

in the minimum energy conformation and also in conformations with parameters ( $n=2$ ,  $h=4.2$  to  $4.3$  Å). It is also seen from Fig. 3 that conformations with  $n=2$  and  $h=4.2$  to  $4.3$  Å, occur very close to the minimum energy. However, from the present calculations based on isolated chain it is not quite clear why the polygalacturonic acid chain prefers a three-fold screw axis rather than a two-fold as in cellulose<sup>10-12</sup>. Probably for pectic acid the intermolecular forces play a major role in stabilizing helical conformations with three fold axis in solid state.

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## INFRARED ABSORPTION SPECTRA OF META- AND PARA-METHYLANISOLE

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#### ABSTRACT

The infrared absorption spectra of meta- and para-methylanisoles have been recorded in the region  $350-4000\text{ cm}^{-1}$  in liquid phase and the vibrational analyses have been performed. The observed fundamental frequencies have been assigned to various modes of vibrations with the assignments proposed for anisole and some of its derivatives and for other disubstituted benzenes.

#### INTRODUCTION

**V**IBRATIONAL analysis of the infrared and Raman spectra of anisole and its mono halogen substituted derivatives have been carried out by Owen and Hester<sup>1</sup>, to investigate possible trends in the vibrational patterns of disubstituted benzenes. The assignments of the observed frequencies in substituted anisoles become somewhat more difficult because of the superposition of, perhaps, several vibrations due to the phenyl ring and those due to the substituents. However, it is possible to assign the substituent vibrational modes from a comparison with assignments of similar substituents in simpler molecules. Josien and coworkers<sup>2</sup> working on a number of substances containing  $\text{CH}_3$  group assigned the frequencies in  $2900\text{ cm}^{-1}$  region to methyl group vibrations. They further observed that the methyl group vibrations are very slightly affected by the nature or position

of other substituents. In the present study the infrared spectra of meta- and para-methylanisoles have been investigated in liquid phase and an attempt has been made to assign the observed frequencies to various modes of vibrations.

#### EXPERIMENTAL

The chemicals used in the present investigations were manufactured by Fluka AG (Switzerland), and were of pure quality. These are liquids at room temperature.

The infrared absorption spectra of *m*- and *p*-methylanisoles were recorded in the region  $650-4000\text{ cm}^{-1}$  in liquid phase. In each case a small amount of the sample was enclosed between two NaCl windows and was pressed without using any spacer and the absorption path length thus available was found sufficient. In the region  $350-650\text{ cm}^{-1}$ , the spectra of the pure liquids (meta- and para-isomers) were recorded by using a KBr cell of

0.05 mm thickness. All these spectra were recorded on a Perkin-Elmer 621 grating spectrophotometer. The specific infrared traces of the two isomeric methylanisoles are reproduced in Figs. 1 and 2.

Varsanyi<sup>15</sup> has pointed out that in the case of substituents like  $-\text{CH}_3$ ,  $\text{OCH}_3$ ,  $\text{CHO}$ , etc., the C-substituent stretching vibration couples strongly with the ring breathing vibration. As a result of which

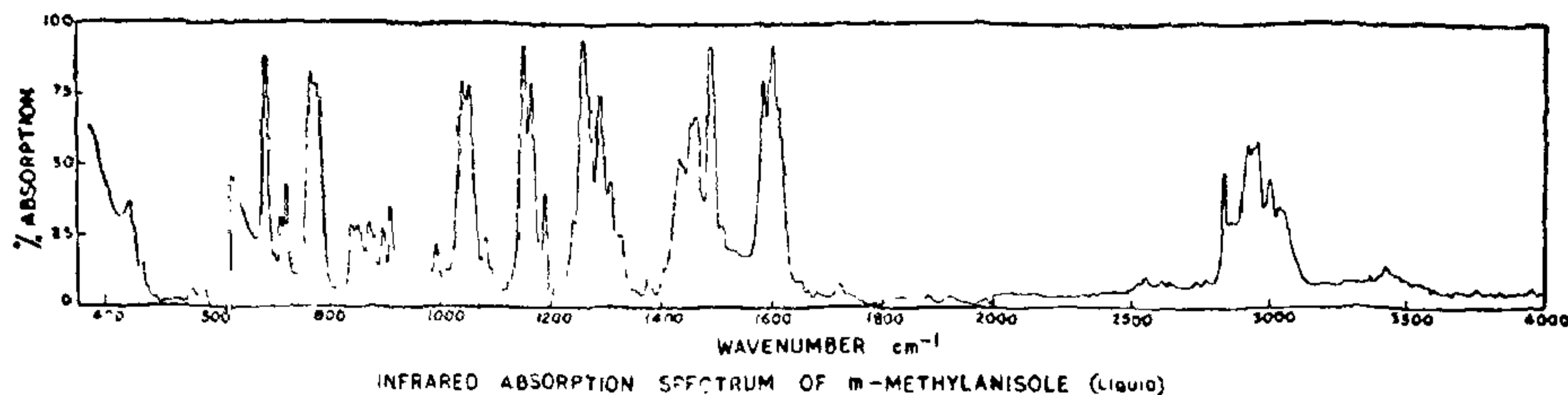


FIG. 1

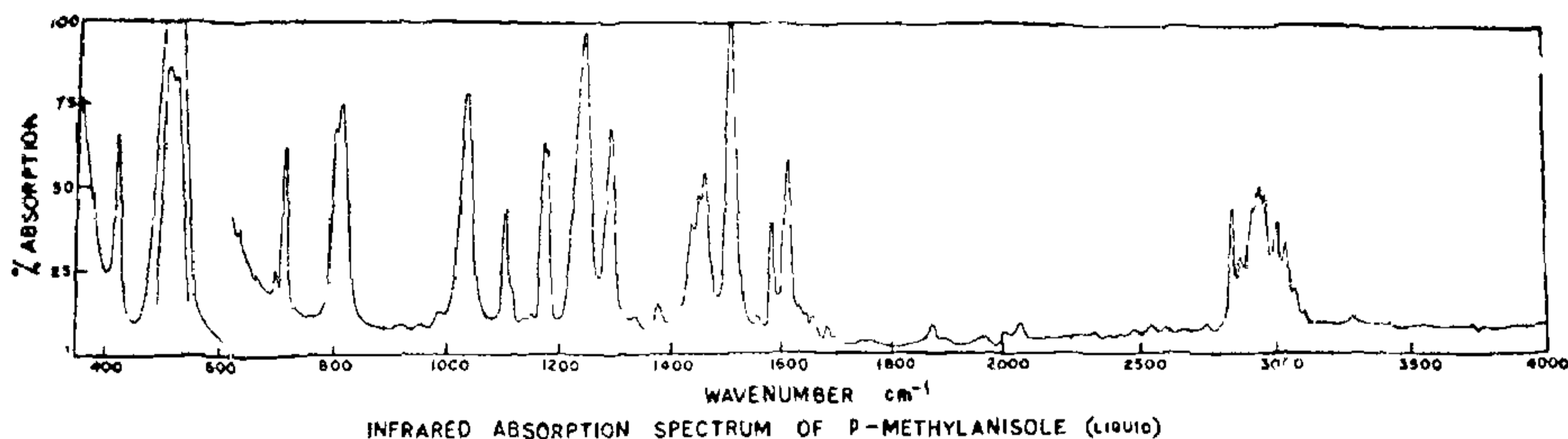


FIG. 2

#### ANALYSIS OF SPECTRA

Methylanisoles having 19 atoms give rise to 51 normal modes of vibrations. If we assume, as an approximation, the  $\text{OCH}_3$  and  $\text{CH}_3$  groups to lie in the plane of the phenyl ring, the *m*- and *p*-methylanisoles would belong to  $C_s$  point group. The 51 normal modes of vibrations can be divided into 35  $a'$  (planar) and 16  $a''$  (non-planar). All these modes are allowed in both the Raman and infrared spectra.

The choice of fundamental frequencies is based on general correlation with the spectra of anisole<sup>3,4</sup> and its derivatives<sup>1,5-7</sup>, disubstituted benzenes<sup>8-11</sup> and other related molecules<sup>12-14</sup>. In assigning the frequencies to various modes of vibrations assistance has also been taken from the relative intensities of the observed infrared bands.

As a result of substitution of one  $-\text{OCH}_3$  and one  $-\text{CH}_3$  group in the benzene ring, we expect six C-substituent vibrations in these molecules. These would include two C-substituent stretching, two in-plane bending and two out-of-plane bending modes for each isomer.

Reviewing the earlier studies on the vibrational spectra of a number of substituted benzenes,

the C-substituent stretching frequency does not drop below  $1050\text{ cm}^{-1}$ . In the case of asymmetric trialkyl benzenes McMurry and Thornton<sup>16</sup> have found this frequency in the region  $1195\text{--}1302\text{ cm}^{-1}$ . The stretching frequency of the methoxy group with the ring (*i.e.*, C- $\text{OCH}_3$  stretching) has been assigned at  $1248\text{ cm}^{-1}$  in anisole<sup>4</sup>; in the region  $1240\text{--}1260\text{ cm}^{-1}$  in halogeno-anisoles<sup>4</sup> and in the region  $1240\text{--}1270\text{ cm}^{-1}$  in isomeric methoxybenzaldehydes<sup>17</sup>. Accordingly, we have assigned the strong bands  $1260$  and  $1246\text{ cm}^{-1}$  in *m*- and *p*-methylanisoles, to C- $\text{OCH}_3$  stretching mode.

The C- $\text{CH}_3$  stretching mode of vibration causes strong absorption in the region  $700\text{--}800\text{ cm}^{-1}$ . Pitzer and Scott<sup>8,11</sup> in toluene, Joshi and Singh<sup>19</sup> in ortho-bromo-toluene and Lal *et al.*<sup>13,14</sup> in isomeric cresols and dimethylphenols have also assigned the frequencies due to this mode in this region. In the present case, the bands at  $770$  and  $805\text{ cm}^{-1}$  observed with strong intensity in *m*- and *p*-methylanisoles, respectively, have been assigned to this mode of vibration.

The  $\text{CH}_3$  group gives rise to two types of vibrations: (i) The internal vibrations which appear even if the group is an isolated one. These vibra-

tions consist of  $\text{CH}_3$  stretching and deformation modes. The magnitudes of the frequencies due to these modes remain practically unchanged. (ii) The external vibrations in which the  $\text{CH}_3$  group does not internally deform but moves as a whole unit and this motion must be compensated by motions of the molecule. These vibrations are rocking and twisting or torsional vibrations (*i.e.*, for one  $\text{CH}_3$  group two rocking and one torsional vibration). The magnitudes of these vibrations are quite variable and depend on the structure of the molecule. The twisting vibration usually lies below  $300\text{ cm}^{-1}$  and is not generally observed probably due to its weak intensity.

In one methyl group there are three C-H stretching vibrations, one of these is symmetric while the other two are asymmetric. The symmetric mode appears quite prominently in the infrared spectrum of methyl substituted benzenes and the asymmetric modes usually appear with variable intensity. These vibrations generally lie in the region  $2815\text{--}2975\text{ cm}^{-1}$ . Fox and Martin<sup>20</sup> examined a large number of hydro-carbons containing methyl groups and found that in all cases two strong bands appear at about  $2872$  and  $2962\text{ cm}^{-1}$  corresponding to C-H symmetric and asymmetric stretching modes in the methyl group. However, the presence of oxygen atom with methyl group in anisole may cause changes in their magnitudes. In the present study, the frequencies  $2868$  and  $2840\text{ cm}^{-1}$  in the case of meta-isomer and  $2870$  and  $2840\text{ cm}^{-1}$  in the case of para-isomer have been assigned to C-H symmetric modes. The C-H asymmetric stretching frequencies have been observed at  $2956$ ,  $2945$  and  $2927\text{ cm}^{-1}$  in meta-methylanisole and at  $2958$ ,  $2940$ ,  $2930$  and  $2915\text{ cm}^{-1}$  in para-methylanisole. These assignments find support from the studies of Singh and Singh<sup>21</sup> on nitrotoluenes, Mooney<sup>22</sup> on halogenated toluenes and Fuson *et al.*<sup>2</sup> on methyl substituted benzenes.

In addition to the above-mentioned stretching vibrations, each methyl group has three C-H deformation modes also, one of these is symmetric and other two asymmetric. The magnitude of the symmetric vibration changes with the electronegativity of the atom to which the  $\text{CH}_3$  group is attached, whereas asymmetric vibrations are less sensitive to the electronegativity of the attached atom. In the present case, the symmetric  $\text{CH}_3$  deformation mode has been identified at  $1375$  and  $1326\text{ cm}^{-1}$  in the meta-isomer and at  $1379$  and  $1336\text{ cm}^{-1}$  in the para-isomer. The frequencies  $1454$ ,  $1442$  and  $1435\text{ cm}^{-1}$  in meta-methylanisole and  $1453$ ,  $1442$  and  $1413\text{ cm}^{-1}$  in para-methylanisole may be assigned to C-H asymmetric bend-

ing modes. These assignments are in agreement with the assignments proposed by Horak *et al.*<sup>23</sup> and Owen and Hester<sup>1</sup> for halogenated anisoles.

For two methyl groups four rocking modes (two planar and two non-planar) are expected. Methyl rocking frequencies are mass sensitive and variable in magnitudes due to interaction with skeletal stretching modes. Randle and Whiffen<sup>24</sup> and Fuson *et al.*<sup>2</sup> have studied a number of methyl substituted benzenes in the region  $1000\text{--}1200\text{ cm}^{-1}$  to determine the rocking frequency associated with the methyl group. In toluene, Wilmschurst and Bernstein<sup>25</sup> have assigned the frequencies  $1040$  and  $1080\text{ cm}^{-1}$  to  $\text{CH}_3$  rocking mode. Mooney<sup>22</sup> has assigned the frequencies  $1041$  and  $1091\text{ cm}^{-1}$  in *o*-chlorotoluene and  $1044$  and  $1091\text{ cm}^{-1}$  in *o*-bromotoluene to methyl rocking modes. In the case of *o*-fluoro, *o*-chloro- and *o*-bromoanisoles, Singh and Singh<sup>5</sup> have assigned the frequencies due to this mode in this region. In agreement with these assignments, in the present case the frequencies  $1083$  and  $1093\text{ cm}^{-1}$  in the case of meta- and  $1108$  and  $1117\text{ cm}^{-1}$  in the case of para-isomer have been assigned to the non-planar  $\text{CH}_3$  rocking mode. The planar  $\text{CH}_3$  rocking mode has been identified at  $1010$  and  $1054\text{ cm}^{-1}$  in meta-isomer but the frequencies due to this mode could not be assigned in the case of para-isomer.

In the present study, the vibrational mode of the methoxy group associated with O- $\text{CH}_3$  stretching has been observed at  $778$  and  $815\text{ cm}^{-1}$  in meta- and para-methyl anisoles, respectively. Both these frequencies appear with strong intensity. These assignments find support from the assignments proposed for anisole and its mono-derivatives<sup>1</sup>.

A correlation of all the fundamental frequencies observed in the infrared spectra of the two isomers along with their relative intensities and proposed assignments are given in Table I. Assignments for the overtones and combination bands are not included in this table.

TABLE I  
Correlation of the vibrational frequencies of meta- and para-methylanisoles

<i>m</i> -methyl-anisole		<i>p</i> -methyl-anisole		Assigned mode of vibration
$\text{cm}^{-1}$	Int.	$\text{cm}^{-1}$	Int.	
447	27	420	46	C C C o.p. bending
468	sh	511	100	C C C i.p. bending
556	9	521	86	O CH <sub>3</sub> i.p. bending
576	12	537	36	C OCH <sub>3</sub> i.p. bending
627	51	637	36	C C C i.p. bending
689	94	702	22	C C C o.p. bending

TABLE I (contd.)

<i>m</i> -methyl- anisole		<i>p</i> -methyl- anisole		Assigned mode of vibration
cm <sup>-1</sup>	Int.	cm <sup>-1</sup>	Int.	
725	48	717	58	C-H o.p. bending
770	88	805	62	C-CH <sub>3</sub> stretching
778	83	815	69	O-CH <sub>3</sub> stretching
873	34	..	..	C-H o.p. bending
896	32	922	8	C-H o.p. bending
910	41	954	8	C-H o.p. bending
994	26	987	11	C-C-C i.p. bending
1010	17	..	..	CH <sub>3</sub> rocking (planar)
1044	86	1036	73	C-C stretching (ring breathing)
1054	83	..	..	CH <sub>3</sub> rocking (planar)
1083	28	1108	40	CH <sub>3</sub> rocking (non- planar)
1093	19	1117	sh	CH <sub>3</sub> rocking (non- planar)
1154	98	1138	9	C-H i.p. bending
1165	85	1152	11	C-H i.p. bending
1190	44	1173	59	C-H i.p. bending
1260	100	1246	91	C-OCH <sub>3</sub> stretching
1290	81	1262	sh	C-H i.p. bending
1310	49	1294	64	C=C stretching
1326	29	1336	9	C-H sym. bending (in CH <sub>3</sub> group)
1375	14	1379	14	C-H sym. bending (in CH <sub>3</sub> group)
1435	56	1413	sh	C-H asym. bending (in CH <sub>3</sub> group)
1442	55	1442	36	C-H asym. bending (in CH <sub>3</sub> group)
1454	69	1453	44	C-H asym. bending (in CH <sub>3</sub> group)
1464	72	1464	51	C=C stretching
1490	97	1503	100	C=C stretching
1586	86	1585	37	C=C stretching
1605	98	1612	55	C=C stretching
2840	53	2840	41	C-H sym. stretching (in CH <sub>3</sub> group)
2868	34	2870	28	C-H sym. stretching (in CH <sub>3</sub> group)
..	..	2915	41	C-H asym. stretching (in CH <sub>3</sub> group)
2927	62	2930	45	C-H asym. stretching (in CH <sub>3</sub> group)
2945	sh	2940	47	C-H asym. stretching (in CH <sub>3</sub> group)
2956	64	2958	45	C-H asym. stretching (in CH <sub>3</sub> group)
3006	50	3008	37	C-H stretching
3035	39	3038	31	C-H stretching
..	..	3070	18	C-H stretching
..	..	3108	11	C-H stretching

N.B.—sh = shoulder, i.p. = in-plane, o.p. = out-of-plane, sym. = symmetric and asym. = asymmetric.

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