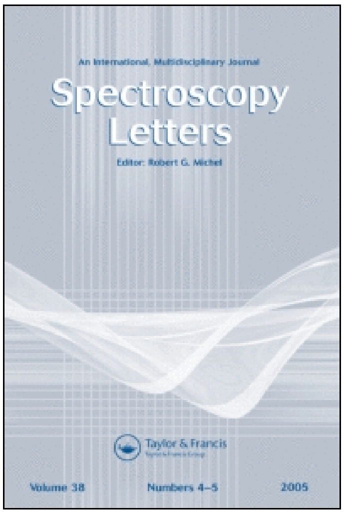

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INTERPRETATION OF THE VIBRATIONAL SPECTRA OF 3,3-DIMETHYL-1-BUTENE

Keywords: 3,3-Dimethyl-1-butene, Raman spectrum, normal coordinate calculations

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ABSTRACT

Infrared and Raman spectra were redetermined for 3,3-dimethyl-1-butene. The spectra were interpreted with the aid of normal coordinate calculations that utilized a forty-five parameter modified valence force field. The Raman spectrum, vibrational assignment, and force constant values are given in this paper.

INTRODUCTION

Nearly half a century ago, Sheppard attempted to interpret the vibrational spectra of the C_6 hydrocarbons 2,2-dimethylbutane, 3,3-

dimethyl-1-butene, and 3,3-dimethyl-1-butyne.[1] Since that time, normal coordinate calculations have been made to aid in the interpretation of the spectra for 2,2-dimethylbutane[2] and more recently for 3,3-dimethyl-1-butyne.[3] The present work was undertaken to complete the normal coordinate analysis of this series of compounds. Apparently, there has been no attempt to interpret the spectra of 3,3-dimethyl-1-butene since Sheppard's work.

Vibrational spectra for several 2-methyl-1-alkenes have been interpreted recently with the aid of normal coordinate calculations.[4-6] Calculations have now been made for the title compound as an aid in interpreting its vibrational spectra. This compound cannot exhibit rotational isomerism, so there is no ambiguity in assigning bands to a particular conformer, as was the case for 1-butene,[7,8] 2-methyl-1-butene,[4] 2-methyl-1-pentene,[5] and 2,3-dimethyl-1-butene.[6] Several force constants had to be adjusted to different values for the separate conformers of each of these compounds in order to obtain a good fit of calculated to observed wavenumbers. The force constants obtained for 3,3-dimethyl-1-butene should be useful for transfer to other alkenes that contain a vinyl group.

The infrared spectrum of 3,3-dimethyl-1-butene is part of the American Petroleum Institute Project 44 collection.[9] The solution spectrum (CCl_4, CS_2) of this compound has also been published in the Coblentz Society Desk Book of Infrared Spectra.[10] Raman data were published long ago by Fenske et al.[11] as part of a table of data for 700 compounds, and the Raman spectrum was included in 1959 as part of the API Project 44.[12] The data in refs. 9 and 11 were used by Sheppard[1] in an attempt to make an approximate fundamental vibrational assignment for this compound. The previous Raman spectra were determined with a mercury source, so this spectrum has been redetermined in the present work with an argon ion laser as the source.

EXPERIMENTAL

Infrared spectra were obtained at 4-cm^{-1} resolution with a Mattson 2020 FTIR spectrometer, which is equipped with a DTGS detector. Raman spectra were obtained at 4 cm^{-1} resolution with a SPEX double monochromator equipped with a Spectra-Physics Model 2020 argon-ion laser. The 514.5-nm line was used at ca. 150 mW power at the sample, which was contained in a 1-ml cell. The compound was obtained from Wiley Organics and had a stated purity of 99%. It was used without further purification.

CALCULATIONS

Normal coordinate calculations were done with the general vibrational analysis system written by McIntosh and Peterson.[13] The program was modified to handle up to twenty-four atoms and sixty force constants. A forty-five parameter modified valence force field was used, which included twenty-one diagonal and twenty-four interaction force constants. The molecular parameters that were used are: C=C = 0.135

nm; -C-C = 0.154 nm; =C-C = 0.1488 nm; C-H = 0.109 nm; =C-H = 0.107 nm; and all angles were assumed to be 120° or 109.47°.

RESULTS AND DISCUSSION

The liquid-state Raman spectrum of 3,3-dimethyl-1-butene is shown in Fig. 1. The IR spectrum is more readily available than is the Raman spectrum, so it will not be given here. The most intense bands in the spectrum, observed at 718 and 1644 cm^{-1}, are normally due to C-C and C=C stretches, and the C-H stretches and CH_3 deformations also lie in their normal regions. In addition, the strong IR bands around 900 and 1000 cm^{-1} are due to out-of-plane bending modes that are characteristic of the vinyl group. These two bands are very weak (1001) or unobserved (910) in the Raman spectrum. Many of the other bands will be due to mixtures of normal modes, and normal coordinate calculations are required for their interpretation.

A molecule of 3,3-dimethyl-1-butene should exist in a C_S conformation with a methyl carbon eclipsing carbon number 1. In this configuration, there would be 27 a' and 21 a" vibrations. In principle, therefore, there would be 27 polarized and 21 depolarized Raman bands, but the depolarization data obtained here were inconclusive for some of the weak bands.

Force constants for the initial normal coordinate calculation were transferred from 2,3,3-trimethyl-1-butene[14] or were estimated (for internal

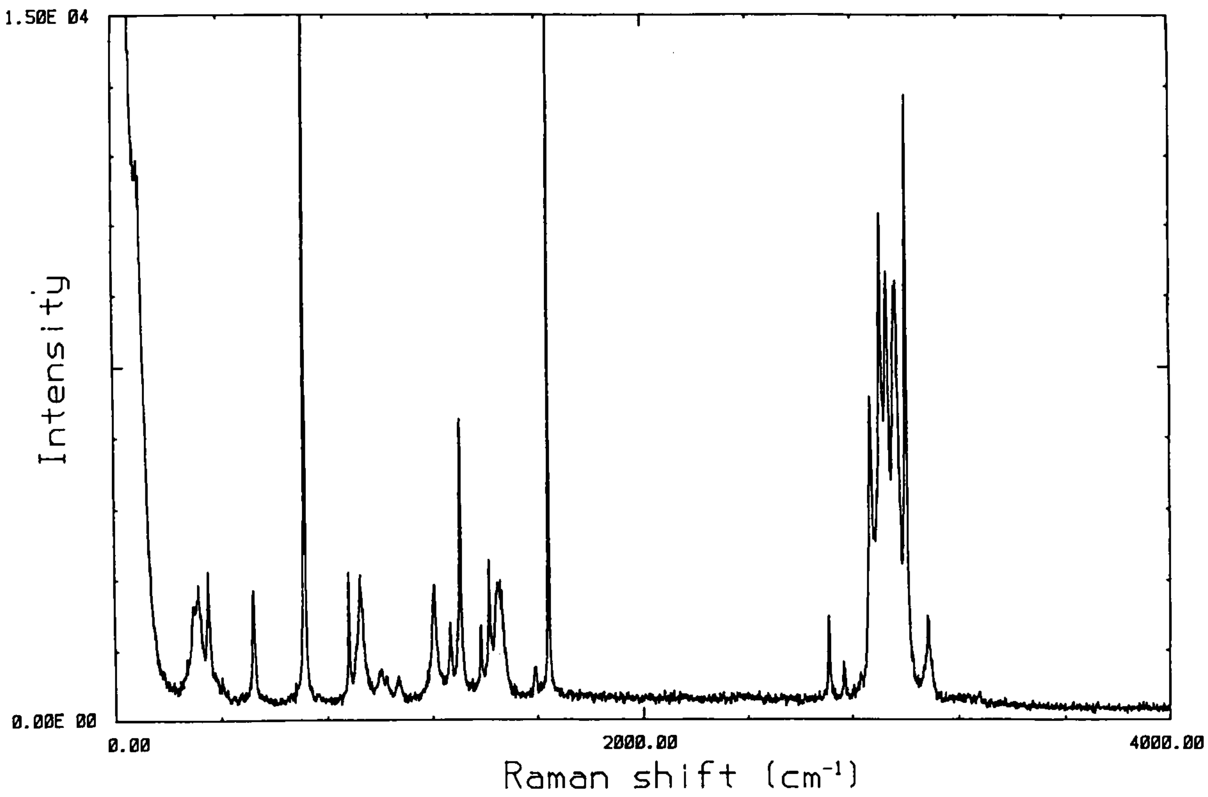

Fig. 1. Raman spectrum of 3,3-dimethyl-1-butene liquid

coordinates that include the lone =C-H). The resulting calculated wavenumbers were in error by an average of almost 16 cm^{-1}, including an average 20 cm^{-1} error for the methyl C-H stretches. The C=C stretch was calculated at 1688 cm^{-1} (obs., 1644), and the lowest-frequency C-C stretch was calculated at 752 cm^{-1} (obs., 718). However, the calculated values seemed to be in the correct order, so refinement should be rather straightforward.

An interaction constant between the C1=C2 stretch and C3-C2-H bend was required to fit the 1644 and 1418 cm^{-1} bands and keep $K_{C=C}$ at a reasonable value. An interaction constant between the =C2-C3 stretch and C3-C2-H bend coordinates was also necessary. A trans H-C=C, C=C-H interaction constant was tried, but non-zero values, both positive and negative, changed the calculated wavenumbers for both 1644 and 1418 cm^{-1} bands significantly. It also had an adverse effect on the 1271 cm^{-1} value. The trans =C-H out-of-plane wag was initially calculated at 1018 cm^{-1} (obs., 1001), and an interaction constant between the $=CH_2$ out-of-plane wag and =C-H out-of-plane wag coordinates was required to lower the calculated value and not make unwanted changes in other frequencies. This constant also increased the calculated value of the C=C twist frequency to the observed value (683 cm^{-1}). The C=C-C and =C-C-C bending diagonal constants and the cis C=C-C,C-C-C interaction constant were used to fit the 520 and 298 cm^{-1} bands. The observed and calculated wavenumbers are given in Table 1, along with an approximate potential energy distribution. The final average difference between observed and calculated wavenumbers was 2.2 cm^{-1}.

Sheppard[1] assigned eleven observed bands below 1350 cm^{-1} to particular normal modes. The assignments given in Table 1 agree with almost all of his assignments, except for the mixing that takes place. Table 1 shows calculated values of 1308 and 1275 cm^{-1} that involve considerable mixing of coordinates, with the largest contribution being from a methyl symmetric deformation. This was also the case for the t-butyl group in 2,2-dimethylbutane,[2] for which the calculations showed large contributions from a methyl symmetric deformation to calculated values of 1303 and 1266 cm^{-1}.

The $=CH_2$ wag for 2-methyl-1-alkenes has been shown to be a good group frequency, with approximately a 90% contribution to the band around 900 cm^{-1}.[4-6] Table 1 shows this to be the case also for 3,3-dimethyl-1-butene. In addition, the C=C twist is more than 90% pure for the 2-methyl-1-alkenes. However, there is considerable mixing of the C=C twist and the lone =C-H out-of-plane wag for both 1001 and 683 cm^{-1} bands of 3,3-dimethyl-1-butene. The C=C stretch for each of the 2-methyl-1-alkenes contributes ca. 70% to the "C=C stretch" band. There is more mixing in 3,3-dimethyl-1-butene, as Table 1 shows (54% C=C stretch, 30% =C-H i-p rock).

TABLE 1

Observed and calculated wavenumbers and approximate potential energy distribution for 3,3-dimethyl-1-butene

Obs. cm^{-1}	Calc. cm^{-1}	P.E.D.(%)[a]
3085p	3086	=CH$_2$ asym. str.(99)
--	3035	=CH str.(93)
3003p	3003	=CH$_2$ sym. str.(94)
2960p	2962	CH$_3$ asym. str.(99)
	2960	CH$_3$ asym. str.(99)
	2960	CH$_3$ asym. str.(99)
	2959	CH$_3$ asym. str.(99)
2931p	2931	CH$_3$ asym. str.(99)
	2930	CH$_3$ asym. str.(99)
2907p	2906	CH$_3$ sym. str.(99)
	2906	CH$_3$ sym. str.(99)
2867p	2868	CH$_3$ sym. str.(99)
1644p	1645	C=C str.(54),=CH i-p rock(30)
1479	1472	CH$_3$ asym. def.(74),CH$_3$ rock(17)
1462	1469	CH$_3$ asym. def.(78),CH$_3$ rock(13)
	1467	CH$_3$ asym. def.(80),CH$_3$ rock(14)
1448dp	1462	CH$_3$ asym. def.(92)
	1456	CH$_3$ asym. def.(84)
	1453	CH$_3$ asym. def.(93)
1418p	1418	=CH$_2$ def.(46),=C-H i-p rock(21), CH$_3$ asym. def.(16),C=C str.(11)
1385	1377	CH$_3$ sym. def,(94)
1364	1367	CH$_3$ sym. def.(61),=CH$_2$ def.(22)
	1362	CH$_3$ sym. def.(80)
1310p	1308	CH$_3$ sym. def.(55),C-C str.(13), =C-H i-p rock(13),=CH$_2$ def.(11)

TABLE 1 (continued)

Obs. cm^{-1}	Calc. cm^{-1}	P.E.D.(%)[a]
1271p	1275	CH_3 sym. def.(33),$=CH_2$ def.(19), C-C str.(17),C=C str.(14)
--	1218	C-C str.(38),CH_3 rock(35)
1208dp	1213	C-C str.(31),CH_3 rock(30)
1068	1070	$=CH_2$ rock(54),CH_3 rock(27)
--	1043	CH_3 rock(75)
1024	1033	CH_3 rock(79)
1001dp	1001	=C-H o-p wag(42),C=C twist(39)
	997	CH_3 rock(90)
927dp	929	C-C str.(54),CH_3 rock(41)
	926	C-C str.(54),CH_3 rock(39)
910dp	910	$=CH_2$ o-p wag(90)
883p	881	C-C str.(52),CH_3 rock(27)
718p	715	C-C str.(86)
683	683	C=C twist(50),=C-H o-p wag(33)
520p	519	C=C-C def.(40),CCC def.(32)
355p	357	CCC def.(83)
	350	CCC def.(80)
318dp	322	CCC def.(83)
	319	CCC def.(83)
298	296	CCC def.(42),$-CH_3$ τ(24),C=CC def.(23)
--	259	$-CH_3$ τ(99)
--	255	$-CH_3$ τ(98)
--	252	$-CH_3$ τ(78),CCC def.(10)
93dp	93	$-C(CH_3)$ τ(93)

[a] Contributions less than 10% are excluded. Abbreviations used: asym. = antisymmetric; sym. = symmetric; str. = stretch; def. = deformation; i-p = in-plane; o-p = out-of-plane; τ = torsion; p = polarized; dp = depolarized

Only two bands were observed in the C-H stretch region of the vinyl group. It was assumed that the lone =C-H stretch was not observed because it is normally observed at a higher frequency than the symmetric $=CH_2$ stretch. The $=CH_2$ symmetric stretch must be assigned to the 3003 cm^{-1} band, as indicated by the Raman intensity. The lone =C-H force constant was arbitrarily assigned a value of 5.00 mdyne/Å, which resulted in a =C-H stretch wavenumber of 3035 cm^{-1}. If the 3003 cm^{-1} band is assigned to both =C-H stretch and symmetric $=CH_2$ stretch, the resulting calculated wavenumbers cannot both be adjusted to this value because of interaction between the two. With a calculated $=CH_2$ symmetric stretch at 3010 and a calculated =C-H stretch at 2996 cm^{-1}, each of these two normal modes contributes ca. 50% to the two calculated wavenumbers.

Harrah[16] has shown the straight-chain 1-alkenes to give rise to two C=C twist bands, which are due to two conformers, at 552 and 634±1 cm^{-1}. It might therefore be expected that the C=C twist wavenumber in 3,3-dimethyl-1-butene would be near one of those values. The candidates for this assignment are the bands observed at 520 and 683 cm^{-1}. The 520 cm^{-1} band is polarized and must therefore be assigned to an a' skeletal bend. The 683 cm^{-1} band (IR) was not observed in the Raman spectrum, which would not be unusual for the C=C twist, so the force constants were adjusted for that assignment. The C=C twist wavenumber is

TABLE 2

Force constants for 3,3-dimethyl-1-butene

Force Constant	Group	Atom(s) common	Value[a]
Stretch			
C-H	$=CH_2$	-	5.050
C-H	$C\text{-}CH_3$[b]	-	4.621
C-H	$C\text{-}CH_3$	-	4.725
C-C	=C-C	-	4.550
C-C	-C-C-	-	4.330
C=C	C=C	-	8.660
C-H	C=CH-C	-	5.000
Stretch-Stretch			
CH,CH	$=CH_2$	C	0.049
CH,CH	CH_3[b]	C	0.060
CH,CH	CH_3	C	0.071
CC,CC	CC_3	C	0.084
C=C,CC	C=CC	=C	0.250
CC,CC	$=C\text{-}CC_3$	C	0.064
Bend			
H-C-H	CH_3	-	0.529
H-C-H	$=CH_2$	-	0.380
C-C-H	$\text{-}C\text{-}CH_3$	-	0.657
C=C-C	C=CC	-	1.200
C=C-H	$CH=CH_2$	-	0.517
C-C-C	=CCC[b]	-	1.400
C-C-C	=CCC	-	0.900

(continued)

TABLE 2 (continued)

Force Constant	Group	Atom(s) common	Value[a]
C-C-C	C-CC$_3$	-	0.835
C-C-H	=CH-C	-	0.657
=CH$_2$ o-p	C=CH$_2$	-	0.216
=C-H o-p	C=CH-C	-	0.330
<u>Stretch-Bend</u>			
CC,CCH	C-CH$_3$	C-C	0.410
CC,CCH	=CH-C	C-C	0.261
CC,C=CC	C=CC	C-C	0.300
CC,CCC	C-CC$_3$	C-C	0.351
C=C,C=CH	C=CH$_2$	C=C	0.300
C=C,C=CC	C=CC	C=C	0.200
C=C,CCH	C=CH-C	=C	-0.200
<u>Bend-Bend</u>			
CCH,CCH	C-CH$_3$[b]	C-C	-0.031
CCH,CCH	C-CH$_3$	C-C	-0.020
=CH$_2$o-p,=CHo-p	C-CH=CH$_2$	C=C	-0.050
C=CH,HCH	C=CH$_2$	=C	0.025
C=CH,CCH	C=CH-C	C-H	-0.019
CCC,CCC	CC$_3$	C-C	-0.041
=CH o-p,C=Cτ	C-CH=CH$_2$	C=C	-0.050
=CCC,=CCC	=CCC$_3$	=C-C	-0.081
CCC, CCH └ trans ┘	CH$_3$-C-C	C-C	0.065
CCC, CCH └ gauche ┘	CH$_3$-C-C	C-C	-0.058

TABLE 2 (continued)

Force Constant	Group	Atom(s) common	Value[a]
C=CC,CCC └─ cis ─┘	C=C-C-C	=C-C	0.340
Torsion			
C=C	C=C	-	0.503
C-C	-C-CH_3	-	0.122
=C-C	=C-CC_3	-	0.069

[a] Stretching constants are in units of mdyn/Å; stretch-bend constants are in units of mdyn/rad; bending constants are in units of mdyn Å/rad². [b]for methyl group cis to C=CH_2

therefore closer to the 2-methyl-1-alkene values than to the unbranched 1-alkene values.

Four methyl C-H stretch bands were observed (2960, 2931, 2907, 2867 cm⁻¹) for 3,3-dimethyl-1-butene. One of these must be assigned to the four antisymmetric stretches of the two equivalent methyl groups, and one must be assigned to the two symmetric stretches of those two groups. The other two bands are due to the two antisymmetric stretches and one symmetric stretch of the methyl group that is cis to the C=CH_2. Several combinations were tried, and because of the K_r and F_r values that were required, it was decided to assign 2931 and 2867 cm⁻¹ to the unique methyl group.

Table 1 shows two calculated wavenumbers that were assigned to the 355 cm^{-1} band and two calculated values that were assigned to the 318 cm^{-1} band. An attempt was made to fit only one calculated value from each of these two pairs to the observed value by lowering the CCC bend and interaction constants. In each of the two cases, the other calculated value also decreased (381, 380 decreased to 357, 350; 343, 341 decreased to 322, 319). These frequencies are apparently accidentally degenerate.

Most of the force constant values that were initially used had to be refined in order to obtain a good fit of calculated to observed wavenumbers. The force constants, their definitions, and their final values are given in Table 2.

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