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The infra-red spectrum of C_2H_5D has been investigated under high resolution. As expected, the bands corresponding to degenerate vibrations of C_2H_6 are split into two components with oscillations in the symmetry plane and normal to the symmetry plane respectively. Analogues of several of the inactive C_2H_6 frequencies have also been observed, including a pair at 1122 cm^{-1} and 1159 cm^{-1} corresponding to a Raman line of ordinary ethane which has been predicted at about 1170 cm^{-1} but has not as yet been found.

ALTHOUGH the infra-red and Raman spectra of ethane have been examined on a number of occasions,[1] several uncertainties remain. ν_{12}, sometimes called the "uncertain frequency" has never been observed in the Raman spectrum and its value has had to be ascertained by indirect methods. The frequency of the internal torsional motion and the height of the barrier hindering free rotation remain open to question. Furthermore, there is not sufficient experimental evidence to decide definitely whether ethane belongs to the point group D_{3h} or to the point group D_{3d}.
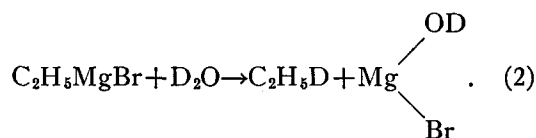
The infra-red spectrum of the slightly asymmetrical mono-deutero-ethane molecule here reported, has been investigated as a means of acquiring more information regarding the existing uncertainties. The only previously published work on C_2H_5D was done by E. Bartholome and H. Sachsse.[2] They used low dispersion and considered only the 12μ and 6.8μ regions. Benedict, Morikawa, Barnes, and Taylor[3] have also published some work on deutero-ethanes but made no attempt to prepare and analyze specific ones.

The replacement of one of the hydrogen atoms in the ethane molecule by a deuterium atom results in the formation of the asymmetric C_2H_5D molecule. This molecule possesses only one element of symmetry which is a plane containing the deuterium atom, the two carbon atoms, and one hydrogen atom. It belongs to the point group C_s and the symmetry type of a vibration is called A' or A'' depending on whether the vibration is symmetric or antisymmetric with respect to the plane of symmetry. It can be shown that eleven of the eighteen fundamental frequencies belong to symmetry class A' while the remaining seven belong to the class A''.

The reduction in symmetry removes the degeneracy of the perpendicular bands of C_2H_6 and allows the possibility of certain bands which are active only in the Raman spectrum of ethane to become observable in the infra-red spectrum of mono-deutero-ethane.

The mono-deutero-ethane was prepared by the well-known Grignard reaction:

$$C_2H_5Br + Mg \rightarrow C_2H_5MgBr, \qquad (1)$$

$$C_2H_5MgBr + D_2O \rightarrow C_2H_5D + Mg\begin{smallmatrix} \diagup OD \\ \diagdown Br \end{smallmatrix} \qquad (2)$$

Precautions were taken to assure the absence of ether and water vapor in the final product. The mono-deutero-ethane was found quite free of impurity except for a trace of ethylene which had probably been left in the system when it was previously used for the preparation of that gas. Only the 950 cm^{-1} band of ethylene, which is indeed a very intense one, appeared in the infrared spectrum of the final product. It is certain that the amount of C_2H_6 was small though the heavy water was not of the highest purity.

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[1] A. Levin and C. F. Meyer, J. Opt. Soc. Am. 16, 137 (1928); E. Bartholome and J. Karweil, Zeits. f. physik. Chemie B39, 1 (1938); J. Karweil and K. Schafer, ibid. B40, 382 (1938); B. L. Crawford, W. H. Avery, and J. W. Linnett, J. Chem. Phys. 6, 682 (1938); P. Daure, Ann. de physique 12, 375 (1929); C. M. Lewis and W. V. Houston, Phys. Rev. 49, 903 (1933); G. Glocker and M. W. Renfrew, J. Chem. Phys. 6, 295 and 409 (1935); G. Goubeau and J. Karweil, Zeits. f. physik. Chemie B40, 376 (1938).
[2] E. Bartholome and H. Sachsse, Zeits. f. physik. Chemie B30, 40 (1935).
[3] Benedict, Morikawa, Barnes, and Taylor, J. Chem. Phys. 5, 1 (1937).

Throughout the experimental observations a grating spectrometer with a rocksalt foreprism was used. This instrument has been described by Barker and Meyer.[4] The individual points used for plotting were obtained as the result of several deflections of the galvanometer with and without the gas cell in the beam. Table I lists the experimental conditions under which various regions of absorption were studied. The observed bands are shown in Figs. 1–5. Recent observations on the perpendicular bands of C_2H_6 are also shown for comparison with their counterparts in C_2H_5D.

The slight asymmetry of the C_2H_5D molecule will result in the splitting of the doubly degenerate perpendicular bands of C_2H_6 into two components of the types called C and B depending on whether the change of electric moment takes place along the major or intermediate axis of inertia. The general nature of the appearance of the infra-red bands of an asymmetric rotator has been discussed by Nielsen[5] for planar molecules and by Badger and Zumwalt[6] in the more general non-planar case. Generally speaking, the C type bands show a central maximum, as a result of a tendency of the K structure to converge toward the center, while the B type bands show a central minimum or gap caused by the tendency of the K structure to diverge from the center. The C_2H_5D bands whose centers are at 804.62 cm⁻¹ and 715.18 cm⁻¹ are excellent examples of the C and B type bands respectively. These two bands are the components into which the 821 cm⁻¹ band (ν_9) of ethane is split because of the asymmetry of the C_2H_5D molecule. The two bands observed at 1159.00 cm⁻¹ and 1121.95 cm⁻¹ are also typical examples of such bands.

TABLE I. Experimental conditions used in observations.

Region (μ)	Center (cm⁻¹)	Grating (lines per inch)	Interval of readings (cm⁻¹)	Effective slit width (cm⁻¹)	Pressure (cm Hg)	Cell length (cm)
13.98	715.18	2400	0.24	0.44	35	10
12.44	804.62	2400	0.17	0.34	18	10
8.8	1121.95	2400	0.36	0.60	70	18
	1159.00					
7.63	1309.76	2400	0.5, 0.25	0.67	18	10
	1311.73					
6.81	1468.55	2400	0.65	0.87	10	10
4.59	2180.55	4800	0.33	0.89	10	10
4.38	2281	4800	0.38	0.90	70	18
3.85	2596	4800	0.97	1.3	70	18
3.63	2753.53	4800	1.1, 0.55	1.5	70	10
3.37	2981.07	7200	0.4	1.1	1	10

It seems probable that this pair is the counterpart of the "uncertain frequency" (ν_{12}) in ethane, for the observations show this to be the only remaining pair having pure C and B type structure. This frequency, which is Raman active in

FIG. 1. The ν_9 band of C_2H_6 and the corresponding pair of bands for C_2H_5D.
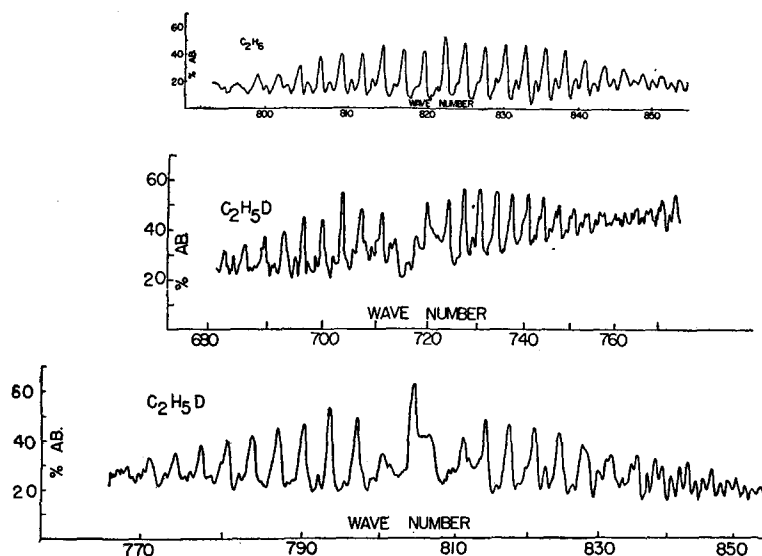
[4] E. F. Barker and C. F. Meyer, Trans. Faraday Soc. 25, 912 (1929).
[5] H. H. Nielsen, Phys. Rev. 38, 1432 (1931).
[6] R. M. Badger and L. R. Zumwalt, J. Chem. Phys. 6, 711 (1938).

C_2H_6 but has never been observed, could be active in the infra-red spectrum of C_2H_5D, and one would expect it to appear with low intensity, which is the case. Since in general the replace-
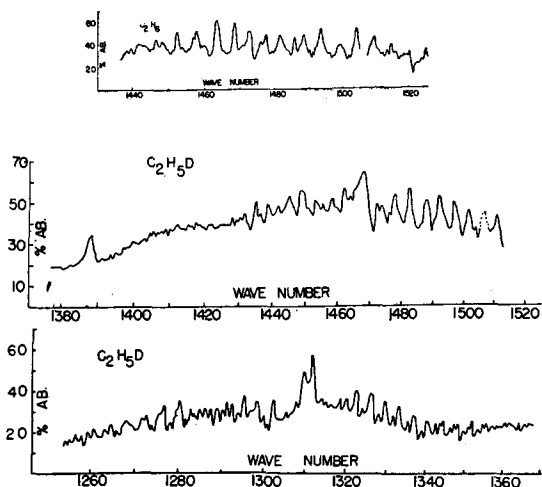

FIG. 2. The ν_8 band of C_2H_6 and the corresponding pair of bands for C_2H_5D. The Q branch at 1388 cm^{-1} in the middle curve corresponds to the frequency ν_6 in C_2H_6.

ment of a hydrogen atom by one of deuterium removes the degeneracy and two components appear, one in approximately the same position as for C_2H_6 and the other at a considerably lower frequency, the value 1170 cm^{-1} calculated by Stitt[7] from his work on C_2D_6 is experimentally substantiated.

It may happen in certain vibrations of an asymmetric molecule that the change of electric moment does not take place purely along one of the principal axes, but has components along two or possibly three of the axes, in which case bands of a two- or threefold hybrid character will appear. A superposition of the corresponding pure band structures will result and the observed band will have neither the appearance of a pure C type nor that of a pure B type band. Examples of such bands observed in the infra-red spectrum of C_2H_5D are the pair at 1311.73 cm^{-1} and 1468.55 cm^{-1} which correspond to the doubly degenerate 1480 cm^{-1} band (ν_8) of C_2H_6 and the pair at 2981.07 cm^{-1} and 2180.55 cm^{-1} corresponding to the doubly degenerate 2989 cm^{-1} band (ν_7) of C_2H_6. It is to be noted that each of the components exhibits a central maximum.

[7] F. Stitt, J. Chem. Phys. 7, 297 (1939).

It is probable that the 1309.76 cm^{-1} band which appears in Fig. 2 as the weaker component of a doublet, is another instance in which the asymmetry of the C_2H_5D molecule allows the appearance of a frequency in the infra-red spectrum the counterpart of which was forbidden in the infra-red spectrum of the symmetrical C_2H_6 molecule. If this band at 1309.76 cm^{-1} is one of the components related to the 1463 cm^{-1} Raman-active vibration (ν_{11}) of C_2H_6 then it would appear that the 1468.55 cm^{-1} band of C_2H_5D should also show a doublet nature. Not only should the E_u** infra-red active band split into two components in going over to C_2H_5D but the E_g Raman-active frequency should do
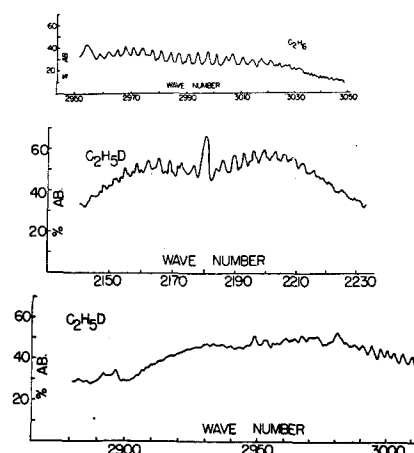

FIG. 3. The ν_7 band of C_2H_6 and the corresponding pair of bands for C_2H_5D. In the upper curve one of the Q branches of ν_5 appears at 2954 cm^{-1}. The low frequency component in the middle curve is a hybrid of types A and B. In the lower curve the Q branch of the band corresponding to ν_7 is found at 2981 cm^{-1}, with the Q branches of the pairs of resonance doublets corresponding to ν_5 and ν_1 on the lower frequency side.

likewise. Again, one of the components will be expected to appear at a frequency only slightly different from the E_g frequency, while the other will be shifted considerably toward lower frequencies. However, in the case of the least shifted frequency, the presence of the deuterium atom has very little effect on the motions of the hydrogen atoms, and if the corresponding frequency in C_2H_6 is inactive in the infra-red

** Naming the symmetry of the vibrations in accord with a D_{3d} configuration is not to be interpreted as eliminating the D_{3h} possibility.

because it involves no change in electric moment, then the change in electric moment will probably be quite small in the case of C_2H_5D. On the other hand, in the component of lower frequency, the deuterium atom has a large effect on the motion of the hydrogen atoms, and the change in electric moment may be correspondingly larger, yielding a greater intensity of absorption. Thus, the 1400 cm⁻¹ component which is to be associated with the 1309.16 cm⁻¹ frequency is probably obscured by the much greater intensity of the 1468.55 cm⁻¹ band while the 1309.16 cm⁻¹ component is observed since its intensity is nearly comparable with that of the 1311.37 cm⁻¹ band.

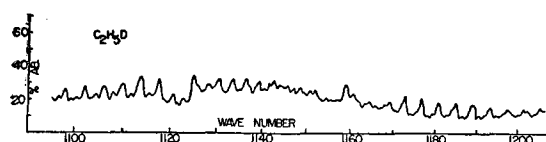FIG. 4. The B type component at 1122 cm⁻¹, and the C type component at 1159 cm⁻¹ of the pair of bands corresponding to ν_{12} in C_2H_6, the uncertain Raman frequency.

The asymmetric rotator also exhibits A type bands which correspond to the parallel bands of a symmetric rotator. In the infra-red spectrum of ethane a Fermi-doublet with components at 2954 cm⁻¹ and 2894 cm⁻¹ is observed. The Raman spectrum exhibits a similar Fermi-doublet with components at 2899 and 2955 cm⁻¹. In the corresponding region of absorption in C_2H_5D, again a Fermi-doublet appears but each component of it appears to be double. The measurements indicate that parallel Q branches appear at 2892.33, 2896.87, 2948.86, and 2952.93 cm⁻¹. There is, then, at least an indication that the C_2H_5D vibration which corresponds to the highest frequency Raman active A_{1g} vibration (ν_1) of ethane, appears in infra-red absorption as well as the vibration which corresponds to the A_{2u} infra-red active frequency (ν_5) in the same region.

The A type band which appears in C_2H_5D at 1388.42 cm⁻¹ is no doubt the counterpart of the 1379 cm⁻¹ band (ν_6) in C_2H_6. The fact that the frequency is higher in C_2H_5D indicates that the presence of the deuterium atom has the effect of changing the motion of the hydrogen atoms

in such a way that a larger restoring force acts upon them in C_2H_5D than in C_2H_6.

The Raman active counterpart (ν_2) of the 1379 cm⁻¹ infra-red active band has never been
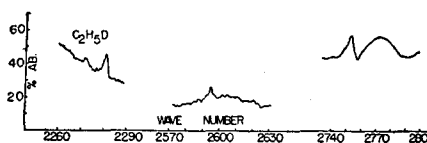

FIG. 5. Observed combination bands in C_2H_5D.

observed. However, its value is estimated by means of the moderately strong parallel type combination band at 2753.6 cm⁻¹. In the infra-red spectrum of C_2H_5D, an almost identical parallel combination band is found at 2753.53

TABLE II. Fundamental frequencies of C_2H_6 and C_2H_5D as suggested on basis of present observations.

Symmetry type in C_2H_6	Assignment	ν(cm⁻¹)	Symmetry type in C_2H_5D	ν(cm⁻¹)
A_{1g}	ν_1	2927* $\begin{cases} 2899 \\ 2955 \end{cases}$	A'	2923* $\begin{cases} 2892 \\ 2953 \end{cases}$
	ν_2	1375**		1365**
	ν_3	993		?
A_{2u}	ν_5	2924* $\begin{cases} 2894 \\ 2954 \end{cases}$	A'	2923* $\begin{cases} 2897 \\ 2949 \end{cases}$
	ν_6	1379		1388
E_u	ν_7	2989	A''	2981
			A'	2180
	ν_8	1480	A''	1468
			A'	1312
	ν_9	821	A''	804
			A'	715
E_g	ν_{10}	2960	A''	?
			A'	?
	ν_{11}	1460	A''	1477**
			A'	1310
	ν_{12}	1170**	A''	1159
			A'	1122

* Arithmetical mean of resonance doublet shown.
** Calculated by means of observed combination bands.
*** Stitt's value of uncertain frequency.

cm^{-1}. No doubt, it is the combination of the 1388 cm^{-1} band and the unobserved parallel fundamental of C_2H_5D in the same region. It

TABLE III. Positions of principal lines of the 715.18 cm^{-1} band of C_2H_5D.

682.84 cm^{-1}	717.80
686.39	719.97
689.78	724.20
693.22	727.30
696.63	730.65
700.03	734.18
703.62	737.35
707.27	740.85
711.20	744.12
713.77	747.47
715.18 (central minimum)	750.78
	754.03

can be estimated, therefore, that the frequency of the latter is 1365 cm^{-1}.

Two other combination bands have been observed in the infra-red spectrum of C_2H_5D. One is the weak band, apparently perpendicular in type, at 2595.63 cm^{-1}. The other appears to

TABLE IV. Positions of principal lines of the 804.62 cm^{-1} band of C_2H_5D.

771.00 cm^{-1}	826.36*
772.95*	827.66
774.20	829.90*
776.08*	831.32
777.27	831.84
780.53	833.60*
782.04*	834.84
783.70	835.72
786.87	837.14
790.18	838.42
791.97*	839.50
793.52	840.76
795.33*	842.02
796.97	843.28
798.95*	844.36
800.38	845.56
804.62 (central maximum)	846.84
811.12	848.22
814.08	849.32
817.43	850.44
820.98	851.72
822.50*	852.84
824.56	854.34

* Weak lines.

be a parallel type band with its Q branch at 2281.11 cm^{-1}.

If it is assumed that the selection rules for the combination bands of ethane still hold in the slightly modified C_2H_5D molecule, the only reasonable assignment for the 2596 cm^{-1} band is

the sum of the 1469 cm^{-1} frequency and the 1120 cm^{-1} frequency. It is gratifying to observe this combination which involves one of the components of the pair of bands at 1120 and 1159 cm^{-1}, for its appearance supports the contention that this pair of bands is the counterpart of the "uncertain frequency" (ν_{12}) of C_2H_6.

The only reasonable assignment for the parallel combination band at 2281 cm^{-1} appears

TABLE V. Line positions in the 1310 cm^{-1} bands of C_2H_5D.

1264.62 cm^{-1}	1305.33*
1268.03	1307.79*
1272.21	1309.76 (central
1276.62	1311.73 maxima)
1280.21	1318.69
1282.71	1320.18
1284.82	1322.70
1286.00	1324.18*
1287.32	1326.21
1288.85	1328.25*
1290.21	1329.79
1291.24	1331.81*
1292.35	1333.33
1293.88	1335.39*
1295.29	1336.94
1298.38	1339.00*
1299.91*	1340.54
1302.42	1342.61*
	1344.19

* Weak lines.

TABLE VI. Line positions in the 1468.55 cm^{-1} band of C_2H_5D.

1431.94 cm^{-1}	1468.55 (central maximum)
1435.53	1473.20
1439.13	1478.27
1442.13	1482.73
1445.47	1488.42
1449.10	1492.13
1453.41	1496.90
1458.67	1501.48
1462.48	—
	1510.70

Q branch of parallel band at 1388.42 cm^{-1}

to be the sum of the 804 cm^{-1} frequency and the unobserved frequency in the 1400 to 1500 cm^{-1} region, corresponding to the E_g band of ethane in this vicinity. Using the combination band to determine the frequency of the unobserved vibration, its value is approximately 1477 cm^{-1}.

Table II gives the suggested set of fundamental frequencies for C_2H_6 and C_2H_5D. It will be noted that the frequencies of all the E_u bands are slightly different from those given by Stitt.[7]

TABLE VII. Line positions in the 2180.55 cm⁻¹ band of C₂H₅D.

2148.52 cm⁻¹	2183.90
2151.85	2185.85
2155.05	2189.68
2158.80	2192.85
2162.58	2195.85
2165.75	2199.53
2169.00	2203.25
2172.90	2206.16
2176.85	2209.21
2180.55 (central maximum)	2212.32
	2216.05

TABLE VIII. Line positions in the 2981 cm⁻¹ band of C₂H₅D.

2981.07 cm⁻¹ (central maximum)	2997.64
2984.29	3000.47
2987.29	3003.07
2990.53	3006.64
2994.20	3010.21
Parallel band doublet	2892.33 2896.87
Parallel band doublet	2948.86 2952.93

These differences are based on recent observations in this laboratory of the ethane spectrum

TABLE IX. Line positions in the 1121.95 and 1159.00 cm⁻¹ bands of C₂H₅D.

1121.95 cm⁻¹ band	1159.00 cm⁻¹ band
1098.27 cm⁻¹	1159.00 cm⁻¹ (central maximum)
1102.30	1160.49
1106.03	1164.34
1110.13	1169.18
1113.92	1172.81
1117.74	1176.70
1120.90	1180.84
1121.95 (central minimum)	1184.97
1122.82	1188.97
1125.13	1193.36
1128.32	1197.40
1130.63	1201.47
1133.71	1205.55
1136.58	
1139.60	
1142.87	

under high resolution. In Tables III to IX the positions of the principal lines in the various observed bands are listed.

These frequencies have not been corrected to vacuum.