent two *gauche* isomers, and they produce

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1) J. K. Brown and N. Sheppard, *Trans. Faraday Soc.*, **50**, 535 (1954).

2) C. Komaki, I. Ichishima, K. Kuratani, T. Miyazawa, T. Shimanouchi, and S. Mizushima, This Bulletin, **28**, 330 (1955).

3) T. N. Sarachman, Smp. Mol. Struct. Spectr., 23rd, Sept. 1968, Columbus, Ohio, N7.

4) N. T. McDevitt, A. L. Rozek, F. F. Bentley, and A. D. Davidson, *J. Chem. Phys.*, **42**, 1173 (1965).

5) K. Tanabe and S. Saëki, Symposium on Molecular Structure, Sendai (1972), paper 5C20 and the private communication.

6) J. T. Neu and W. D. Gwinn, *J. Chem. Phys.*, **18**, 1642 (1950).

7) M. de Hemptinne, *Contrib. etude structure mol. Vol. commem Victore Henri*, 151 (1947/48).

8) H. J. Bernstein, A. D. E. Pullin, S. B. Rabinovitch, and N. R. Larson, *J. Chem. Phys.*, **20**, 1227 (1952).

9) A. Streitwieser, Jr., *J. Amer. Chem. Soc.*, **75**, 5014 (1953).

10) M. S. Kharasch, M. C. McNab, and F. R. Mayo, *ibid.*, **55**, 2531 (1933).

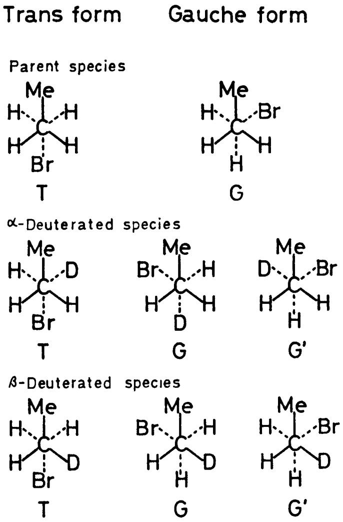

Fig. 1. Rotational isomers of propyl bromide and its asymmetrically-deuterated species.

two non-equivalent pairs of the four *gauche* forms if one of the hydrogens in the CH_2 groups is replaced by a deuterium, while the *trans* isomer produces two equivalent forms. Therefore, the infrared bands for the *gauche* isomers may be expected to be split into doublets for the asymmetrically-deutetrated species.

Spectra in the Region from 300 to 1000 cm^{-1}. In Fig. 2, the observed infrared spectra in the region from 300 to 1000 cm^{-1} are shown; the solid and the dotted lines indicate the spectra in the liquid and crystalline states respectively.

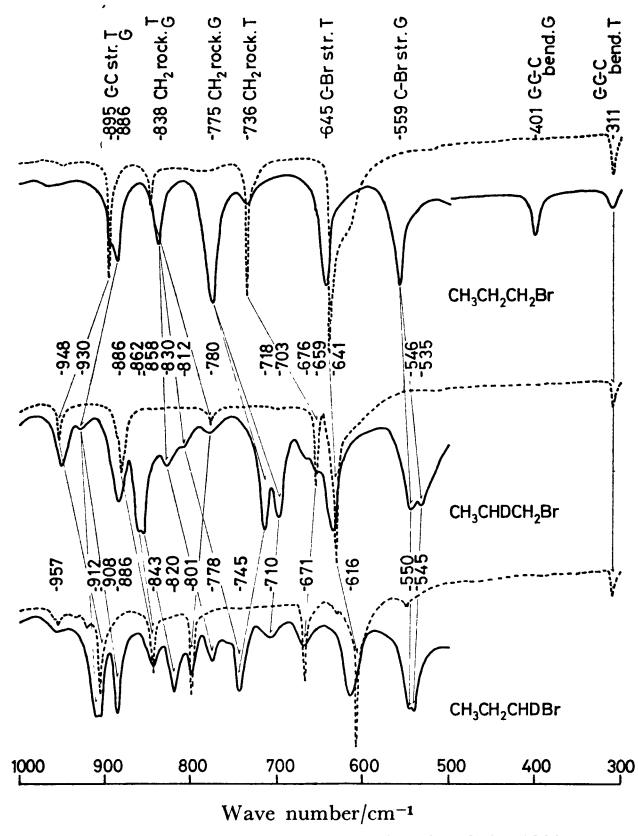

Fig. 2. Observed infrared spectra in the 300—1000 cm^{-1} region for the parent, β-deuterated, and α-deuterated species of propyl bromide. Solid and dotted lines indicate the spectra in the liquid and the crystalline states, respectively.

According to the reported vibrational assignments,[1,2] the strong infrared bands at 645 and 559 cm^{-1} of the parent species are the C–Br stretching vibrations for the *trans* and *gauche* isomers respectively. For the α- and β-deuterated species, the corresponding bands are found with nearly equal frequencies, and the band vanishing in the crystalline state appears to be a doublet, as is expected, while the band persisting in the crystalline state is a singlet.

As Shimanouchi and Suzuki[11] have already pointed out in their paper on dichloromethylene, upon asymmetrical deuteration the CH_2 rocking mode keeps its original mode, with relatively smaller modifications than the other hydrogen deformation modes. In the case of propyl bromide, the shifts of the CH_2 rocking modes are also expected to be relatively simple, though the shifts of the other vibrational modes between the parent and the deuterated species may be complicated.

For the parent species of propyl bromide, according to the reported assignments,[2] one of the two CH_2 rocking modes is the band at 736 cm^{-1} persisting in the crystalline state for the *trans* isomer and the band at 775 cm^{-1} appearing in the liquid state for the *gauche* isomer.

For the asymmetrically-deuterated species, there are two kinds of CH_2 rocking modes; they can be regarded as the CHD and CH_2 rocking modes, though a larger mutual mode mixing is expected. The CHD rocking mode is expected to be at a lower frequency than the CH_2 rocking mode.

For the β-deuterated species, the band at 659 cm^{-1} persisting in the crystalline state can be assigned to the CHD rocking mode for the *trans* isomers, which is a singlet. For the *gauche* isomer, the doublet around 710 cm^{-1} can be easily assigned to this mode.

For the α-deuterated species, the band at 671 cm^{-1} persisting in the crystalline state can be assigned to this mode for the *trans* isomer, which is a singlet. For the *gauche* isomer, although the band at 710 cm^{-1} appearing only in the liquid state can be easily assigned to one of components of the doublet of this mode, there are two possibilities for the other component of the doublet; that is, either the band at 710 cm^{-1} is the unsplit doublet or the band at 745 cm^{-1} appearing only in the liquid state is another component of the doublet.

Since the band at 710 cm^{-1} is too weak to be regarded as the unsplit doublet when comparison is made with the corresponding doublet of the β-deuterated species, the band at 745 cm^{-1} must be the component of the doublet with the band at 710 cm^{-1}. The present assignments are also supported by the result of the normal vibration calculations, as will be described later.

The doublet spacing for the *gauche* isomer of the α-deuterated species (35 cm^{-1}) is larger than that for the β-deuterated species (15 cm^{-1}), according to the

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[11] T. Shimanouchi and I. Suzuki, *J. Mol. Spectrosc.*, **8**, 222 (1962).

present assignments, in the same manner as the calculated spacings (the calculated spacings are 32 and 4 cm^{-1} respectively).

From the tendency found in the frequency separations between the two CH_2 rocking modes for a series of molecules with $-CH_2-CH_2-$ groups, as has already been reported,[12] the bands around 840 cm^{-1} for the parent species can be assigned to another CH_2 rocking mode, which corresponds to the CH_2 rocking mode for the deuterated species. The bands at 780 and 801 cm^{-1} for the β- and α-deuterated species respectively can be assigned to the corresponding CH_2 rocking mode for the *trans* isomer.

However, the assignment cannot be made immediately for the *gauche* isomer. For the β-deuterated species, there is no possible band if the corresponding mode for the *gauche* isomer is considered to have a lower frequency than that for the *trans* isomer, as is the case in the parent species. If bands at higher frequencies are permitted for this mode, there is a weak doublet around 820 cm^{-1} with a reasonable spacing for this mode.

For the α-deuterated species, there is a single band at a lower frequency than that for the *trans* isomer; in explaining this, there are three possibilities: 1) this band may be regarded as an unsplit doublet; 2) another component may overlap with the band at 745 cm^{-1}, which is assigned to the CHD rocking mode for the *gauche* isomer, and 3) this unknown component may have a higher frequency than that for the *trans* isomer.

In order to find the correct assignments in view of the above possibilities, the results of the normal vibration calculation are useful, as is shown in Tables 5—7.

From the calculation, the localization of the higher-frequency mode of two CH_2 rocking vibrations is found to be rather worse than that of the lower-frequency mode, though both of them are well localized from the other mode, as is to be expected. Furthermore, if the rocking modes for the *trans* and *gauche* isomers are designated as T and G respectively, they are possibly arrayed in the order of GTGT from higher to lower frequencies for the β-deuterated species, while for the α-deuterated species they are arrayed in the same order (TGGT) as that for the parent species.

Therefore, for the β-deuterated species, the doublet around 820 cm^{-1} can be assigned to this mode, while for the α-deuterated species, the band at 745 cm^{-1} can be regarded as containing one of the components of the doublet which has the band at 778 cm^{-1} as another component with reasonable spacing.

There are two C–C stretching modes for one isomer; one of them can be expected around 900 cm^{-1}. For the parent species, the bands at 895 and 886 cm^{-1} can be assigned to this mode for the *trans* and *gauche* isomers respectively.

For the deuterated species, one of the two CH_2 twisting modes, which should be more properly called a CD deformation mode,[11] can also be expected in the same region for the C–C stretching mode. In this region, there are two distinct bands in the crystalline state for both α- and β-deuterated species.

For the β-deuterated species, the bands at both 886 and 948 cm^{-1} persisting in the crystalline state accompany the bands in the liquid state on the lower-frequency side. The band accompanying the band at 886 cm^{-1} is a strong doublet with a small spacing, while the band accompanying the band at 948 cm^{-1} is a shoulder and seems to be a singlet.

According to the normal vibration calculation, the CD deformation mode should not only have a lower frequency for both the *trans* and *gauche* isomers, but should have a larger spacing of the doublet for the *gauche* isomer than that for the C–C stretching mode. Therefore, the band at 886 cm^{-1} and the doublet around 860 cm^{-1} can be assigned to the CD deformation mode for the *trans* and *gauche* isomers respectively, while the bands at 948 and 930 cm^{-1} can be assigned to the C–C stretching mode for the *trans* and *gauche* isomers respectively.

For the α-deuterated species, the calculation indicates that: 1) the C–C stretching mode has a higher frequency than the CD deformation mode; 2) both the C–C stretching and CD deformation modes have relatively large spacing of the doublet for the *gauche* isomer, and 3) one of the components of the doublet of the C–C stretching mode for the *gauche* isomer has a higher frequency than that for the *trans* isomer.

Taking the above results into account, for the *trans* isomer the bands at 843 and 908 cm^{-1} can be assigned to the CD deformation and the C–C stretching modes respectively. The band at 820 cm^{-1} can be assigned to one of the components of the doublet for the CD deformation mode for the *gauche* isomer, where the other component can be regarded to overlap the band at 843 cm^{-1} for the *trans* isomer. The band at 886 cm^{-1} assigned to the C–C stretching mode for the *gauche* isomer forms a doublet with a reasonable spacing and with a shoulder of the band at 908 cm^{-1} of the *trans* isomer.

Spectra in the Region from 1000 to 1200 cm^{-1}. In this region, one of the C–C stretching modes and two of the CH_3 rocking modes can be expected for one isomer. Actually, three bands exist, at 1022, 1036, and 1097 cm^{-1}, in the crystalline state for the parent species; they can be assigned to the C–C stretching mode, the CH_3 rocking mode belonging to the A″ species, and that belonging to the A′ species for the *trans* isomer respectively, taking into account the results of the calculation.

There are three corresponding bands, at 1017, 1064, and 1143 cm^{-1}, in the crystalline state for the β-deuterated species.

For the α-deuterated species, the band for the C–C stretching mode is at 1020 cm^{-1} in the crystalline state. However, the assignments cannot be made immediately for the two CH_3 rocking modes. As no other mode is possible in the expected region from 1000 to 1200 cm^{-1} for these two CH_3 rocking modes, some of the four bands appearing in the crystalline state are probably the modes in question. Among these

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[12] M. Hayashi, Y. Shiro, and H. Murata, This Bulletin, **39**, 112 (1966).

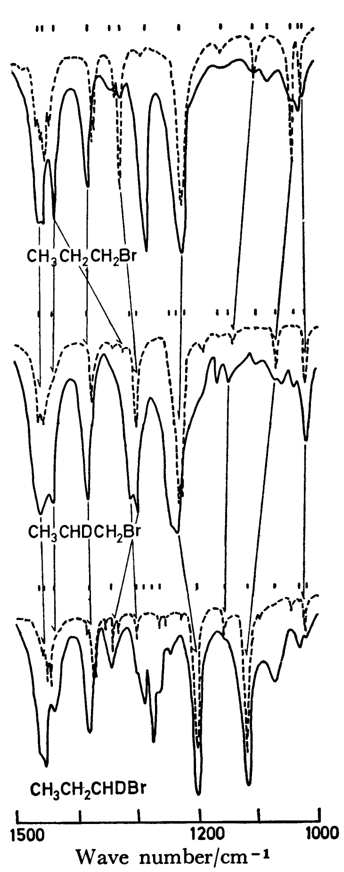

Fig. 3. Observed infrared spectra in the 1000—1500 cm^{-1} region for the parent, β-deuterated, and α-deuterated species of propyl bromide. Solid and dotted lines indicate the spectra in the liquid and the crystalline states, respectively.

four bands, the strongest band, at 1118 cm^{-1}, may be assigned to the CH_3 rocking mode corresponding to the strong band belonging to the A″ species for the parent species, though the difference between the calculated and observed frequencies seems to be a little large.

This assignment seems suspect because the band at 1118 cm^{-1} is too strong compared with the corresponding bands for the parent and the β-deuterated species. However, a similar strong band has also been found in this region for the monodeuterated ethyl bromide, CH_3CHDBr, reported by Bak *et al.*[13] Therefore, this may be a permissible assignment.

Another CH_3 rocking mode corresponding to the mode belonging to the A′ species for the parent species may be assigned to either the weak band at 1154 cm^{-1} or the band considered to overlap the band at 1118 cm^{-1}. There is no way to find which is correct, since the calculated frequency is probably not reliable. Therefore, we will tentatively assign the band at 1154 cm^{-1} to the CH_3 rocking mode.

For the *gauche* isomer, the tentative assignments for the C–C stretching and the two CH_3 rocking modes are shown in Tables 5—7; they have been made taking into account the results of the calculation and the assignments of the *trans* isomer.

Spectra in the Region from 1200 to 1500 cm^{-1}. In this region, there are nine CH_2 and CH_3 hydrogen deformation modes for one isomer.

For the deuterated species, since one of the CH_2 groups is replaced by a CHD group, when the results for $CHDCl_2$ described earlier are taken into account the set of CH_2 hydrogen deformation modes can be expected to change in their characteristic and to be more or less shifted to a lower-frequency side.

Among these shifted modes, the CHD rocking mode and the CD deformation mode originating from the CH_2 twisting mode have previously been assigned. The CHD scissoring mode and the CH deformation mode originating from the CH_2 wagging mode can be expected around 1290 and 1220 cm^{-1} respectively.

On the assignments of the spectra for the parent species, the potential energy distributions of the normal vibrations for propyl chloride calculated by Snyder and Schachtschneider[14] give a suitable point of reference, though they did not report any explicit assignments of the observed spectra.

The CH_2 wagging modes can be assigned to the strong bands at 1224 and 1326 cm^{-1} in the crystalline state for the *trans* isomer and to a strong band at 1282 cm^{-1} and a weak band at 1326 cm^{-1} in the liquid state for the *gauche* isomer.

As is shown in Table 5, judging from the calculated frequency it seems better to regard the CH_2Br wagging mode for the *gauche* isomer as overlapping the strong band at 1224 cm^{-1}. However, if this assignment is chosen, the intensity change of the band at 1282 cm^{-1} between the liquid state and the crystalline state cannot be understood unless the band for the CH_2 twisting mode exhibits a drastic intensity change between that for the *trans* isomer and that for the *gauche* isomer.

As for the two CH_2 twisting modes, since the spectra are expected to be weak and since, actually, no remarkable bands exist in the expected region, it is not easy to make any definite assignments. Therefore, the weak bands and the shoulders in this region are only tentatively assigned to these modes.

Only one band, at 1380 cm^{-1}, exists in the liquid state in the expected region for the CH_3 symmetric deformation mode; this band appears in the crystalline state at 1378 cm^{-1} as a doublet due to the crystalline field. As the difference in the molecular forms is considered to have a negligible influence on this mode, these may be regarded as overlapping bands due to the *trans* and *gauche* isomers.

Around 1440 cm^{-1}, there exist complicated bands which correspond to the CH_3 asymmetric deformation and CH_2 scissoring modes, where the lowest band at 1435 cm^{-1} existing in the liquid and crystalline states is probably one of the CH_2 scissoring modes due to both the *trans* and *gauche* isomers, in view of the finding on ethyl chloride reported by Miller and Kiviat.[15]

For the β-deuterated species, the strong bands at 1230 and 1295 cm^{-1} can be easily assigned to the CH_2 wagging mode and the CH deformation mode originating from the CHD wagging mode for the *trans* isomer.

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[13] B. Bak, D. H. Christensen, J. Møller, and S. Detoni, *Acta Chem. Scand.*, **12**, 2021 (1958).

[14] R. G. Snyder and J. H. Schachtschneider, *J. Mol. Spectrosc.*, **30**, 290 (1969).

[15] F. A. Miller and F. E. Kiviat, *Spectrochim. Acta*, **25A**, 1363 (1969).

For the *gauche* isomer, the CH_2 wagging mode and the CH deformation mode can be assigned to the bands at 1230, 1235, and 1308 cm^{-1}, taking into account the results of the calculation where the band at 1308 cm^{-1} is regarded as the overlapping band of two spectra due to two kinds of *gauche* isomers.

Since one of the CH_2 twisting modes (CD deformation mode) is shifted to the lower-frequency side around 900 cm^{-1}, there is one CH_2 twisting mode for one isomer which can be assigned to the shoulder at 1210 cm^{-1} for the *trans* isomer. For the *gauche* isomer, as the calculation indicates that only a slight frequency shift can be expected for the CH_2 twisting mode among the one *trans* isomer and the two kinds of *gauche* isomers, and as the lower-frequency side of the band at 1230 cm^{-1} seems to be too broad, the other weak band assigned to the CH_2 twisting mode may be considered to be hidden somewhere near the foot of the band.

Corresponding to the CH_2 scissoring mode at 1435 cm^{-1} for the parent species, either the band at 1319 or 1331 cm^{-1} in the crystalline state can be regarded as the CHD scissoring mode for the *trnas* isomer. Though there is no way to decide which is the correct assignment, the band at 1319 cm^{-1} may be considered to be preferable on the basis of the results of the calculation.

For the *gauche* isomer, since the band around 1295 cm^{-1} is too much weakened in the crystalline state, the band may consist of several overlapping bands due to the *gauche* isomer. Therefore, the CHD scissoring modes for the *gauche* isomers can be regarded as overlapped on this band.

For the α-deuterated species, the strong band at 1200 cm^{-1} can be easily assigned to the CH deformation mode originating from the CHD wagging mode for the *trans* isomer on the basis of a comparison of the spectra with those for CH_3CHDBr.

There are several weak bands in the crystalline state in the expected region for the higher-frequency CH_2 wagging mode. As the corresponding band at 1296 cm^{-1} for the β-deuterated species is also not very strong, the weak band can be assigned to this mode. However, in this region, the CHD scissoring and CH_2 twisting modes are expected, both of which are also expected to be weak. As the results of the calculation indicate that the CH_2 wagging mode has the highest frequency, while the CH_2 twisting mode has the lowest, if the relatively stronger bands are selected from the observed bands in this region, the bands at 1341, 1296 and 1260 cm^{-1} can be assigned to the CH_2 wagging, CHD scissoring, and CH_2 twisting modes respectively.

For the *gauche* isomer, though the assignments become more ambiguous than those for the *trans* isomer, the tentative assignments shown in Table 7 have been made taking into account the results of the calculation.

The assignments of the other modes, such as the CH_3 symmetric deformation, CH_2 scissoring, and CH_3 asymmetric deformation modes, are obtained from a comparison of the spectra with those for the other species.

Spectra for the C–H and C–D Stretching Modes. As is shown in Fig. 4, the C–H and C–D stretching vibrations are found in the regions around 2950 and 2200 cm^{-1} respectively.

A comparison of the spectra between the parent and deuterated species and between those in the liquid and crystalline states leads to the conclusion that the band at 2848 cm^{-1} is due to the β–CH_2 group of the *gauche* isomer, while the band at 3003 cm^{-1} is due to the α-CH_2 group of the *trans* isomer. For the β-deuterated species, one of the two C–H stretching modes of the β–CH_2 group is shifted to the region around 2200 cm^{-1} by replacing one of the hydrogens with a deuterium. The shifted bands consist of three bands; one of them (2197 cm^{-1}) persists in the crystalline state and can be assigned to the *trans* isomer, while the two other bands, which vanish in the crystalline state, can be assigned to the *gauche* isomer. Again, the spectra assigned to the *gauche* isomer are doublets, as is seen for the spectra below 900 cm^{-1}.

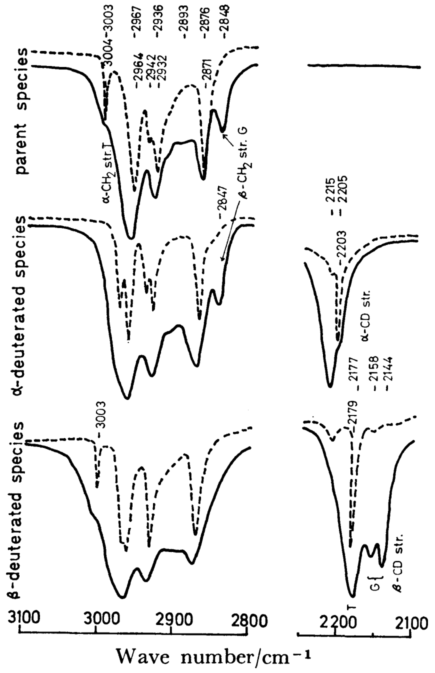

Fig. 4. Observed infrared spectra of the C-H and C-D stretching vibrations for the parent, α-deuterated, and β-deuterated species of propyl bromide. Solid and dotted lines indicate the spectra in the liquid and the crystalline states, respectively.

For the α-deuterated species, though the shifted bands are seen at 2215 and 2205 cm^{-1}, and though the band at 2215 cm^{-1} can be assigned to the *gauche* isomer, the band for the *gauche* isomer seems to be a singlet, although it may be an unresolved doublet with a smaller spacing.

Spectra in the Region below 550 cm^{-1}. As for the skeletal deformation and torsional modes, McDevitt *et al.*[4] have already reported the observed infrared and Raman spectra in the liquid state below 400 cm^{-1}, along with the assignments for the parent species. However, the assignments in Table 1 are very different from those reported by McDevitt *et al.*

They made their assignments on the basis of a comparison of the spectra of propyl chloride and bromide with those of isopropyl and *t*-butyl chlorides and bromides in the liquid state. Not only does this comparison of the spectra seem to us to be inadequate, but the lack of the spectra in the crystalline state leads to incorrect assignments for the rotational isomers.

Table 1. Infrared spectra of $CH_3CH_2CH_2Br$ (cm^{-1})[a]

Liquid	Int.	Crystal	Int.	Assignment
133[b]				CH_2–CH_2 torsion T, G
202[b]				C–C–Br bend. G
220[b]				C–C–Br bend. T, CH_3-C torsion T
273[b]				CH_3–C torsion G
311	vw	311	m	C–C–C bend. T
401	w	—		C–C–C bend. G
559	s	—		C–Br str. G
		623 sh	m	
645	s	637	vs	C–Br str. T
736	m	737	s	CH_2 rock. T
775	s	—		CH_2 rock. G
838	ms	—		CH_2 rook. G
		849 851	w	CH_2 rock. T
886	ms	—		C–C str. G
895	ms	893 897	m	C–C str. T
953	vvw	951	vw	
1022	m	1023	m	C–C str. T
1028	m	—		C–C str. G
1036	m	1038	m	CH_3 rock. A″ T, G
1078	w	—		CH_3 rock. A′ G
1097	w	1100	w	CH_3 rock. A′ T
1152	w	1154	vw	
		1214 sh	ms	CH_2 twist. T, G
1224	vs	1221	vs	CH_2 wag. T
1282	vs	1288	vw	CH_2 twist. T, G, CH_2 wag. G
1326	w	1325	s	CH_2 wag. T, G
1238	w	1335	w	
1380	s	1365 1370	ms	CH_3 sym. def. T, G
1435	s	1433 1439	ms	CH_2 sci. T, G
		1447	ms	
		1450 sh	ms	
1456	s	1456	ms	CH_3 asym. def. A′, A″ T, G
1463	s	1463	ms	
2848	ms	—		CH_2C sym. str. G
2876	s	2871	s	C–H str. T, G
2893 sh	s			
		2903 sh	m	
2918 sh	s			
		2932	ms	
2936	vs	2942	s	
2967	vs	2964	vs	
3003	ms	3004	m	CH_2Br antisym. str. T

a) Int.=intensity; s, m, w=strong, medium, weak; v=very; sh=shoulder; b=broad; T, G=*trans* form, *gauche* form.

b) Infrared frequencies were measured by McDevitt *et al.*, Ref. 4.

Table 2. Infrared spectra of CH_3CHDCH_2Br (cm^{-1})[a]

Liquid	Int.	Crystal	Int.	Assignment
		310	m	C–C–C bend. T
535	s	—		C–Br str. G
546	s	—		
607	w	—		
		616	m	
641	s	633	vs	C–Br str. T
659	m	659	s	CHD rock. T
676	m	—		
703	s	—		CHD rock. G
718	s	—		
780	w	780	w	CH_2 rock. T
812 sh	w	—		CH_2 rock. G
830	m	—		
858	s	—		CD def. G
862	s	—		
886	s	882 895	m	CD def. T
930	w	—		C–C str. G
948	m	953	m	C–C str. T
		1009 sh	vw	
1017	s	1019	m	C–C str. T, G
1036	m	—		CH_3 rock. G
1053	m	—		
1064	m	1063	m	CH_3 rock. T
1095	w	—		CH_3 rock. G
1143	w	1138	mw	CH_3 rock. T, G
1157	vw	1157	w	
1191 sh	w	1187	m	
1210 sh	m	1224	vs	CH_2 twist. T, G
1230	vs	1228	vs	CH_2 wag. T, G
1235 sh	vs	—		CH_2 wag. G
1295	s	1295 1299	s	CH def. T, CHD sci. G
1308	s	—		CH def. G
		1319	w	CHD sci. T
		1331	w	
1379	s	1366 1369	s	CH_3 sym. def. T, G
1437	s	—		CH_2 sci. T, G
		1451	s	CH_3 asym. def. T, G
1459	s	1462	s	
2144	m	—		C–D str. G
2158	m	—		
2177	m	2179	m	C–D str. T
2876	s	2872	m	CH_3 sym. str. T, G
2895 sh	s			C–H str. T, G
2935	s	2932	s	
2965	vs	2961 2968	vs	
3003 sh	m	3003	mw	CH_2Br antisym. str. T

a) See footnote a) of Table 1.

TABLE 3. INFRARED SPECTRA OF CH_3CH_2CHDBr (cm^{-1})[a]

Liquid	Int.	Crystal	Int.	Assignment
		311	m	C–C–C bend. T
545	s	—		C–Br str. G
550	s	550	vw	
		555	vw	
		596	w	
616	s	607	vs	C–Br str. T
		638	w	
671	w	669	s	CHD rock. T
710	w	—		CHD rock. G
745	s	—		
759 b	w	—		
778	m	—		CH_2 rock. G
801	m	799 801	s	CH_2 rock. T
820	s	—		CD def. G
843	m	844	s	CD def. T, G
886	s	—		C–C str. G
908	s	907	s	C–C str. T
912	s	—		C–C str. G
		921	w	
957	w	954	w	
1020 sh	w	1020	w	C–C str. T, G
1027	w	—		C–C str. G
		1041	w	
1068	m	—		CH_3 rock. G
1118	vs	1118	vs	CH_3 rock. T, G
1154	vw	1154	w	CH_3 rock. T
1200	vs	1201 1206	vs	CH def. T, G
		1223	w	
1242	w	1249	w	
1260	w	1260	w	CH_2 twist. T
1272	s	—		CH_2 twist. G, CHD sci. G
1289	m	—		
1296	m	1300	w	CHD sci. T
		1328	w	
1341	mw	1338	mw	CH_2 wag. T, G
1349 sh	w	1349	w	
1381	s	1366 1370	m	CH_3 sym. def. T, G
		1382	w	
1435	m	—		CH_2 sci. T, G
1455	s	1453	m	
		1457	m	CH_3 asym. def. T, G
1461 sh	s	1465	mw	
2205	m	2203	w	C–D str. T
2215	m	—		C–D str. G
2847	s	—		CH_2C sym. str. G
2875	vs	2873	s	C–H str. T, G
2910 sh	s			
2934	vs	2934 2942	s	
2967	vs	2965	s	
		2975	vs	

a) See footnote a) of Table 1.

The incorrectness of their assignments can be clearly seen if their assignments for propyl chloride are compared with those reported by Komaki *et al.* and by Snyder *et al.*

The assignments in Table 1 have been obtained from a comparison of the spectra of propyl bromide with those of propyl chloride, both in the liquid and crystalline states, and have been confirmed from the normal vibration calculations to be described in the next section.

Normal Vibration Calculation

In order to confirm the vibrational assignments, a normal vibration study based on a modified Urey-Bradley force field has been carried out.

The bond lengths used in the calculation were transferred from those of ethyl bromide determined by microwave study by Flanagan and Pierce.[16] They were $r(C\text{–}Br)=1.950$, $r(C\text{–}C)=1.518$, $r(C\text{–}H)_{CH_3}=1.093$, and $r(C\text{–}H)_{CH_2}=1.087$ Å. On the other hand, all of the valency angles were assumed to be tetrahedral in disregard of the observed values. The internal symmetry coordinates were taken from those given in the papers by Takahashi[17] and by Clark.[18]

At first, the force constants were transferred from those for propane[19] and for ethyl bromide[20] in the simple Urey-Bradley force field; the force constants for ethyl bromide were obtained in order to fit the calculated frequencies to the observed frequencies for the parent ethyl bromide and its three deuterated species, CH_3CD_2Br, CD_3CH_2Br, and CD_3CD_2Br, by the least-squares technique.

The internal rotation force constant for the skeletal torsion was assumed to be the value obtained from the reported far-infrared band for the CH_3 torsion of ethyl chloride.[15] This value of the force constant corresponds to the barrier height of 3.49 kcal/mol. The force constant for the CH_3 torsion was assumed to be the value obtained from the barrier height of 2.77 kcal/mol. This barrier height is the average of the observed barrier height of the CH_3 group in the *trans* and the *gauche* isomers of propyl fluoride, as determined by means of microwave spectroscopy.[21]

However, the calculated frequencies could not reproduce the observed frequencies well enough, especially for the CH_2 deformation, C–Br stretching, and C–H stretching modes.

Therefore, the force field was modified as follows: 1) the *trans* and *gauche* coupling terms between the CH_3 and CH_2C groups and between the CH_2C and CH_2Br groups were added; 2) the C–H bond interac-

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[16] C. Flanagan and L. Pierce, *J. Chem. Phys.*, **38**, 2963 (1963).

[17] H. Takahashi, *Nippon Kagaku Zasshi*, **82**, 1304 (1961).

[18] E. A. Clark, *J. Chem. Phys.*, **45**, 1759 (1966).

[19] H. Takahashi, *Nippon Kagaku Zasshi*, **83**, 978 (1962).

[20] K. Ohno, to be published.

[21] E. Hirota, *J. Chem. Phys.*, **37**, 283 (1962).

Table 4. Force constants for propyl bromide[a)] ($F'=-0.1F$)

K(C–Br)	1.784 (1.874)[e)]	$\kappa(CH_2Br)$	−0.032 (−0.047)
K(C–C)	2.695 (2.568)	$\kappa(CH_2C)$	−0.045
K(C–H), CH_2Br	4.401 (4.499)	$\kappa(CH_3)$	−0.036 (−0.010)
K(C–H), CH_2C	4.115	$Y(CH_2–CH_2)$	0.109[b)]
K(C–H), CH_3	4.209 (4.229)	$Y(CH_2–CH_3)$	0.087[c)]
H(C–C–Br)	0.033	F(C···C···Br)	0.669
H(C–C–H)	0.258	F(C···C···H)	0.406
H(H–C–Br)	0.164 (0.192)	F(H···C···Br)	0.303
H(H–C–H)	0.352	F(H···C···H)	0.250
H(C–C–C)	0.275[d)]	F(C···C···C)	0.335[d)]
$t(CH_3, CH_2)$	0.056	$g(CH_3, CH_2)$	−0.018
$t(CH_2, CH_2)$	0.001	$g(CH_2, CH_2)$	−0.033
		p(C–H)	−0.144 (−0.128)

a) The units of the force constants are in mdyn/Å for stretching, K; bending, H; repulsion, F; and bond interaction, p; and in mdyn·Å for intramolecular torsion, κ; internal rotation, Y; *trans* coupling, t; and *gauche* coupling, g.
b) The value of Y is assumed from the barrier height of 3.49 kcal/mol.
c) The value of Y is assumed from the barrier height of 2.77 kcal/mol.
d) Force constants are transferred from propane, Ref. 19.
e) ( ) indicates the values for ethyl bromide.

Table 5. Observed and calculated frequencies of $CH_3CH_2CH_2Br$ (cm^{-1})

No.	Obsd	Calcd	P.E.D.[a)]
Trans form			A′ species
1	2967	2953	CH_3 asym. str. (100)
2	2936	2944	CH_2Br sym. str. (98)
3	2876	2865	CH_3 sym. str. (70), CH_2C sym. str. (31)
4	2876	2883	CH_2C sym. str. (70), CH_3 sym. str. (31)
5	1463	1475	CH_3 asym. def. (38), CH_2C sci. (34)
6	1456	1461	CH_2Br sci. (27), CH_3 asym. def. (46)
7	1435	1429	CH_2C sci. (47), CH_2Br sci. (52)
8	1380	1384	CH_3 sym. def. (100)
9	1326	1323	CH_2C wag. (85)
10	1224	1231	CH_2Br wag. (100)
11	1097	1070	CH_3 rock. (40), C–C str. (31)
12	1022	1023	C–C str. (67)
13	895	909	C–C str. (46), CH_3 rock. (40)
14	645	641	C–Br str. (82), C–C–C bend. (20)
15	311	309	C–C–C bend. (54), C–Br str. (26)
16	220	216	C–C–Br bend. (90)
			A″ species
17	3003	3005	CH_2Br antisym. str. (100)
18	2967	2955	CH_3 asym. str. (93)
19	2936	2935	CH_2C antisym. str. (93)
20	1456	1464	CH_3 asym. def. (87)
21	1288	1281	CH_2C twist. (78)
22	1214	1222	CH_2Br twist. (78)
23	1036	1054	CH_3 rock. (48)
24	850	830	CH_2 C rock. (43), CH_2Br rock. (28), CH_3 rock. (27)
25	736	738	CH_2Br rock. (46), CH_2C rock. (42)
26	220	228	CH_3–C torsion (96)
27	133	106	$CH_2–CH_2$ torsion (90)

No.	Obsd	Calcd	P.E.D.[a)]
Gauche form			A species
1	3003	3005	CH_2Br antisym. str. (100)
2	2967	2955	CH_3 asym. str. (92)
3	2967	2953	CH_3 asym. str. (100)
4	2936	2944	CH_2Br sym. str. (90)
5	2936	2934	CH_2C antisym. str. (85)
6	2876	2865	CH_3 sym. str. (71), CH_3 sym. str. (30)
7	2848	2884	CH_2C sym. str. (70), CH_3 sym. str. (29)
8	1463	1472	CH_3 asym. def. (65)
9	1456	1465	CH_3 asym. def. (85)
10	1435	1453	CH_2Br sci. (49), CH_2C sci. (27)
11	1435	1443	CH_2C sci. (55), CH_2Br sci. (39)
12	1380	1384	CH_3 sym. def. (100)
13	1326	1348	CH_2C wag. (65)
14	1282	1286	CH_2C twist. (76)
15	1282	1226	CH_2Br wag. (65)
16	1214	1204	CH_2Br twist. (67)
17	1078	1065	CH_3 rock. (39)
18	1036	1044	CH_3 rock. (43)
19	1028	1022	C–C str. (73)
20	886	901	C–C str. (54), CH_3 rock. (35)
21	838	830	CH_2C rock. (30), CH_2Br rock. (34), CH_3 rock. (23)
22	775	753	CH_2Br rock. (49), CH_2C rock. (33)
23	559	571	C–Br str. (97)
24	401	407	C–C–C bend. (61)
25	273	264	CH_3–C torsion (42), C–C–Br bend. (31)
26	202	189	C–C–Br bend. (35), CH_3–C torsion (52)
27	133	95	$CH_2–CH_2$ torsion (75)

a) Potential energy distributions are shown in percent for the internal symmetry coordinates, where only contributions greater than 20% are included.

TABLE 6. OBSERVED AND CALCULATED FREQUENCIES OF CH_3CHDCH_2Br (cm^{-1})

No.	Obsd	Calcd	P.E.D.[a]
Trans form			A species
1	3003	3005	CH_2Br antisym. str. (100)
2	2965	2954	CH_3 asym. str. (100)
3	2965	2953	CH_3 asym. str. (100)
4	2935	2944	CH_2Br sym. str. (99)
5	2876	2909	CHC str. (97)
6	2876	2870	CH_3 sym. str. (99)
7	2177	2130	CDC str. (100)
8	1459	1467	CH_3 asym. def. (84)
9	1459	1464	CH_3 asym. def. (87)
10	1459	1448	CH_2Br sci. (95)
11	1379	1384	CH_3 sym. def. (100)
12	1295	1309	CHDC wag. (54), CHDC twist. (25)
13	1319	1299	CHDC sci. (75)
14	1230	1230	CH_2Br wag. (90)
15	1210	1208	CH_2Br twist. (79)
16	1143	1133	CH_3 rock. (24), CHDC twist. (29), C–C str. (32)
17	1064	1060	CH_3 rock. (44), C–C str. (29)
18	1017	1021	C–C str. (35), CH_3 rock. (39)
19	948	910	C–C str. (58), CH_3 rock. (28)
20	886	886	CHDC twist. (18), CHDC wag. (30)
21	780	789	CH_2Br rock. (54)
22	659	660	CHDC rock. (66)
23	641	640	C–Br str. (82)
24	310	307	C–C–C bend. (54), C–Br str. (26)
25	—	226	CH_3–C torsion (96)
26	—	212	C–C–Br bend. (88)
27	—	103	CH_2–CHD torsion (90)
Gauche form(G)			A species
1	3003	3004	CH_2Br antisym. str. (100)
2	2965	2954	CH_3 asym. str. (99)
3	2965	2953	CH_3 asym. str. (100)
4	2935	2943	CH_2Br sym. str. (100)
5	2876	2910	CHC str. (97)
6	2876	2870	CH_3 sym. str. (99)
7	2158	2130	CDC str. (100)
8	1459	1467	CH_3 asym. def. (85)
9	1459	1464	CH_3 asym. def. (87)
10	1437	1447	CH_2Br sci. (95)
11	1379	1384	CH_3 sym. def. (100)
12	1308	1337	CHDC wag. (44), CHDC twist. (21)
13	1295	1305	CHDC sci. (79)
14	1230	1220	CH_2Br wag. (68), C–C str. (28)
15	1210	1207	CH_2Br twist. (69)
16	1095	1130	CH_3 rook. (27), C–C str. (33), CHDC twist. (23)
17	1036	1042	CH_3 rock. (51)
18	1017	1015	C–C str. (40), CH_3 rock. (35)
19	930	904	C–C str. (50)
20	862	877	CHDC twist. (17), CHDC wag. (24), C–C str. (25)
21	812	792	CH_2Br rock. (58)
22	718	699	CHDC rock. (55)
23	546	563	C–Br str. (93)
24	—	400	C–C–C bend. (64)
25	—	254	CH_3–C torsion (52), C–C–Br bend. (27)
26	—	185	C–C–Br str. (41), CH_3–C torsion (44)
27	—	94	CH_2–CHD torsion (77)
Gauche form(G′)			A species
1	3003	3005	CH_2Br antisym. str. (100)
2	2965	2954	CH_3 asym. str. (100)
3	2965	2953	CH_3 asym. str. (100)
4	2935	2944	CH_2Br sym. str. (98)
5	2876	2909	CHC str. (95)
6	2876	2870	CH_3 sym. str. (98)
7	2144	2130	CDC str. (100)
8	1459	1467	CH_3 asym. def. (84)
9	1459	1464	CH_3 asym. def. (86)
10	1437	1448	CH_2Br sci. (93)
11	1379	1384	CH_3 sym. def. (100)
12	1308	1324	CHDC wag. (49), CHDC twist. (17)
13	1295	1295	CHDC sci. (89)
14	1235	1239	CH_2Br wag. (91)
15	1210	1209	CH_2Br twist. (69)
16	1143	1133	CH_3 rock. (24), C–C str. (40), CHDC twist. (27)
17	1053	1051	CH_3 rock. (49)
18	1017	1019	C–C str. (48), CH_3 rock. (36)
19	930	900	C–C str. (54), CH_3 rock. (33)
20	858	865	CHDC twist. (30), CHDC wag. (36)
21	830	803	CH_2Br rock. (68)
22	703	695	CHDC rock. (56)
23	535	550	C–Br str. (85)
24	—	404	C–C–C bend. (62)
25	—	256	CH_3–C torsion (49), C–C–Br bend. (28)
26	—	186	C–C–Br bend. (39), CH_3 torsion (47)
27	—	94	CH_2–CHD torsion (77)

a) See a) of Table 5. Potential energy distributions are shown in percent for the internal symmetry coordinates of $CH_3CH_2CH_2Br$. Though the designations of the CH and CD deformation modes are used in Tables 2—3 and in the text, in this table, the designations of the CHD wagging and twisting modes are used for the convenience of the comparison with the results for the parent species.

Table 7. Observed and calculated frequencies of CH_2CH_2CHDBr (cm^{-1})

No.	Obsd	Calcd	P.E.D.a)
Trans form			A species
1	2967	2976	CHBr str. (99)
2	2967	2955	CH_3 asym. str. (93)
3	2967	2953	CH_3 asym. str. (100)
4	2934	2935	CH_2C antisym. str. (93)
5	2875	2865	CH_3 sym. str. (72), CH_2C sym. str. (29)
6	2875	2884	CH_2C sym. str. (71), CH_3 sym. str. (29)
7	2205	2177	CDBr str. (100)
8	1461	1471	CH_3 asym. def. (70)
9	1455	1464	CH_3 asym. def. (87)
10	1455	1449	CH_2C sci. (82)
11	1381	1384	CH_3 sym. def. (100)
12	1341	1327	CH_2C wag. (80)
13	1296	1295	CHDBr sci. (57)
14	1260	1274	CH_2C twist. (72)
15	1200	1214	CHDBr wag. (47), CHDBr twist. (33)
16	1154	1091	CH_3 rock. (32), C–C str. (20)
17	1118	1064	CH_3 rock. (46), C–C str. (28)
18	1020	1028	C–C str. (63)
19	909	936	C–C str. (37), CH_3 rock. (28)
20	843	866	CHDBr twist. (18), CHDBr wag. (17), CH_3 rock. (26), C–C str. (24)
21	801	795	CH_2C rock. (51), CH_3 rock. (23)
22	671	663	CHDBr rock. (65)
23	616	603	C–Br str. (63)
24	311	309	C–C–C bend. (53), C–Br str. (26)
25	—	226	CH_3–C torsion (95)
26	—	213	C–C–Br bend. (87)
27	—	104	CHD–CH_2 torsion (90)
Gauche form(G)			A species
1	2967	2976	CHBr str. (100)
2	2967	2955	CH_3 asym. str. (93)
3	2967	2953	CH_3 asym. str. (100)
4	2934	2935	CH_2C antisym. str. (93)
5	2875	2865	CH_3 sym. str. (72), CH_2C sym. str. (29)
6	2847	2884	CH_2C sym. str. (71), CH_3 sym. str. (29)
7	2215	2176	CDBr str. (100)
8	1461	1471	CH_3 asym. def. (71)
9	1455	1464	CH_3 asym. def. (87)
10	1435	1447	CH_2C sci. (84)
11	1381	1384	CH_3 sym. def. (100)
12	1341	1335	CH_2C wag. (79)
13	1289	1293	CHDBr sci. (67)
14	1289	1285	CH_2C twist. (61)
15	1200	1210	CHDBr wag. (40), CHDBr twist. (26)
16	1118	1104	CH_3 rock. (30), C–C–str. (41)
17	1068	1060	CH_3 rock. (44), CH_2C rock. (21)
18	1020	1023	C–C str. (73)
19	912	942	C–C str. (22), CH_3 rock. (50)
20	820	828	CHDBr twist. (20), CHDBr wag. (17), CH_2C rock. (26)
21	745	795	CH_2C rock. (29)
22	710	666	CHDBr rock. (74)
23	550	557	C–Br str. (93)
24	—	399	C–C–C bend. (56)
25	—	259	CH_3–C torsion (45), C–C–Br bend. (28)
26	—	188	C–C–Br bend. (37), CH_3–C torsion (49)
27	—	94	CHD–CH_2 torsion (76)
Gauche form(G′)			A species
1	2967	2975	CHBr str. (100)
2	2967	2955	CH_3 asym. str. (99)
3	2967	2953	CH_3 asym. str. (100)
4	2934	2935	CH_2C antisym. str. (99)
5	2875	2865	CH_3 sym. str. (73), CH_2C sym. str. (28)
6	2847	2884	CH_2C sym. str. (72), CH_3 sym. str. (29)
7	2215	2177	CDBr str. (100)
8	1461	1471	CH_3 asym. def. (72)
9	1455	1464	CH_3 asym. def. (87)
10	1435	1446	CH_2C sci. (86)
11	1381	1384	CH_3 sym. def. (100)
12	1341	1364	CH_2C wag. (57)
13	1272	1289	CH_2C twist. (54), CHDBr sci. (34)
14	1272	1268	CHDBr sci. (41), CH_2C twist. (32)
15	1200	1203	CHDBr wag. (46), CHDBr twist. (23)
16	1118	1092	CH_3 rock. (33), CHDBr twist.(21)
17	1068	1054	CH_3 rock. (24), C–C str. (39)
18	1027	1032	C–C str. (45), CH_3 rock. (36)
19	886	916	C–C str. (44), CHDBr twist. (22), CH_3 rock. (24)
20	843	861	CHDBr twist. (15), CHDBr wag (17), C–C str. (22), CH_3 rock. (27)
21	778	783	CH_2C rock. (50)
22	745	699	CHDBr rock. (69)
23	545	545	C–Br str. (90)
24	—	390	C–C–C bend. (55)
25	—	260	CH_3–C torsion (43), C–C–Br bend. (27)
26	—	188	C–C–Br bend. (36), CH_3–C torsion (50)
27	—	94	CHD–CH_2 torsion (77)

a) See a) of Table 6.

tion constants were introduced; 3) the C–H stretching force constants of the CH_2 groups were considered to be not necessarily equal for the CH_2C and CH_2Br groups, and 4) the stretching force constants of K(C–C) and K(C–Br), the bending force constant of H(H–C–Br), and the intramolecular torsions were also considered to be different from the values transferred from similar molecules.

These force constants were determined by the least-squares technique in order to reproduce the observed frequencies for the parent species. They are shown in Table 4, together with the other transferred force constants. The calculated and observed frequencies for the parent and two asymmetrically-deuterated species are given in Tables 5—7, together with the potential energy distributions. A good agreement has been obtained between the calculated and observed frequencies for the two deuterated species as well as for the parent species. Since the force constants were adjusted for the parent species, this agreement for the deuterated species is considered to indicate the reasonableness of the present assignments.

From the potential energy distributions, for the parent species larger mode mixings are obvious between the two CH_2 scissoring modes, between the C–C stretching and CH_3 rocking modes, and between the two CH_2 rocking modes.

Although the mode mixing has been found to be relatively large between two skeletal bending vibrations, as had been expected, the mode designations in the internal coordinates still seem to be valid for this molecule. Therefore, the designations of the C–C–C and C–C–Br bending modes are more adequate for the description of the actual modes of the vibrations than the designations of the symmetric and antisymmetric deformation modes of the two skeletal bendings.

Discussion

Mizushima *et al.*[22] pointed out that when a heavier atom or group, such as the halogen atom or the CH_3 group, occupies the position *trans* to the halogen atom, the stretching vibration of the carbon-halogen bond is observed at a higher frequency than in the other configurations.

This tendency is also found in the cases of the deuterated species and the parent species of propyl bromide. That is, the C–Br stretching vibrations for the *trans* isomers of the three isotopic species were always observed at higher frequencies than those for the *gauche* isomers. Furthermore, even for the two different *gauche* isomers of the α- and β-deuterated species, the C–Br stretching vibration appears at a higher frequency for the *gauche* isomers with the deuterium atom at the posittion *trans* to the bromine atom than that for the other, *gauche* isomer with its hydrogen atom at the posittion *trans* to the bromine atom.

As for the frequency splittings of the *gauche* isomers resulting from the asymmetrical deuteration, the bands in the range from 500 to 1000 cm^{-1} give more obvious patterns of the doublets than the bands in the other range. Although the spacings of the doublets for the CH_2 deformation modes are found to be larger, in general, for the α-deuterated species than for the β-deuterated species, the patterns of the doublets seem to be more distinct for the β-deuterated species than for the α-deuterated species. Therefore, the β-deuterated species may be preferable in the determination of the molecular forms of the rotational isomers for the $XCH_2CH_2CH_3$-type molecules.

The authors wish to express their thanks to Dr. Kazutoshi Tanabe and Dr. Shinnosuke Saëki of the Government Chemical Industrial Research Institute of Tokyo for their pre-publication information on their vibrational assignments.

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[22] S. Mizushima, T. Shimanouchi, K. Nakamura, M. Hayashi, and S. Tsuchiya, *J. Chem. Phys.*, **26**, 970 (1957).