

## Raman and Infrared Spectra of 3-Methylbutene-1

JOSEPH S. ZIOMEK,\* *Chemistry Department, DePaul University,  
Chicago, Illinois*

and

JOHN E. FORRETTE, *Roy C. Ingersoll Research Center,  
Borg-Warner Corporation, Des Plaines, Illinois*

### INTRODUCTION

In recent years much attention has been focussed on the monoolefins as monomers in the preparation of polymers, especially the stereospecific type. As a result, extensive investigations have been carried out on the chemical and spectroscopic properties of such monomers as ethylene, propylene, and styrene. However, very little has been done on 3-methylbutene-1. The purpose of this paper is to report on the spectral studies made on 3-methylbutene-1.

### EXPERIMENTAL

The sample of 3-methylbutene-1 used in this investigation was obtained from Phillips Petroleum Co., Special Products Division. Its purity was specified at 99 mole-% minimum.

A saturated solution of 3-methylbutene-1 in methyl alcohol and carbon tetrachloride were used for the Raman spectrum measurements. The Raman displacements obtained in the region from the exciting line to 1000  $\text{cm.}^{-1}$  were from measurements on the methyl alcohol solution, and those in the region 1000-3100  $\text{cm.}^{-1}$  were obtained from measurements on carbon tetrachloride solutions.

The instrument used was the Cary 81 Raman spectrophotometer. Depolarization measurements on the displacements were made on these solutions in the corresponding regions by a two-exposure method involving Polaroid cylinders (furnished by the Applied Physics Corporation). No corrections for convergence error were made and the results are listed, in Table I, as polarized (p) or depolarized (dp) and, in addition, a numerical value is given in parentheses after the symbol when possible.

The infrared absorption measurements in the region 700-3000  $\text{cm.}^{-1}$  were made for the vapor with the Perkin-Elmer 221G spectrophotometer. In the region 3000-9000  $\text{cm.}^{-1}$  measurements were made on the vapor of 3-methylbutene-1 and a thin film of poly-3-methylbutene-1 polymer with

\* Present address: Martin Co., Orlando, Florida.

TABLE I  
 Raman and Infrared Spectra of 3-Methylbutene-1<sup>a</sup>

Gerding	Raman		Infrared vapor $\nu$ , cm. <sup>-1</sup>	Assignments
	This work			
	$\Delta\nu$	$\rho$		
249 (0,d)	—	—	—	$a''$ fund., C—C—C bend
298 (3,d)	—	—	—	$a'$ fund., C—C—C bend
321 (4,d)	325	dp	—	$a''$ fund., C—C—C bend
350 (3)	359	dp	—	$a''$ fund., C—C=C bend
378 (0)	—	—	—	$a''$ fund., 912 - 533 = 379
458 (0,d)	462	dp	—	$a''$ fund., 779 - 321 = 458
506 (4)	509	p (0.333)	—	$a'$ fund., 799 - 298 = 501
533 (1,d)	539	dp	—	$a''$ fund., 249 + 298 = 547, 799 - 249 = 550
665 (2,d)	662	dp	672 m	$a''$ 298 + 378 = 676, 912 - 249 = 663
—	—	—	686 m	$a'$ 321 + 350 = 671
779 (4)	786	p	784 vw	$a'$ fund., C—C stretch 533 + 249 = 782
799 (7)	802	p	794 vw	$a'$ fund., C—C stretch 506 + 298 = 804
—	—	—	801 vw	—
921 (5,d)	922	p (0.635)	912 vs	$a'$ fund., CH <sub>2</sub> wag, 2 × 458 = 916
—	—	—	919 vs	$a'$ fund., CH <sub>2</sub> wag
956 (2)	958	p (0.333)	—	$a'$ fund., 458 + 506 = 964
992 ( $\frac{1}{2}$ )	—	—	990 vs	$a''$ fund., C=C twist
—	—	—	998 vs	$a''$ fund. —
1027 (o)	1032	dp	—	$a''$ 779 + 249 = 1028
1098 (3,d)	1100	p (0.795)	1098 w	$a'$ fund., CH <sub>2</sub> rock, methyl
—	—	—	1103 w	$a'$ 779 + 321 = 1100
—	—	—	1112 w	$a''$ fund., 321 + 799 = 1120
1192 ( $\frac{1}{2}$ b)	—	—	1173 vw	$a'$ fund., CH <sub>2</sub> rock, methyl 506 + 665 = 1171
1288 (7,d)	1290	p (0.656)	1288 m	$a'$ fund., H—C=C stretch

(continued)

the Beckman DK-2 spectrophotometer. The thin film of polymer was made by hot pressing a product obtained by polymerizing 3-methylbutene-1 with a Zeigler type catalyst.<sup>1-3</sup> The product so obtained was considered highly ordered on the basis of x-ray diffraction and melting point data.

### RAMAN AND INFRARED SPECTRAL DATA

The previously and presently reported Raman spectral data are given in Table I. The values of the displacements obtained for the solutions agreed in general with those reported by Gerding and van der Vet<sup>4</sup> for the liquid. Since the depolarization measurements were not previously reported, no such comparison could be made for them.

TABLE I (continued)

Raman			Infrared vapor $\nu$ , cm. <sup>-1</sup>	Assignments
Gerding	This work			
$\Delta\nu$	$\Delta\nu$	$\rho$		
1325 (0)	—	—	1305 m	$a'$ fund., H—C=C stretch
—	—	—	1362 m	$a''$ CH <sub>3</sub> sym. bend
—	—	—	1375 m	$a''$ fund., CH <sub>3</sub> sym. bend
1381 ( $\frac{1}{2}$ )	1382	p (0.389)	1384 m	$a'$ fund., CH <sub>3</sub> sym. bend
1417 (3)	1420	p (0.275)	1420 m	$a'$ fund., (2) C—H in-plane bend
1457 (4,d)	1460	dp	1468	$a''$ fund., (2) CH <sub>3</sub> unsym. bend
			ms	
1504 (0)	—	—	—	1192 + 321 = 1513
—	1545	p (0.456)	1577	$a'$ 784 + 794 = 1578
			vw	
—	1590	p	1587	$a'$ 2 × 794 = 1588
			vw	
1642 (10)	1644	p	1650	$a'$ fund., C=C stretch
			vw	
1678 (0)	—	—	—	$a'$ 1381 + 298 = 1679
1716 (o)	—	—	—	$a'$ 1417 + 298 = 1715
—	—	—	1835 m	$a'$ CH <sub>2</sub> ethylenic 1st overtone
—	—	—	2584	$a'$ 2 × 1288 = 2576
			vw	
2654 (0)	—	—	—	$a'$ 1457 + 1192 = 2649
2716 ( $\frac{1}{2}$ )	2715	p	—	$a'$ 2963 - 249 = 2714
—	—	—	2740	— 2 × 1375 = 2750
			vw	
2827 (1)	—	—	—	$a'$ fund., 2 × 1417 = 2834
2868 (10)	2870	p (0.400)	—	$a''$ fund., (2) C—H sym. stretch
—	—	—	2898 s	$a'$ C—H sym. stretch
2914 (6)	2920	p (0.250)	—	$a'$ fund., C—H asym. stretch
—	2940	p	—	
2963 (5)	2968	dp	2958	$a''$ fund., C—H asym. stretch
			vs	
2999 (7)	3004	p (0.233)	—	$a'$ fund., (2) C—H olefinic stretch
3082 (1)	—	—	3086	$a''$ fund., C—H olefinic stretch
			ms	

\*  $\Delta\nu$  = Raman displacement,  $\rho$  = depolarization factor (dp = depolarized, p-polarized),  $\nu$  = absorption frequency (m = medium, vs = very strong, s = strong, w = weak, vw = very weak, ms = medium strong).

As for the results of the infrared absorption measurements, the wave numbers observed in the rock-salt region agreed with those reported in the American Petroleum Institute Spectrum No. 360 Sheet. Some early work by Errera et al.<sup>5</sup> reported a limited number of absorption bands in the 2800–7700 cm.<sup>-1</sup> region. These bands, however, do not agree with those observed in the present investigation.

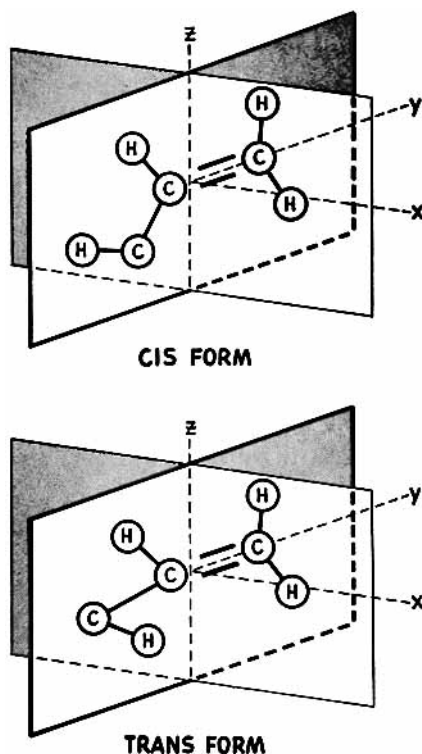


Fig. 1. The *cis-trans* Models showing all the atoms in the plane with the ethylenic carbon-carbon linkage.

### MODEL

The examination of the literature indicated that the model for 3-methylbutene-1 is that of isopropyl ethylene. This was supported by deductions made from the modes of synthesis of this substance,<sup>6-8</sup> and deductions made by Kistiakowsky et al.<sup>9</sup> on data obtained from heats of hydrogenation, which indicated a branched-chain molecule with terminal unsaturation. Thus there are three possible models: the *cis* ( $C_s$ ), *trans* ( $C_s$ ) and the *gauche* form ( $C_1$ ).

For the *cis* and *trans* forms the vinyl group lies in the plane of symmetry

TABLE II  
Selection Rules for the Three Possible Forms of 3-Methylbutene-1

Structure	No. of Raman-active <sup>a</sup>	No. of infrared-active
<i>Trans</i> $C_s$	23 $a'$ p 16 $a''$ dp	23 $a'$ 16 $a''$
<i>Cis</i> $C_s$	23 $a'$ p 16 $a''$ dp	23 $a'$ 16 $a''$
<i>Gauche</i> $C_1$	39 p	39

<sup>a</sup> Polarized = p; depolarized = dp.

of the molecule, as shown in the figures. The selection rules for these three models have been determined and are shown in Table II.

Examination of the Raman spectrum in Table I indicates that only thirty-four Raman displacements are present and that at least one of them is depolarized. The fact that one of the displacements is depolarized eliminates the *gauche* form, since the selection rules require that all displacements be polarized. Next, an examination of Table II shows that it is not possible to distinguish between the *cis* and *trans* forms on the basis of the selection rules. Thus, the model must be one of the two  $C_2$  models given.

## ASSIGNMENTS

### Group Frequencies

The 3-methylbutene-1 can be considered isopropyl ethylene. An attempt was made to make assignments on the basis of group frequencies, i.e., frequencies assigned to both the isopropyl group and the vinyl group.

TABLE III  
Raman Displacements for Compounds Which Are Structurally Related to 3-Methylbutene-1

Dimethyl ether	Isobutyraldehyde	Isopropyl acetylene	3-Methylbutene-1
162	—	185	—
—	—	215	249
—	—	268	—
—	281	—	298
316	—	—	321
—	343	—	350
413	—	—	—
—	451	—	458
—	—	—	506
—	546	527	533
—	630	630	665
—	—	775	779
—	798	—	799
920	917	927	921
—	971	958	956
—	—	—	992
1102	1111	1107	1098
1155	1176	1170	1192
—	1279	1296	1288
—	—	—	1325
—	1392	—	1381
—	—	—	1417
1450	1455	1444	1457
—	—	—	—
—	2716	—	2716
2813	2811	—	2827
2865	2872	2875	2868
2915	2911	—	2914
2950	2934	2941	2963
2987	2976	2980	2999

First, the isopropyl group frequencies were considered. For this purpose the Raman and infrared spectra of isobutyraldehyde<sup>10</sup> (isoelectronic with 3-methylbutene-1) and isopropylacetylene<sup>11</sup> were collected and these were compared with that for 3-methylbutene-1, as shown in Table III. It was found that the frequencies common to the three substances match those given by Sheppard<sup>12</sup> as listed in Table IV for the isopropyl group obtained by him on examination of isopropyl chloride, isopropyl bromide, isopropyl iodide, and isopropyl mercaptan. Furthermore, Sheppard, for these substances, had made assignments of frequencies which were used in making assignments for 3-methylbutene-1. Also, these

TABLE IV  
Raman and Infrared Spectra for the Isopropyl Group (in  $\text{cm.}^{-1}$ )

Frequency assign.	Isopropyl chloride		Isopropyl bromide		Isopropyl iodide		3-MB-1	
	Raman	Infr.	Raman	Infr.	Raman	Infr.	Raman	Infr.
CH <sub>2</sub> asym. stretch (2)	<i>a'</i>	2982		2984		2982		2999
	<i>a''</i>	2944		2956		2963		3963
	<i>a'</i>	2928		2921		2915		2914
CH <sub>2</sub> sym. stretch	<i>a'</i>	2965		—		2872		2868 (2)
	<i>a''</i>	2909		2894		(2900)		2898
C—H stretch	<i>a'</i>	(2890)		(2890)		(2890)		(2890)
CH <sub>2</sub> asym. (2) deform (2)	<i>a'</i>	1455	1461	—	1456	—	1456	1417
	<i>a''</i>		1438	1442	1442	1448	—	1457
CH <sub>2</sub> sym. deform	<i>a'</i>	1388	1385	1380	1385	1373	1382	1381
	<i>a''</i>	—	1372	—	1370	—	1369	—
C—H deform	<i>a''</i>	1337	—	1325	—	1313	1320	1325
	<i>a'</i>	1256	1261	1219	1227	1199	1201	1192
C—C stretch	<i>a''</i>	1126	1131	1119	1133	—	1125	1027
	<i>a'</i>	1059	1062	1038	1038	1019	1018	1098
CH <sub>2</sub> wag	<i>a'</i>	1161	1160	1154	1157	1146	1147	—
	<i>a''</i>	—	949	946	—	—	941	990
	<i>a''</i>	937	932	—	931	925	928	912
	<i>a''</i>	884	881	879	877	874	872	(799)

TABLE V  
The Ethylenic Group Frequencies Assigned to the 3-Methylbutene-1 Molecule

Wave number, $\text{cm.}^{-1}$	Freq. type	Wave number, $\text{cm.}^{-1}$	Freq. type
<i>a''</i> 3082	C—H stretch	<i>a'</i> 921	CH <sub>2</sub> wag
<i>a'</i> 2999		<i>a'</i> 956	
<i>a'</i> 1642	C=C stretch	992	C=C twist
<i>a'</i> 1417	CH <sub>2</sub> wag	1835	CH <sub>2</sub> 1st overtone
<i>a'</i> 1288	H—C=C stretch	665	
<i>a''</i> 458	C—C=C bend		

same frequencies were used in making the assignments for the bands in the near infrared region for the monomeric 3-methylbutene-1 as well as for the polymer.

Second, the vinyl group frequencies were considered. On the basis of the work reviewed by Potts and Nyquist<sup>13</sup> on the out-of-plane modes and the study made by Herzberg<sup>14</sup> and Tarkington<sup>15</sup> on the in-plane modes of ethylenic compounds, the frequencies listed in Table V are assigned to the vinyl group.

### Fundamentals

Examination of Table II shows that there are 23 fundamentals of the  $a'$  type and 16 of the  $a''$  type for both forms. The bands at 506, 779, 799, 921, 956, 1098, 1288, 1381, 1417, 1642, 2914, and 2999  $\text{cm.}^{-1}$  were chosen as

TABLE VI  
Observed Near-Infrared Spectrum for the Monomer and Polymer of 3-Methylbutene-1  
( $\text{cm.}^{-1}$ )<sup>a</sup>

3-Methyl- butene-1	Poly-3-Methyl- butene-1	Assignments	Vibration type
—	3151 s	2914 + 249 = 3163	$a''$
—	3322 m	3082 + 249 = 3331	$a'$
3460 w	3413 w	2963 + 458 = 3421	$a'$
—	3484 w	2963 + 533 = 3496	$a'$
3630 w	—	2963 + 665 = 3628	$a'$
3752 w	3731 w	3082 + 655 = 3747	$a'$
3824 m	3824 m	2914 + 921 = 3835	$a'$
3882 m	3883 m	2963 + 921 = 3884	$a''$
4056 s	4058 s	2963 + 1098 = 4058	$a''$
4158 ms	4124 ms	2963 + 1192 = 4152	—
4255 s	4255 s	2963 + 1288 = 4251	$a''$
4320 s	4301 s	2868 + 1457 = 4325	$a''$
4396 s	4380 s	2963 + 1417 = 4380	$a''$
4484 ms	—	2(1642) + 1192 = 4476	$a'$
4612 m	—	2(1642) + 1325 = 4609	—
4721 ms	—	3082 + 1642 = 4724	$a''$
4784 vw	—	2(1642) + 1504 = 4788	—
4866 vw	—	2(1642) + 1590 = 4874	$a'$
5449 w	5464 w	2999 + 1642 + 799 = 5440	$a'$
5666 m	5650 w	2827 + 2868 = 5695	$a'$
5747 m	—	2(2868) = 5736	$a'$
5899 ms	5865 m	2963 + 2914 = 5877	$a'$
6098 ms	—	3082 + 2999 = 6081	$a''$
7194 vw	—	2(2898) + 1417 = 7213	$a'$
7353 vw	—	2(2963) + 1417 = 7343	$a'$
8333 w	—	2(2868) + 2584 = 8318	$a'$
8474 w	—	3(2827) = 8481	$a'$
8696 w	—	3(2898) = 8694	$a'$
8849 w	—	3(2963) = 8889	$a'$

<sup>a</sup> See Table I for code.

$a'$ -type fundamentals on the basis of the values of the Raman displacements, infrared wave numbers, relative intensities, and depolarization factors. Also, the bands at 321, 458, 533, 665, 1457, 2868, 2963, and 3082  $\text{cm}^{-1}$  were taken as  $a''$  fundamentals according to the correlation of Potts and Nyquist.<sup>13</sup> Bands at 298, 378, 998, 1172, 1192, 2827, and 2999  $\text{cm}^{-1}$  were taken as  $a'$  fundamentals, and the bands at 249, 1112, and 1375  $\text{cm}^{-1}$  as  $a''$  fundamentals, according to Sheppard<sup>12</sup> and Jones and Sandorfy,<sup>16</sup> and these bands were used to make assignments of the observed bands in the Raman, infrared, and near infrared spectra of 3-methylbutene-1. This, then, accounts for 33 of the total 39 fundamental frequencies: 19 of the  $a'$  type and 14 of the  $a''$  type. To account for the remaining 6 fundamentals, additional bands at 2898 and 1457  $\text{cm}^{-1}$  were taken as the remaining two  $a''$  fundamentals and additional bands at 1417, 2914, 2999 (with 1325)  $\text{cm}^{-1}$  as the  $a'$  type. Moreover, certain of the above bands have also been assigned as difference tones, summation tones, or overtones because of the possibility of Fermi resonance or Coriolis interactions. All these assignments are given in Table I.

### Near-Infrared Region

In this region a considerable number of bands were observed for the monomer and a smaller number for the polymer, as shown in Table VI. It was possible to make assignments for the bands of the monomer with the fundamentals listed above. Furthermore, the bands of the polymer could be explained in terms of the frequencies listed for the isopropyl group and, if a comparison was made between the bands of the monomer and those of the polymer, the bands due to the olefinic group could be determined. These agreed with those previously reported for olefins,<sup>17</sup> and the fundamentals for the olefinic part of the monomer were used to make assignments of these bands.

### CONCLUSION

The assignments given above for 3-methylbutene-1 appear to be satisfactory. First, the assignments of most of the fundamentals were made on the basis of the values of the depolarization factors, displacements, and infrared wave numbers. Second, the fundamentals so assigned explained all other bands in the Raman and infrared spectra, as well as the near infrared bands. Third, the assignments given explain all the strong infrared and Raman bands in a manner that is consistent with the assignments for the corresponding structurally related hydrocarbons and other molecules.

The authors wish to express their gratitude to Charles Parsons for preparation of the polymer and to Elma Lanterman for the x-ray data.



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### Synopsis

Infrared and near-infrared spectra of 3-methylbutene-1 were observed for the vapor phase at room temperature. Also, Raman displacements and depolarization factors of 3-methylbutene-1 in methanol and carbon tetrachloride were obtained at the same temperature. Tentative assignments of the observed Raman and infrared bands were made, and a classification of bands on the basis of group frequencies is given.

### Résumé

Les spectres d'absorption d'infra-rouge et le proche-infrarouge du 3-méthyl-butène-1 ont été étudiés à température ordinaire en phase vapeur. Les spectres de diffusion et les facteurs de dépolarisation Raman ont également été obtenus pour le même produit dans l'alcool méthylique et le tétrachlorure de carbone à la même température. Les bandes infra-rouges et Raman observées ont été provisoirement attribuées, et une classification des bandes est donnée sur la base de fréquences de groupe.

### Zusammenfassung

Infrarotspektren von 3-Methylbuten-1 und auch solche im nahen Infrarot wurden in der Dampfphase bei Raumtemperatur gemessen. Bei der gleichen Temperatur wurden auch Ramanverschiebungen und Depolarisationsfaktoren für 3-Methylbuten in Methanol und Tetrachlorkohlenstoff erhalten. Eine versuchsweise Zuordnung der beobachteten Raman- und Infrarotbanden wurde vorgenommen und eine Klassifizierung der Banden nach Gruppenfrequenzen wird gegeben.

Received March 19, 1962