THE INFRA-RED SPECTRUM OF DEUTEROMETHYL ACETYLENE $CH_3C\equiv CD$

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Received 15*th October*, 1953

The vibration spectrum of $CH_3C\equiv CD$ has been measured over the range 3-40 μ with medium dispersion and some of the bands have been examined with very high resolving power. The fundamental vibration frequencies have been determined, and the rotational constants have been derived from a parallel band. Coriolis coupling coefficients ζ have been determined from the perpendicular-type bands, and all the results have been compared with those found earlier for methyl acetylene.

The structure of methyl acetylene involves one feature of interest, in that the length of the carbon-carbon single bond is shorter than was originally expected. The spectra of this molecule and its isotopic species are therefore important since they provide values for the moments of inertia and molecular vibration frequencies. Herzberg, Patat and Verleger[1] first measured the rotational structure of some bands of methyl acetylene in the photographic infra-red, and Boyd and Thompson[2] recently surveyed the vibrational spectrum and resolved fine structure of a fundamental band. From photographic infra-red bands of $CD_3C\equiv CH$, Herzberg, Jones and Leitch[3] have also recently determined the rotational constants of this isotopic molecule, while the rotational spectra of several isotopic species have been measured by Trambarulo and Gordy[4] from which the molecular geometry has been fully established.

The spectrum of $CH_3\equiv CD$ in the region of the fundamental vibration bands 3-40 μ has not been described previously. In the present work the vibration frequencies have been determined and other molecular constants have been obtained from the rotational structure of certain bands.

EXPERIMENTAL AND RESULTS

$CH_3C \equiv CD$ was prepared by the action of deuterium chloride on the mercury derivative of methyl acetylene. Magnesium carbide, prepared according to the method of Leitch and Renaud, was treated with deuterium oxide (99·97 %). The resulting methyl acetylene, containing a small proportion of allene, was passed into an alkaline solution of potassium mercuric iodide. The precipitate was filtered off, washed with acetone and further purified by Soxhlet extraction with this solvent, white crystals of m.p. 202-4° C being obtained.

Deuterium chloride was made by dropping deuterium oxide on to powdered phosphorus pentachloride which had been heated in a vacuum, or on to redistilled trichloroacetyl chloride, and a solution was prepared in deuterium oxide. In spite of all precautions it was impossible to obtain a product entirely free from hydrogen chloride.

The solution of deuterium chloride was slowly added to the mercury methyl acetylide, and the gaseous product was collected in a trap at low temperature and finally refractionated *in vacuo*. It contained a very small amount of methyl acetylene, revealed by the band of acetylenic C—H bond near 3μ, and allowance was made for this where necessary.

THE VIBRATIONAL SPECTRUM

The whole absorption spectrum was measured between 3-40 μ with a Perkin Elmer 12C spectrometer, using prisms of rock salt, lithium fluoride, potassium bromide and thallium bromoiodide. It is shown in fig. 1 and the positions of bands are listed in table 1. The nomenclature for the fundamentals is the same as that used previously for methyl acetylene.[2]

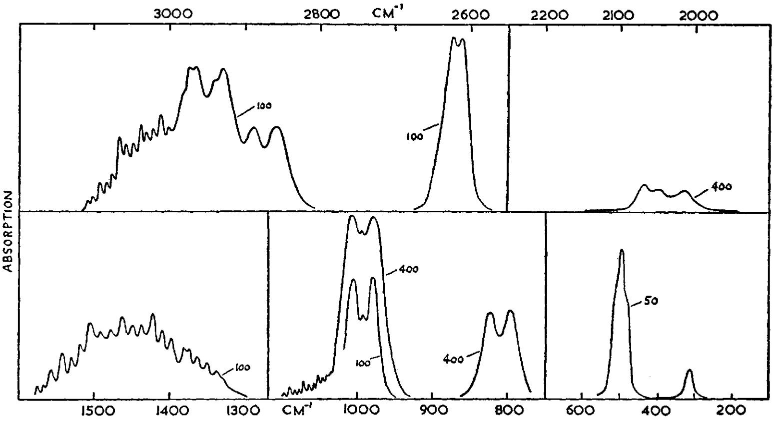

FIG. 1.—Spectrum of $CH_3C \equiv CD$. Path length 10 cm, pressures recorded on curves in mm mercury. The lowest fundamental at 328 mm was measured in a cell of 10 cm length, with 50 mm pressure of $CH_2C \equiv CD$ and 700 mm of air.

The discrepancy between the observed values of ν_1 and ν_3, and those calculated from the potential energy function and constants suggested by Meister,[6] presumably arises from the neglect of an interaction constant between the stretching of $C \equiv C$ and C—D bonds. The calculated value for ν_6 for both methyl acetylene and the deutero derivative indicates that some other modification in the potential function is required.

THE PARALLEL BANDS

With methyl acetylene it was possible to resolve the fine structure of parallel bands between 3μ and 6μ using the high resolving power now available when a lead telluride cell is used as detector in a grating spectrometer.[7] The band ν_3 associated with the stretching of the $C \equiv C$ bond was well resolved and a rotational analysis could be carried out. In the present case of $CH_3C \equiv CD$, the corresponding band ν_3 was found to be much weaker than with methyl acetylene, and when higher pressures were used the pressure broadening appeared to be too severe. The marked difference of intensity in the two cases is noteworthy. It has not yet been possible to examine the band using a much longer path and lower pressure.

The band ν_1 of $CH_3C{\equiv}CD$ lying near 2617 cm^{-1}, connected with the stretching of the C—D link, has been resolved, and is shown in fig. 2. It contains *R*, *Q* and *P* branches and at least one, and probably two, " hot " transitions are superimposed with origins near 2613·5 and 2609 cm^{-1}. Wavelength calibration was carried out with absorption lines of hydrogen chloride. Table 2 gives the positions of lines attributed to the main band, no satisfactory values being obtainable between *R*(5) and *R*(15), and from *P*(0) to *P*(8), owing to the overlapping bands. These results were examined by the usual combination relationships. If, as a first approximation, we neglect the centrifugal stretching terms in D_{JK} and D_K, and the difference $(D'_J - D''_J)$, we have

TABLE 1.—POSITIONS OF BANDS IN cm^{-1}

The frequencies calculated for $CH_3C{\equiv}CD$ were determined using the potential function and constants of Meister [6]

	$CH_3C{\equiv}CH$	$CH_3C{\equiv}CD$		
	$\nu_{obs.}$	$\nu_{obs.}$	$\nu_{calc.}$	
ν_1	3334·0	2616·78	2674	
ν_2	2941·0	2941·0	2941	
ν_3	2142·2	2960·3	2009	
ν_4	(1382)	1378	1376	
ν_5	930·7	—	914	
ν_6	3008·3	3008·9	3059	$\zeta_6 = 0·074$
ν_7	1452·0	1453·5	1454	$\zeta_7 = -0·37$
ν_8	1052·5	1051·0	1037	$\zeta_8 = 0·40$
ν_9	633·2	497·5	518	$0·92 < \zeta_9 < 1·0$
ν_{10}	328·0	314	309	$0·92 < \zeta_{10} < 1·0$
$2\nu_7$	2881·0	2881		
$2\nu_9$	1255·0	993		
$(\nu_9 + \nu_{10})$		812		
$(\nu_1 + \nu_{10} - \nu_{10})$		2613·8		
$(\nu_1 + \nu_9 - \nu_9)$		2610		

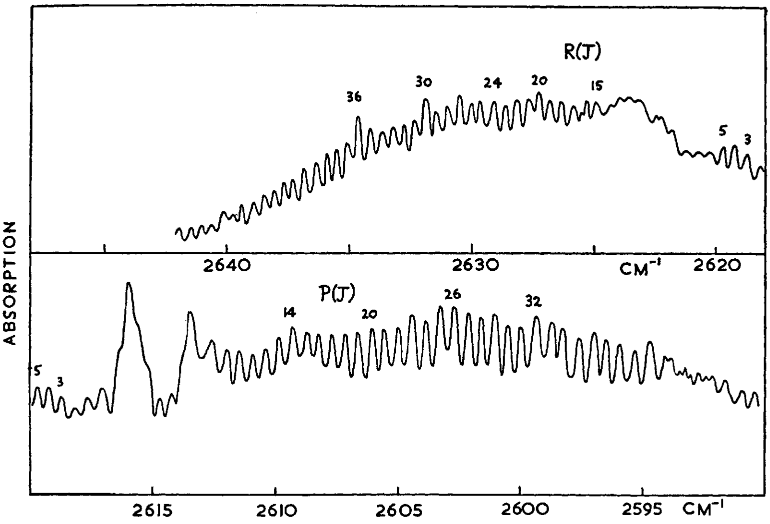

FIG. 2.—The band ν_1 of $CH_3C{\equiv}CD$. Path length 10 cm, pressure 20 mm.

$$\Delta_2F(J, K) = (4B - 6D_J)(J + \tfrac{1}{2}) - 8D_J(J + \tfrac{1}{2})^3,$$

and

$$[R(J-1) + P(J)] = 2\nu_0 + 2K^2[(A' - A'') - (B' - B'')] + 2J^2(B' - B'').$$

The plots of $\Delta_2F(J_1K)$ against $(J + \frac{1}{2})$ for both lower and upper states were satisfactorily linear except at the highest values of J where the effect of D_J becomes noticeable. From the graphical analysis, and also by fitting the data to the relations by least squares, the following mean values were obtained:

$$B'' = 0{\cdot}2596 \pm 0{\cdot}0003\ \text{cm}^{-1},$$
$$\alpha = (B'' - B') = +\,0{\cdot}00091_6 \pm 0{\cdot}00001\ \text{cm}^{-1},$$
$$D''_J \sim 6{\cdot}5 \times 10^{-7}\ \text{cm}^{-1},$$
$$\nu_0 \sim 2616{\cdot}78\ \text{cm}^{-1}.$$

The value of B'' determined from the microwave spectrum was 0·25977 cm^{-1} so that the agreement is better than might have been expected in view of errors caused by the overlapping " hot " transitions.

TABLE 2.—BAND ν_1

Positions in cm^{-1} (vac.)

J	$R(J)$	$P(J)$	J	$R(J)$	$P(J)$
0	(2617·05)	—	28	2630·99	2601·60
1	(17·63)	—	29	31·46	1·02
2	18·19	—	30	31·94	2600·49
3	18·72	—	31	32·36	2599·88
4	19·22	(2614·71)	32	32·79	99·35
5	19·73	(14·19)	33	33·25	98·75
6	—	—	34	33·66	98·22
7	—	—	35	34·12	97·59
8	—	2612·56	36	34·60	96·98
9	—	12·00	37	35·03	96·44
10	—	11·46	38	35·50	95·89
11	—	10·95	39	35·93	95·31
12	—	10·41	40	36·37	2594·66
13	—	2609·88	41	36·83	—
14	—	9·35	42	37·28	—
15	2624·87	8·74	43	37·65	—
16	25·31	8·21	44	38·10	—
17	25·80	7·72	45	38·51	—
18	26·27	7·16	46	38·93	—
19	26·76	6·61	47	39·40	—
20	27·29	6·05	48	39·79	—
21	27·65	5·51	49	40·14	—
22	28·20	4·96	50	40·65	—
23	28·68	4·40	51	41·05	—
24	29·15	3·83	52	41·57	—
25	29·65	3·24	53	2641·93	—
26	30·08	2·76	54	—	—
27	2630·54	2602·15			

Neither of the parallel bands ν_2 and ν_4 could be analyzed. The former has the correct contour, and the latter is submerged beneath the perpendicular band ν_7.

The magnitude of the vibration frequency ν_5 can be estimated from the five known A_1 class vibration frequencies of methyl acetylene by use of the product rule.

Thus,

$$\omega_5' = \frac{\omega_1\omega_2\omega_3\omega_4\omega_5}{\omega'_1\omega'_2\omega'_3\omega'_4}\sqrt{\frac{m_{\mathrm{H}}}{m_{\mathrm{D}}}\,\frac{M'}{M}} = 886.$$

With methyl acetylene, the corresponding band at 930 cm^{-1} is weak, and in the deutero derivative it seems too weak for detection with the pressures we have used. The observed band at 812 cm^{-1} is almost certainly to be interpreted as $(\nu_9 + \nu_{10})$.

THE PERPENDICULAR BANDS

The band ν_6 associated with the degenerate stretching mode of the CH_3 group is overlapped by the parallel band ν_2. Using a lithium fluoride prism the ${}^RQ_K$ lines are resolved, their positions being given in table 3.

For this molecule of C_{3v} symmetry and with the three identical hydrogen atoms, the lines with $K = 0, 3, 6, 9 \ldots$ should be relatively intense, and on this basis $^RQ_0$ is located at 3013·5 cm^{-1}. The Q branches will be given by the expression

$$\nu = \nu_0 + [A'(1 - \zeta)^2 - B'] \pm 2[A'(1 - \zeta) - B']K + [(A' - A'') - (B' - B'')]K^2$$

and the observed values can be fitted to the equation,

$$\nu = 3013{\cdot}13 \pm 9{\cdot}16\,K - 0{\cdot}036\,K^2.$$

If we assume that $A' \sim A''$, $B' \sim B''$, and take $A'' = 5{\cdot}21$ cm^{-1} as found for methyl acetylene and $B'' = 0{\cdot}26$ cm^{-1} determined above from the band ν_1, then $\zeta = 0{\cdot}07_1$ and $\nu_0 = 3008{\cdot}9$ cm^{-1}. The corresponding values with methyl acetylene were $0{\cdot}07_4$ and 3008·3 cm^{-1}.

TABLE 3.—BAND ν_6

Positions in cm^{-1}

$^PQ_1$	3003·5	$^RQ_6$	3067·3
$^RQ_0$	13·5	$^RQ_7$	75·5
$^RQ_1$	22·5	$^RQ_8$	84·2
$^RQ_2$	31·1	$^RQ_9$	93·2
$^RQ_3$	39·8	$^RQ_{10}$	3102·0
$^RQ_4$	48·7	$^RQ_{11}$	3108·4
$^RQ_5$	3057·7		

The perpendicular band ν_7 was measured with the Perkin Elmer spectrometer, the positions of the Q branches being given in table 4. The assignment of these is based upon the assumption that the strong peak at 1463 cm^{-1} is $^RQ_0$. The following combination relationship applies:

$$[^RQ_K + {}^PQ_K] = 2[\nu_0 + A'(1 - \zeta)^2 - B'] + 2[(A' - A'') - (B' - B'')]K^2.$$

The plot of $[^RQ_K + {}^PQ_K]$ against K^2 was satisfactorily linear, the slope giving

$$[(A' - A'') - (B' - B'')] = -\,0{\cdot}05\ \text{cm}^{-1}.$$

Also, the positions of the ^RQ_K and ^PQ_K lines are given by

$[\nu_0 + A'(1 - \zeta)^2 - B'] \pm 2K[A'(1 - \zeta) - B'] + [(A' - A'') - (B' - B'')]K^2$, and from the plots of $\{^RQ_K - [(A' - A'') - (B' - B'')]K^2\}$, or $\{^PQ_K - [(A' - A'') - (B' - B'')]K^2\}$ against K, we find $2[A'(1 - \zeta) - B'] = 13{\cdot}8$ cm^{-1}. Using the same assumptions as were made already in the analysis of the band ν_6 we find $\zeta_7 = 0{\cdot}37$, $\nu_0 = 1453{\cdot}5$ cm^{-1}.

TABLE 4.—BAND ν_7

Positions in cm^{-1}

K	^RQ_K	^PQ_K
0	1463	
1	1478	1449
2	1491	1436
3	1505	1422
4	1517	1408
5	1530	1396
6	1543	—
7	1558	1362
8		1350
9		1336
10		1324

Another perpendicular band ν_8 lies between 1040-1090 cm^{-1} on the higher frequency side of the intense parallel band $2\nu_9$, the positions and assignment of the Q branches being given in table 5.

These Q branches are well represented by the equation,

$$\nu = 1052{\cdot}58 \pm 5{\cdot}71\,K + 0{\cdot}09\,K^2,$$

and making the same assumptions as above, $\zeta_8 = 0{\cdot}4_0$ and $\nu_0 = 1051{\cdot}0$ cm^{-1}. The values thus found for ζ_7 and ζ_8 agree within the experimental error with those previously found for the corresponding coefficients with methyl acetylene.

The remaining pair of perpendicular bands ν_9 and ν_{10} lie at low frequencies and were measured with the prism of thallium bromoiodide. They lie at 497 cm^{-1} and 314 cm^{-1} and, as was to be expected, were not resolved into the separate Q branches. According to the Coriolis sum rule,[9]

$$\Sigma\zeta_i = 4 - [2 - (B/2A)],$$

so that, using the values already determined,

$$\zeta_9 + \zeta_{10} = 1{\cdot}92.$$

Since both ζ_9 and $\zeta_{10} \leq 1$, both must be positive and lie between 0·92 and unity. This result is exactly similar to that found with methyl acetylene previously.

TABLE 5

Positions in cm^{-1}

$^PQ_2$	1040·0	$^RQ_3$	1069·7
$^PQ_1$	1046·4	$^RQ_4$	1077·5
$^RQ_0$	1052·8	$^RQ_5$	1083·4
$^RQ_1$	1057·9	$^RQ_6$	1089·9
$^RQ_2$	1064·9		

The frequencies now determined for the perpendicular type modes of methyl acetylene and the deutero derivative, agree with the Teller-Redlich rule, Thus,

$$\frac{\omega'_6\omega'_7\omega'_8\omega'_9\omega'_{10}}{\omega_6\omega_7\omega_8\omega_9\omega_{10}} = 0{\cdot}751, \text{ and } \sqrt{\frac{m_{\text{H}}}{m_{\text{D}}}\,\frac{M'}{M}\,\frac{I'_B}{I_B}} = 0{\cdot}750.$$

COMBINATION AND OVERTONE BANDS

The assignment of bands to $2\nu_7$, $2\nu_9$,

$$(\nu_1 + \nu_{10} - \nu_{10}) \text{ and } (\nu_1 + \nu_9 - \nu_9)$$

given above in table 1 involves no ambiguity. The intense band near 812 cm^{-1} is assigned to $(\nu_9 + \nu_{10})$ rather than to the parallel-type fundamental ν_5 which is expected to be weak and to lie at a rather higher frequency.

We acknowledge gratefully a grant from the Hydrocarbon Research Group of the Institute of Petroleum.

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