

Vibrational spectra and thermodynamic functions of allyl acetate

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Abstract. Raman spectrum of allyl acetate molecule has been photographed in liquid phase using 4358 Å line of mercury arc as the exciting line. Infrared absorption spectrum of the molecule has been recorded in liquid phase in the frequency range 200-4000 cm^{-1} . Both the spectra have been analysed to identify the fundamental frequencies. Assuming C_s symmetry, the observed fundamental frequencies have been assigned to various modes of vibration and compared with the frequencies of allyl halides and acetic acid. On the basis of present assignments of fundamental vibrational frequencies and assumed approximate structural parameters of the molecule, thermodynamic functions have been computed.

Keywords. Vibrational spectra ; thermodynamic functions ; allyl acetate.

1. Introduction

The vibrational spectra of propene ($\text{CH}_2=\text{CH}-\text{CH}_3$) molecule have been studied in detail by several workers using infrared and Raman methods (Herzberg 1945; Herschbach 1962; Lin and Swalen 1959; Silvi *et al* 1973). Fateley and Miller (1963) studied the torsional vibration of this molecule in the far infrared. Recently, vibrational spectra and normal coordinate analysis of four isotopic species of propene have appeared in literature (Silvi *et al* 1973). The microwave spectrum of the above molecule has been studied and structure parameters determined (David and Mann 1957; Herschbach and Krisher 1958). Among the substituted propene molecules the infrared, Raman as well as microwave spectra of a large number of compounds have been studied in recent years (Gunde and Azman 1975; Hirota 1965; McLachlan and Nyquist 1968; Siegel 1957; Torgrimsen and Klaoe 1974). It has also been established from these studies that allylic compounds substituted in the 3-position ($\text{CH}_2=\text{CH}-\text{CH}_2\text{X}$, where $\text{X}=\text{F}$, Cl , Br , I , CN , NH_2 , OH , SH , NCO and NCS) have *cis* and *gauche* conformations (Torgrimsen and Klaoe 1974 and references therein). By using the proton magnetic resonance method to study rotational isomerism Bothner-By and his coworkers (Bothner-By and Naar-Colin 1961; Bothner-By and Gunter 1962; Bothner-By *et al* 1962) have shown that when the size of the substituent in the 3-carbon position is increased, the

population of the *cis* form decreases perhaps due to the steric repulsion between the substituent and the =CH₂ group (Hirota 1965). However, a detailed study of vibrational spectra of allyl acetate (CH₂=CH-CH₂OCOCH₃) is not available in literature, although its infrared spectrum has been reported briefly by Nakanishi (1966). The present work comprises the detailed study of vibrational spectra of allyl acetate molecule in liquid phase both by Raman and infrared methods to identify the fundamental frequencies. This gives evidence of the presence of only one rotamer in liquid phase as the infrared and Raman bands do not show any splitting and the number of identified fundamental frequencies is just as expected. Thus *gauche* structure closer to the planar *trans* conformation of the molecule as in figure 1 has been assumed for simplicity. On this basis the frequencies have been assigned to various modes of vibration of the molecule and its thermodynamic properties computed statistically on a TDC-316 computer using the assigned frequencies.

2. Experimental details

Chemically pure allyl acetate obtained from A G Fluka, Switzerland, was used. The compound was used for recording Raman spectrum only after twice distillation under vacuum. The Raman spectrum was recorded on a Russian ESP-51 constant deviation glass spectrograph with a linear dispersion of 19 Å/mm at 4000 Å. An evacuated 6 cc Raman cell was filled with fresh compound and then sealed. A low pressure mercury arc running at 230 volts ac and 3 amp served as the source of excitation. Raman cell and the Hg-arc were put along two focal axes of an ellipsoidal mirror reflector forming the inner surface of a double-walled housing through which continuous water circulation was maintained to avoid extra heating. The 4358 Å line of Hg-arc was isolated with NaNO₂ solution filter. The exposures varied between 15 and 30 hr with a slit width of 40 μ. The ORWO-27 cut films were used to photograph the spectrum. Measurements were made on a comparator (Optical Instruments, New Delhi) with a least count of 0.0001 cm and accurate to within ± 3 cm⁻¹ for strong lines and ± 8 cm⁻¹ for weak lines. Infrared spectrum of the compound was recorded in the liquid phase on a Perkin-Elmer 621 double-beam grating infrared spectrophotometer using a cell of thickness 0.05 mm. The wave numbers are noted at peak absorption positions of the bands.

3. Results and discussion

Table 1 shows comparison of the fundamental frequencies identified in the spectra of the molecule with those of allyl bromide and acetic acid molecules.

With assumed structure and approximate bond lengths and bond angles of figure 1 allyl acetate molecule possesses the plane of the molecule as the only symmetry element in which lie 11 atoms including 5 carbon, 2 oxygen and 4 hydrogen. Two pairs of hydrogen atoms each attached at C₃ and C₅ carbon atoms are situated symmetrically above and below the plane of symmetry. As such the molecule belongs to C_s point group and has a total of 39 vibrational frequencies including 14 stretching, 20 angle deformation and 5 torsional frequencies. It is also worked out that 25 of these frequencies belong to in-plane

(a') and 14 of them to out-of-plane (a'') vibrational modes. Both these types of vibrations are infrared as well as Raman active. While totally symmetric planar vibrations should be polarised in the Raman spectrum, the non-totally symmetric non-planar ones are depolarised. The polarisation measurements, however, could not be made as very long exposures were required in the present experimental set-up.

Considering allyl acetate molecule as a mono-substituted propene on position-3 on the one hand and a substituted acetic acid replacing H atom of the OH group by the allyl group on the other, observed fundamental frequencies can be grouped as (i) allyl group frequencies and (ii) acetate group frequencies. These two groups of frequencies are discussed separately as follows:

3.1. Allyl group frequencies

As the allyl group consists of one pair of hydrogen atoms attached to the first carbon atom, one hydrogen atom attached to the second carbon atom and another pair of hydrogen atoms attached to the third carbon atom, we expect one $=\text{CH}_2$ asymmetric stretching, one $=\text{CH}_2$ symmetric stretching, one CH stretching, one methylene CH_2 asymmetric stretching and one methylene CH_2 symmetric stretching frequencies in the region $2950\text{--}3100\text{ cm}^{-1}$. Assignments of suitable frequencies to the above modes of vibration of molecule have been made by comparison with similar assignments in other mono-substituted propenes as shown in table 1. For the remaining two aliphatic C=C stretching and C-C stretching modes frequencies around 1650 and 931 cm^{-1} respectively have been assigned. One of the frequencies of propene molecule associated with stretching of CH bond which has been replaced by CO bond in the present molecule will correspond to a non-totally symmetric (a'') twisting mode of vibration. A weak Raman fundamental at 293 cm^{-1} has been assigned to this mode. Similarly, frequencies for angle deformation and other torsional modes have been assigned by comparison with their counterparts in mono-substituted propenes (McLachlan and Nyquist 1968; Torgriksen and Klabe 1974).

3.2. Acetate group frequencies

Considering allyl group as a single unit Y, CH_3COOY ($\text{Y} = \text{C}_3\text{H}_5$) molecule will possess two CH_3 asymmetric stretching, one CH_3 symmetric stretching, one C=O stretching, one C-C stretching, one C-O stretching and one O-C stretching vibrations. Suitable fundamental frequencies have been assigned to the first six stretching modes of vibration by comparison with their assignments in acetic acid molecule (Fukushima and Zwolinski 1969; Wilmschurst 1956). A very strong fundamental observed in the Raman spectrum at 783 cm^{-1} has been assigned to the O-C stretching vibration. Assignments of the frequencies to the angle deformation modes compare well with their counterparts in acetic acid molecule in table 1. Assignment of a frequency around 433 cm^{-1} to O-COCH₃ torsional vibration is, however, tentative. The corresponding frequency in formic acid has been observed by Millikan and Pitzer (1957) at 636 cm^{-1} . On substitution of allyl group in acetic acid the C-O-H bent mode is replaced by the C-O-C deformation mode. So we expect much reduction in the corresponding frequency in the present molecule as

Table 1. Correlation of fundamental frequencies (in cm^{-1}) of allyl acetate with those of allyl bromide and acetic acid.

Symmetry C_s	Allyl bromide (Mc Lachlan and Nyquist 1968)	Acetic acid (Wilmshurst 1956)	Allyl acetate		Assignment
			Infrared spectrum	Raman spectrum	
a'	3093	..	3098 (m)	3100 (vwb)	$\nu(=\text{CH}_2)$ asym.
a''	..	3048	3030 (sh)	..	$\nu(\text{CH}_3)$ asym.
a'	3022	2995 (w)	$\nu(=\text{CH}_2)$ sym.
a''	2986	..	2983 (sh)	..	$\nu(\text{CH}_2)$ asym.
a'	2986	..	2983 (sh)	..	$\nu(\text{CH})$
a'	..	2947	2983 (sh)	..	$\nu(\text{CH}_2)$ asym.
a'	2968	..	2938 (vs)	2947 (s)	$\nu(\text{CH}_2)$ sym.
a'	..	2961	2938 (vs)	2947 (s)	$\nu(\text{CH}_2)$ sym.
a'	..	1799	1723 (vs)	1743 (m)	$\nu(\text{C}=\text{O})$
a'	1638
a''	1647*	..	1643 (m)	1658 (vs)	$\nu(\text{C}=\text{C})$
a''	..	1445	1436 (vs)	1470 (vvw)	$\nu(\text{CH}_3)$ asym.
a'	1442	..	1423 (vs)	1430 (mb)	(CH_2) scissoring
a'	..	1401	1408 (vs)	..	$\beta(\text{CH}_2)$ asym.
a'	1409	..	1361 (vs)	1361 (vwb)	$=\text{CH}_2$ scissoring
a'	..	1340	..	1336 (w)	$\beta(\text{CH}_2)$ sym.
a'	..	1279	..	1297 (sb)	$\nu(\text{C}-\text{O})$
a'	1294	..	1250 (sh)	1259 (mw)	$\beta(\text{C}-\text{H})$
a'	1208
a'	1245*	..	1210 (vs)	1191 (vw)	CH_2 wagging
a'	1195
a''	1042*	..	1086 (vs)	..	$=\text{CH}_2$ rocking
a''	1071
a''	1154*	..	1153 (sh)	..	CH_2 twisting
a''	..	1068	1015 (vvs)	1033 (w)	CH_3 rocking
a'	..	990	989 (vvs)	979 (vw)	CH_3 rocking
a''	984	..	989 (vvs)	979 (vw)	$\phi(=\text{CH}_2)$
a'	935	..	931 (vvs)	931 (vw)	$\nu(\text{C}-\text{C})$
a''	926	..	901 (sh)	890 (w)	$=\text{CH}_2$ wagging
a'	..	846	833 (ms)	836 (s)	$\nu(\text{C}-\text{C})$
a'	783 (vs)	$\nu(\text{O}-\text{C})$
a''	..	1192	..	744 (vvw)	$\alpha(\text{C}-\text{O}-\text{C})$
a''	866	..	759 (vvwb)	744 (vvw)	CH_3 rocking
a''	..	654	651 (sh)	..	$\alpha(\text{O}=\text{C}-\text{O})$
a''	..	582	611 (s)	623 (vw)	CO_2 wagging
a'	..	536	554 (m)	558 (vvw)	CO_2 rocking
a''	575 ^(a)	..	575 (sh)	..	$\gamma(\text{C}-\text{H})$
a''	..	636 ^(b)	430 (vvw)	433 (vw)	$\phi(\text{O}-\text{COCH}_3)$
a'	392
a''	458*	..	342 (m)	341 (vw)	skeletal bending
a'	291 (vw)	293 (vw)	$\phi(\text{C}-\text{OCOCH}_3)$
a'	254
a''	215*	191 (vw)	skeletal bending
a''	119*	146 (vvw)	$\phi(\text{CH}_2 \text{ X})$
a''	..	93 ^(c)	..	95 (vw)	$\phi(\text{CH}_3)$

Note: Explanation of footnotes is given in p. 207.

shown in table 1. Although Fateley and Miller (1961) have observed a fundamental in the vapour phase of acetic acid at 130 cm^{-1} and have assigned the same to C-CH₃ torsional vibration, more recent values recommended for this mode by Fukushima and Zwolinski (1969), Shimanouchi (1972) and Chao *et al* (1978) are as 101, 93 and 75 cm^{-1} respectively. On the other hand the C-CH₃ torsional frequency assigned in the propene molecule is at 188 cm^{-1} (in gas, Silvi *et al* 1973) and 177 cm^{-1} (in liquid, Herzberg 1945). In halogenated propenes the frequencies in the range $163\text{--}107\text{ cm}^{-1}$ (McLachlan and Nyquist 1968) have been assigned to C-CH₂X (where X=F, Cl, Br and I) torsional mode. In view of the above two frequencies observed in Raman spectrum of allyl acetate at 146 and 95 cm^{-1} in the present study could be assigned to C-CH₂X (where X=OCOCH₃) torsion and C-CH₃ torsion modes respectively.

4. Thermodynamic properties

Thermodynamic functions of the allyl acetate molecule have been calculated by utilising standard expressions (Herzberg 1945; Colthup 1964; Pitzer and Gwinn 1942) and the assigned fundamental frequencies of table 1. In order to determine rotational contribution, we make use of the assumed approximate structural parameters of the molecule as given in the figure on the basis of the microwave spectral studies of propene and acetic acid molecules by David and Mann (1957) and Tabor (1957) respectively. This molecule possesses five torsional frequencies in all but the barrier height V_0 for each of the four internal rotations excepting the one around C-CH₃ bond is very large as calculated in the harmonic approximation using the relationship (Miller *et al* 1967)

$$v_i = \sigma_i (V_0 F)^{1/2} \quad (1)$$

where $F = h/8\pi^2 c I_m$ in cm^{-1} , v_i is the observed torsional frequency in the respective internal rotation mode and σ_i is the number of potential minima per revolution; also the symmetry number of the internal rotation and I_m the reduced moment of

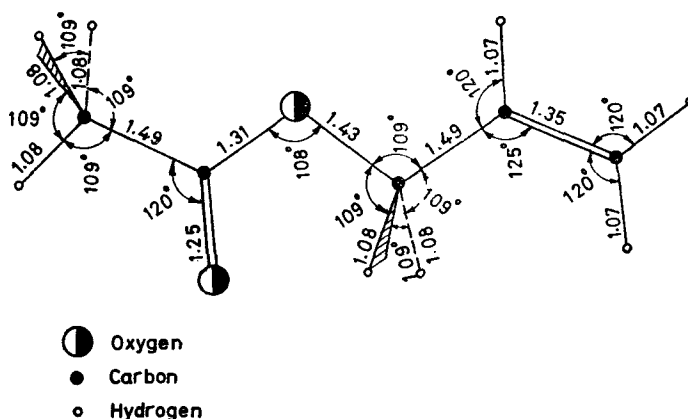


Figure 1. Structural parameters for allyl acetate (scale: $2.54\text{ metres} = 100\text{Å}$)

inertia of the rotating top. Thus for the purpose of computing the contributions of internal rotations to the partition function all the four torsional frequencies for which barriers hindering internal rotations are very high have been taken as ordinary vibrations (Herzberg 1945). In C-CH₃ torsion the rotational constant has been calculated as 5.6330 cm⁻¹. With this value of F , 95 cm⁻¹ for ν_i and 3 for σ_i , equation (1) has been used to find the barrier height hindering internal rotation V_0 as 509 cal/mole which is an intermediate value. Hence, for computing the contribution of this mode to the various thermodynamic functions it has been omitted from the list of ordinary vibrations and instead appropriate corrections have been made using Pitzer and Gwinn's (1942) table with the knowledge of an additional factor Q_i , appearing with overall rotational partition function in completely free internal rotation, which is given as (Herzberg 1945)

$$Q_i = (8\pi^3 I_m kT)^{1/2} / \sigma_i h \quad (2)$$

where symbols have their usual meanings.

The symmetry number for overall rotation is taken as 1. The principal moments of inertia are calculated as 66.6041, 74.6276, 9.0583 and the reduced moment of inertia as 0.4965 in units of 10⁻³⁹ gcm². The calculation of total contribution of $(H^0 - H_0^0)/T$, $-(G^0 - H_0^0)/T$, S^0 and C_p^0 at various temperatures (100–1500° K) were carried out in the rigid rotor harmonic oscillator approximation and these relate to 1 mole of perfect gas at 1 atmosphere and are tabulated in table 2. The computations have been done on a TDC-316 Computer. However, the experimental values for these functions in the present molecule are not available in literature and hence no comparison could be made.

Table 2. Thermodynamic functions (in cal °K⁻¹ mole⁻¹) of allyl acetate.

Temperature (° K)	$\frac{(H^0 - H_0^0)}{T}$	$-\frac{(G^0 - H_0^0)}{T}$	S^0	C_p^0
100	10.27	51.94	62.21	13.29
200	13.34	62.99	73.33	19.98
273.15	15.91	64.55	80.46	26.06
298.15	16.88	65.97	82.85	28.22
300	16.95	66.08	83.03	28.38
400	20.81	71.48	91.28	36.47
500	24.65	76.54	101.20	43.32
600	28.26	81.35	109.61	48.92
700	31.55	85.95	117.51	53.53
800	34.64	90.38	125.02	57.38
900	37.27	94.60	131.87	60.63
1000	39.75	98.65	138.41	63.41
1100	42.00	102.56	144.56	65.78
1200	44.07	106.30	150.37	67.82
1300	45.98	109.90	155.88	69.58
1400	47.71	113.38	161.09	71.11
1500	49.28	116.72	165.99	72.43

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Footnotes

* Bands assigned to *cis* isomer

X = OCOCH₃.

s = strong, vs = very strong, vvs = very very strong, m = medium, mw = medium weak, w = weak, vw = very weak, vvw = very very weak and b = broad.

ν = stretching, α = angle deformation, β = in-plane bending, γ = out-of-plane bending and ϕ = torsional deformation.

(^a) Value in agreement with that of Silvi *et al* (1973).

(^b) Millikan and Pitzer (1957) and (^c) Shimanouchi (1972).