

The vibrational spectrum of allene- d_1

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Abstract—The i.r. spectra of allene- d_1 in the vapour phase and as a crystalline solid at 90 K were recorded in the region 5000–200 cm^{-1} . Raman spectra, including semi-quantitative polarization data, of the vapour and of the neat liquid, contained in a sealed tube at ambient temperature, were obtained. The fundamental frequencies were assigned in good agreement with results from earlier normal coordinate calculations.

INTRODUCTION

Being the simplest hydrocarbon with cumulated double bonds, allene has been very thoroughly studied by a variety of physical methods. Therefore, it is not surprising that numerous i.r. and Raman studies of allene have been published, the earlier work has been listed by TANABE and SAËKI[1]. Certain isotopic substituted molecules like allene- d_4 [2, 3] and allene-1,1- d_2 [4] have been prepared and the spectra reported. Various force fields[1, 5–7] have been developed for allene which with varying success reproduce the observed fundamentals of the parent molecule and the deuterated species as well as the mean amplitudes of vibration, the centrifugal distortion constants and the Coriolis coupling constants.

Recently, we have prepared allene- d_1 and used it in various syntheses. This compound has to our knowledge not been synthesized previously. In view of the great interest in the spectra of allene, we decided to make a thorough spectral study of this compound.

EXPERIMENTAL

A 500-ml three-necked round flask containing 40 g (0.61 mol) zinc powder and 12 ml (0.60 mol) D_2O in 80 ml dioxane was heated to the boiling point. The flask was fitted with an electric stirrer and with a 50-cm long watercooled condenser leading to three U-shaped traps connected in series. The first trap was cooled with ice-water, the second and third were cooled with methanol/dry ice.

43.3 ml (0.60 mol) of 3-chloropropyne (propargyl chloride) was added dropwise to the reaction mixture and boiled for 30 min. With a gentle stream of nitrogen, the vapour formed by the reaction were collected in the traps. The product from the second trap was distilled once under atmospheric pressure and contained ca. 80% allene- d_1 . A pure sample of allene- d_1 was obtained by preparative gaschromatography on a 6 m 25% OPN (oxydipropionitrile) column at 25°C.

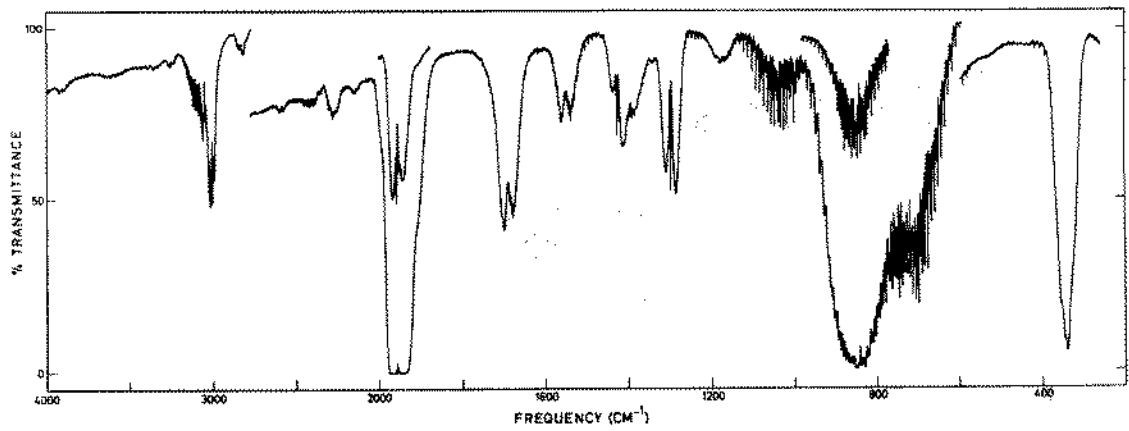
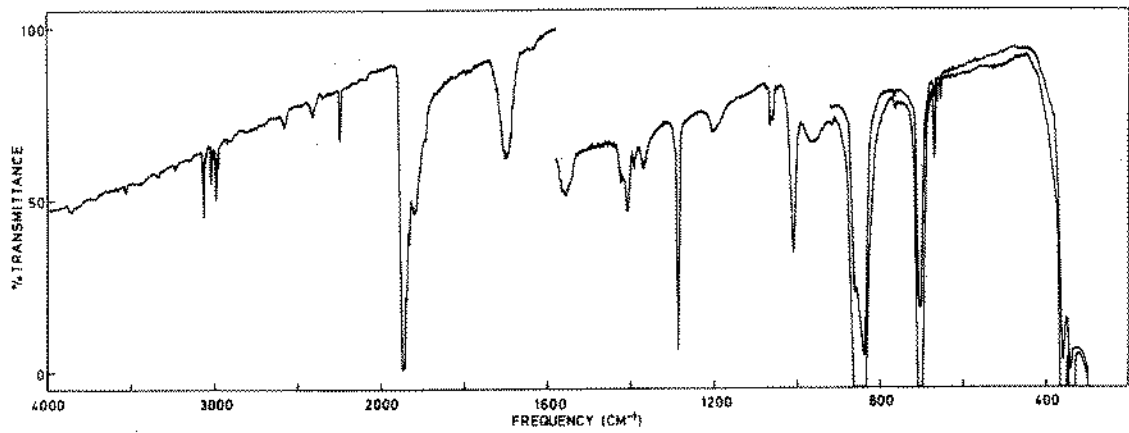
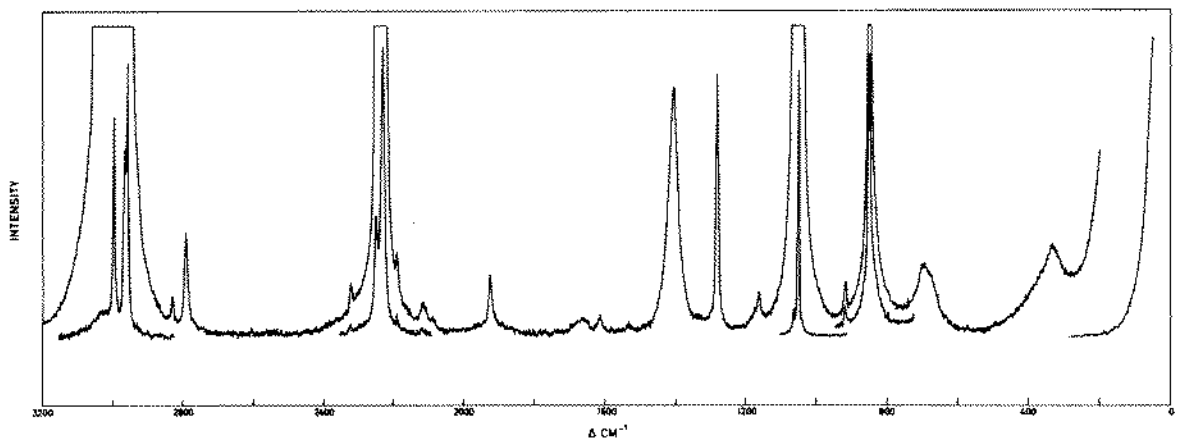
The i.r. spectra were recorded on a Perkin-Elmer model 225 spectrometer and on a Bruker model IFS 114C fast scan evacuable Fourier transform spectrometer. With no fundamentals below 300 cm^{-1} , the whole spectral region could be covered with cells having windows of CsI. The compound was studied in a 10-cm vapour cell and in a cryostat cooled with liquid nitrogen. In the latter cell, the sample was shock frozen on the window and the spectra recorded of a partly crystalline film at ca. 90 K.

Raman spectra of the liquid and of the vapour was obtained at ambient temperature in a thick-walled capillary tube of ca. 2-mm inner diameter. Approximately half of the tube was filled with liquid, the remaining half contained vapour under equilibrium pressure. The laser beam was directed axially through the tube. A quite satisfactory Raman spectrum, including polarization measurements, was recorded for the liquid. Because of the adverse geometry (no multiple reflection of the laser beam or back scattering of the Raman signal) only the most intense Raman bands of the vapour were detected. The spectra were recorded with a Cary 81 spectrometer modified for 90° illumination, excited by a CRL 52 G argon ion laser.

RESULTS

The i.r. survey spectra of allene- d_1 in the vapour phase and as a partly crystalline solid are shown in Figs. 1 and 2, respectively, a Raman spectrum of the liquid is given in Fig. 3. The wave numbers of the observed i.r. and Raman bands are listed in Table 1 while the assigned fundamentals are given in Table 2.

A moderately high resolution (ca. 0.25 cm^{-1}) vapour spectrum was recorded with the Fourier transform spectrometer and a part of this spectrum (1100–600 cm^{-1}) is shown in Fig. 4. A very large number of rotational lines were resolved (e.g. ca. 400 between 1100 and 600 cm^{-1}). We have not attempted to analyze this spectrum in detail in the present communication, and these data are therefore not included in Table 1.

Fig. 1. Infrared vapour spectrum of allene-*d*₁.Fig. 2. Infrared spectrum of allene-*d*₁ as a crystalline solid at *ca.* 90 K.Fig. 3. Raman spectrum of allene-*d*₁ as a liquid under pressure.

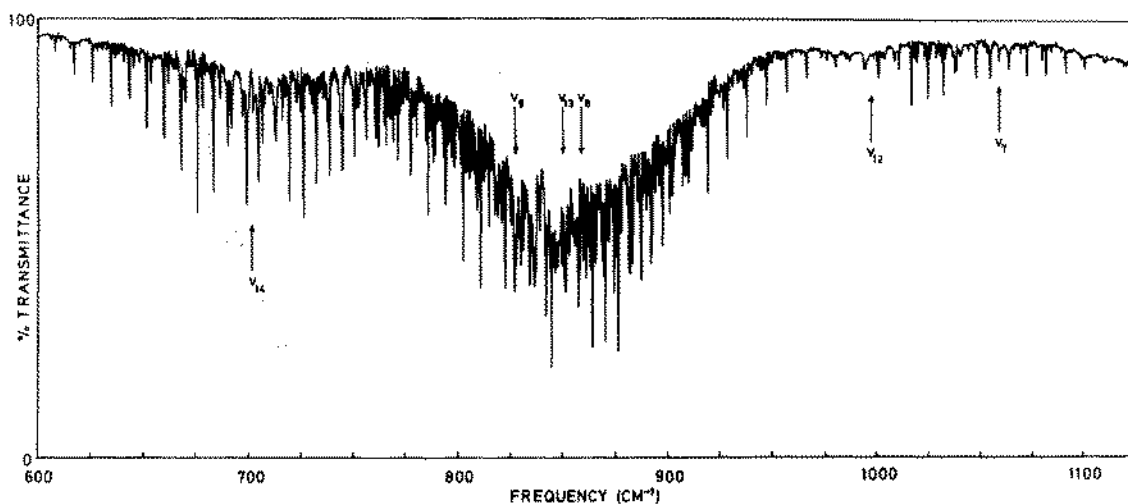


Fig. 4. Infrared vapour spectrum of allene- d_1 in the region 600–1100 cm^{-1} , resolution 0.25 cm^{-1} . The position of the band centres for ν_8 and ν_{13} have not been determined accurately.

Table 1. Vibrational spectral data for allene- d_1

Infrared		Raman		Interpretation
vapour	solid 90K	vapour	liquid	
4492 m, \perp	4460 m			$\nu_5 + \nu_{11}$ A"
~4430 w, sh, \parallel	4440 w, sh			$\nu_1 + \nu_5$ A'
	4385 vw			$\nu_2 + \nu_5$ A'
	4350 w			$\nu_6 + \nu_{11}$ A"
4328 w, \perp	4300 m			$\nu_1 + \nu_6$ A"
4246	4225 vw			$\nu_2 + \nu_6$ A'
4233 Q } w, \parallel				
4220				
	4115 vw			$\nu_7 + \nu_6$ A'
4090	4070 vw			$\nu_1 + \nu_7$ A'
4078 Q } w, \parallel				
4065				
~4000 vw, \perp	3985 vw			$\nu_2 + \nu_7$ A', $\nu_1 + \nu_{12}$ A"
~3895 w, \parallel/\perp	3870 w, bd			$2\nu_4$, $\nu_{11} + \nu_{13}$ A', $\nu_9 + \nu_{11}$ A"
	3805 vw			$\nu_2 + \nu_9$ A', $\nu_2 + \nu_{13}$ A"
~3550 vw	3530 w			$\nu_3 + \nu_6$ A'
3402 w, \parallel/\perp	3420 vw			$\nu_{11} + \nu_{15}$ A', $\nu_{10} + \nu_{11}$ A"
3346	3345 w, bd			$\nu_4 + \nu_5$ A'
3334 Q } w, \parallel				
3333 Q				
3324				
	3300 vw			$\nu_3 + \nu_7$ A'
	3260 vw			$\nu_3 + \nu_{12}$ A"
3260	3225 w			$\nu_4 + \nu_6$ A'
3250 Q } w, \parallel				
3237				
3084 m, \perp	3060 m	3070 s, D		ν_{11} a"

Table 1 (Contd.).

Infrared		Raman		Interpretation
vapour	solid 90K	vapour	liquid	
3046 m, $\frac{1}{2}$ L	3020 m	3048 s	3035 vs,P 3004 vs,P	V_1 a' V_4+V_7 A' FR
3014 3005 q } s,H 2992	2990 m	3016 s	2996 vs,P	V_2 a'
~2970 w, sh	2980 w 2920 vw			V_4+V_{12} A"
2847 2835 q } w,H 2822	2840 vw		2863 w,P	$2V_5$ A'
2805 w	2810 vw		2826 m,P 2801 vw	V_4+V_8 A' V_5+V_6 A'
2720 vw	2700 vw			V_5+V_6 A'
2596 2588 q } w,H 2586 q 2575	2570 w			$2V_6$ A'
2404 w, L	2403 w		2398 vw	V_5+V_{12} A"
2330 w, H	2320 vw		2348 vw	V_6+V_7 A'
			2278 s, sh, P	V_4+V_{10} , V_5+V_8 A' FR
2268 w, $\frac{1}{2}$ L	2242 m	2271 m	2260 vs,P	V_3 a'
			2219 w,P	V_5+V_9 A'
2143 w, $\frac{1}{2}$ L	2140 vw 2120 vw		2142 vw	V_6+V_8 A'
			2110 vw	V_6+V_9 A', V_6+V_{13} A"
2088 vw, H				
2007 1997 q } m, sh, H 1966			~1980 vw	$2V_{12}$ A' FR
1956 q } vs, H 1951 q 1942	1943 vs		1947 w,P	V_4 a'
~1910 m, sh, H	1916 m, sh 1888 w, sh		~1915 vw	V_7+V_8 A' V_7+V_9 A'
			1711 vw	$2V_8$ A'
			~1700 vw	$V_{12}+V_{14}$ A'
			1696 vw	V_8+V_{13} A"
1687 s, $\frac{1}{2}$ L	1692 s, bd		1684 vw	V_8+V_9 A'
			1677 vw	$2V_9$, $2V_{13}$ A', V_9+V_{13} A"
			1633 vw	V_6+V_{10} A', V_6+V_{15} A"
1550 m, $\frac{1}{2}$ L	1555 m, bd 1420 w, sh		1553 vw	V_8+V_{14} A"
1435 1424 q } m, H 1419 q 1442	1405 m		1422 m,P	V_5 a'

Table 1 (Contd).

Infrared		Raman		Interpretation
vapour	solid 90K	vapour	liquid	
1398	} m,l	1389 w		$2\nu_{14} A'$
1388 q				
1377				
~1370 w, \perp	1365 w		~1350 vw	
1309	} s,l	1282 s	1294 m,P	$\nu_6 a''$
1297 q				
1286				
~1265 w, \perp				
	1195 w,bd		1191 vw	$\nu_8 + \nu_{10} A', \nu_8 + \nu_{15} A''$
1180 m, \parallel	1180 w, sh		1175 w,P	$\nu_9 + \nu_{10} A', \nu_9 + \nu_{15} A''$
			1075 s,P	
~1060 w, \perp	1061 w	1063 s	1061 vs,P	$\nu_7 a'$
	1055 w		1049 s,P	$\nu_{14} + \nu_{15} A', \nu_{10} + \nu_{14} A''$
	1045 vw			
997 m, \perp	1005 s		1005 w, sh, D	$\nu_{12} a''$
	960 w, vbd			
	915 vw		928 w,P	
	860 vs		858 vs,P	$\nu_8 a'$
	845 m, sh		841 w, sh, D	$\nu_{13} a''$
828 vs, \perp	838 vs			$\nu_9 a'$
	762 vw			
701 vs, \perp	702 vs		707 w, D	$\nu_{14} a''$
	668 m			
	663 vw		~680 w, sh, D	$2\nu_{10}, 2\nu_{15} A', \nu_{10} + \nu_{15} A''$
	653 vw			
340 vs, \perp	360 vs		337 w, bd	$\nu_{10} a', \nu_{15} a''$
	342 vs			

Abbreviations: s, strong; m, medium; w, weak; v, very; FR, Fermi resonance; \parallel , parallel and \perp , depolarized; sh, shoulder; bd, broad; P, polarized; D, perpendicular.

Whereas the parent compound allene and the perdeuterated molecule allene- d_4 have D_{2d} symmetry, the dideuterated species allene-1,1- d_2 has C_{2v} symmetry, allene- d_1 only has C_s symmetry. A correlation diagram between the symmetry species of allene (or allene- d_4) (D_{2d}), allene-1,1- d_2 (C_{2v}) and allene- d_1 (C_s) is given in Table 3. As apparent, the 15 normal modes of vibration in allene- d_1 divide into: $10a' + 5a''$. The a'' modes will have perpendicular (\perp) contours while those of species a' should have parallel/perpendicular contours (\parallel/\perp).

From the well established structure of allene[8] the moments of inertia for allene- d_1 were calculated. The band contours were calculated by a program[9] based upon the method of UEDA and

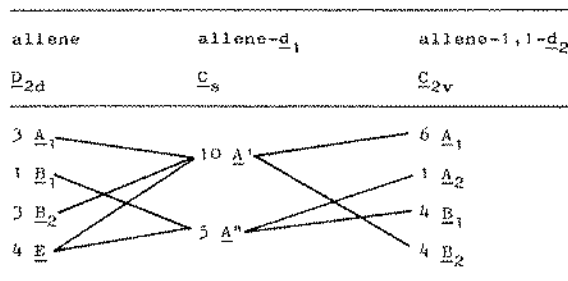
SHIMANOUCI[10], giving the following results: (1) The A-bands (\parallel) (a') should have a sharp medium intense Q-branch, the rotational lines should have a spacing of less than 0.5 cm^{-1} , but well defined P and R envelopes with a separation of ca. 23 cm^{-1} . (2) The B-bands (\perp) (a'') should have a spacing between the sub branches of ca. 7 cm^{-1} , all the central bands having approximately the same intensities. (3) The C-bands (\perp) (a'') should appear very similar to the B-bands with approximately 7 cm^{-1} spacing between the sub bands. At the centre, the bands will be slightly more intense and have a somewhat closer spacing corresponding to the $K = 0 \leftrightarrow 1$ transitions.

Since practically all the vibrations in allene- d_1 to some extent involves the hydrogen (deuterium)

Table 2. Observed and calculated fundamental frequencies of allene- d_1

No		Vapour	Liquid	Solid	Calculated	
		i.r.	Raman	i.r.	I ^a	II ^b
\underline{a}'	ν_1	3046	3035	3020	3045	3067
	ν_2	3005	2995	2990	2995	3023
	ν_3	2268	2260	2242	2267	2252
	ν_4	1956	1947	1943	1955	1955
	ν_5	1424	1422	1405	1435	1440
	ν_6	1296	1294	1282	1319	1309
	ν_7	1063 ^c	1061	1061	1048	1072
	ν_8	-	858	860	860	880
	ν_9	828	-	838	830	804
	ν_{10}	340	337	342	337	338
\underline{a}''	ν_{11}	3084	3070	3060	3089	3105
	ν_{12}	997	1005	1005	1025	1000
	ν_{13}	-	841	845	851	856
	ν_{14}	701	707	702	712	715
	ν_{15}	340	337	360	338	346

^aRef. [6]; ^bRef. [7]; ^cRaman vapour frequency.

Table 3. Correlation diagram of symmetry species in allene, allene- d_1 and allene-1,1- d_2 

atoms, it is difficult to predict both the relative intensities and the band contours of the a' modes from the correlation diagram. Instead, we have attempted to calculate the relative transition moments using results from a normal coordinate analysis and *ab initio* values for the gross charge distribution[11]. In this method one neglects polarization effects, which make it impossible to compare the relative intensities of two different modes. However, within one vibrational mode, the relative intensities of the parallel/perpendicular components should be reliable. The ν_2 , ν_4 , ν_5 and ν_6 modes were calculated to be pure parallel bands, the ν_7 - ν_{10} modes to be pure perpendicular bands and the ν_1 and ν_3 modes to be of the mixed parallel/perpendicular type. The experimentally observed band shapes are actually in close agreement with this calculation and the only surprising result is that the symmetrical C=C=C

stretching mode, ν_7 , should (and does) appear as a perpendicular band (see later).

The spectral features are quite similar to those observed for propyne-3- d_1 [12]. However, the rotational fine structure of the perpendicular bands are still better resolved for allene- d_1 than for propyne-3- d_1 [12].

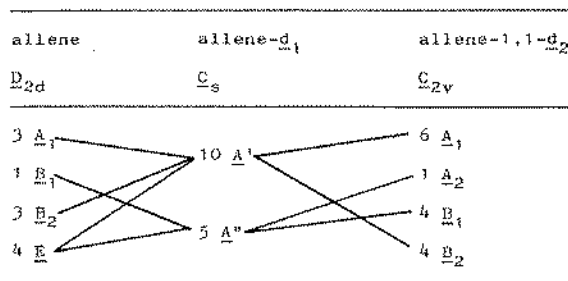
Many of the rotational bands of neighbouring fundamentals overlap and the band centres cannot easily be determined from the vapour spectra without a thorough analysis of the bands. This is particularly true for the region 1100-600 cm^{-1} (Fig. 4) in which the bands ν_7 - ν_9 and ν_{12} - ν_{14} all with perpendicular contours are expected, in addition to some overtones and combination bands.

Based upon the i.r. and Raman vapour contours and the Raman polarization measurements the fundamental frequencies for allene- d_1 were assigned. Although the compound has not previously been studied, two independent force constant calculations have been reported by SVERDLOV and BORISOV[6] and by ANDERSEN *et al.*[7]. The actual force fields have not been published but they were derived from data on allene, allene- d_4 and allene-1,1- d_2 [6,7]. The frequencies listed by both groups agreed quite well with our experimentally determined fundamentals, particularly when the uncertainty in determining the band centres of the perpendicular bands were taken into account. Although the Coriolis coupling constants determined for allene and allene- d_4 showed significant discrepancies from the calculated values of ANDER-

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SEN *et al.* [7], their fundamental frequencies reproduce our wave numbers to a high degree (Table 2).

As expected, the bands assigned to ν_2 (CH_2 sym. stretch), ν_4 ($\text{C}=\text{C}=\text{C}$ asym. stretch), ν_5 (CH_2 scissor) and ν_6 (CHD scissor) all had parallel contours since the dipole changes were clearly close to the axis of the smallest moment of inertia. It was surprising that ν_7 has distinct perpendicular contours. This fundamental is supposedly predominantly the symmetric $\text{C}=\text{C}=\text{C}$ stretch and the corresponding Raman band is the most intense in the entire spectrum. Apparently, this mode involves to a large extent also $\text{C}-\text{H}$ and $\text{C}-\text{D}$ deformations. Moreover, the wave number for ν_7 at 1063 cm^{-1} does not follow the order for $\text{C}=\text{C}=\text{C}$ sym. stretch of the allene derivatives: 1088 (allene), 924 (allene-1, 1- d_2) and 865 cm^{-1} (allene- d_4).

Of the three fundamentals ν_8 , ν_9 and ν_{13} , all expected around 850 cm^{-1} (Fig. 4), only the rotational bands due to the strong ν_9 mode centred at 828 cm^{-1} could be identified. Coriolis coupling between ν_7 (*ca.* 1060 cm^{-1}), ν_8 (*ca.* 860 cm^{-1}), ν_9 (828 cm^{-1}), ν_{12} (*ca.* 1000 cm^{-1}) and ν_{13} (*ca.* 840 cm^{-1}) adds to the complexity of the spectrum in this region and only some distance from the band centres can series of sub bands be recognized.

The two lowest modes, ν_{10} and ν_{15} , connected with the nearly degenerate in-plane and out-of-plane $\text{C}=\text{C}=\text{C}$ bending modes was observed at *ca.* 340 cm^{-1} in the vapour phase. The perpendicular contours are difficult to interpret but in the i.r. crystal spectrum the two modes appear at 342 and 360 cm^{-1} . Following the results of the normal

coordinate calculations we have tentatively assigned ν_{10} to the low and ν_{15} to the higher frequency mode.

As apparent from Table 1 the bands not considered as fundamentals can in most cases be explained as overtones or combination modes, often enhanced by Fermi resonance from neighbouring fundamentals.

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REFERENCES

- [1] K. TANABE and S. SAÉKI, *Bull. Chem. Soc. Japan* **47**, 1847 (1974).
- [2] R. C. LORD and P. VENKATESWARLU, *J. Chem. Phys.* **20**, 1237 (1952).
- [3] A. G. MAKI and A. TOTR, *J. Mol. Spectr.* **17**, 136 (1965).
- [4] W. E. SCHULER and W. H. FLETCHER, *J. Mol. Spectr.* **1**, 95 (1957).
- [5] K. VENKATESWARLU and M. G. K. PILLAI, *Z. Phys. Chem.* **18**, 396 (1958).
- [6] L. M. SVERDLOV and M. G. BORISOV, *Opt. Spectrosc.* **9**, 227 (1961).
- [7] B. ANDERSEN, R. STOLEVIK, J. BRUNVOLL, S. J. CYVIN and G. HAGEN, *Acta Chem. Scand.* **21**, 1759 (1967).
- [8] LANDOLT-BÖRNSTEIN, *Neue Serie*, Band 7, p. 227. Springer, Berlin (1976).
- [9] C. J. NIELSEN, program *IRBAND*, available upon request.
- [10] T. UEDA and T. SHIMANOCHI, *J. Mol. Spectr.* **28**, 350 (1968).
- [11] J. M. ANDRÉ, M. CL. ANDRÉ, G. LEROY and J. WEHLER, *Int. J. Quantum Chem.* **3**, 1013 (1969).
- [12] H. PRIEBE, C. J. NIELSEN and P. KLAEBOE, *Spectrochim. Acta* **36A**, 1017 (1980).