

Preparation and Infrared Spectra of 1 D-, 2 D-, 1,2 D₂-, and 1,2,2' D₃- Ethyl Fluorides and Bromides

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1 D-, 2 D-, 1,2 D₂-, and 1,2,2' D₃-ethyl fluorides and bromides were prepared. Infrared absorption curves were recorded. In the spectra of the bromides the existence of rotational isomers is demonstrated.

In connection with a microwave determination of the structure of ethyl fluoride, the five isotopic species CH₃CH₂F (I), CH₂DCH₂F (II), CH₂CHDF (III), CH₂DCHDF (IV) and CHD₂CHDF (V) (b. p. —32°C), were prepared. A brief record of their preparation is given here together with the infrared absorption curves of the five intermediates, CH₃CH₂Br (I'), CH₂DCH₂Br (II'), CH₃CHDBr (III'), CH₂DCHDBr (IV') and CHD₂CHDBr (V') (b. p. +38°C), referring to the substances in the liquid and the gas phase, and the infrared absorption curves of I—V, referring to the substances in the gas phase.

EXPERIMENTAL

A. Preparations. Henne¹ prepared ethyl fluoride from ethyl bromide and HgF₂. Later, he suggested² the use of the more easily available HgF which can be applied at the cost of yield. All five fluorides were prepared by us by the latter procedure, modified, for sake of simplicity, by using sealed-off glass ampullæ instead of metal vessels. After twenty experiments in which the temperature, the reaction period, and the C₂H₅Br/HgF ratio were systematically varied it was found most advantageous to work at 110°C for 20 h with a 1:2 ratio between ethyl bromide and mercurous fluoride. Usually, $\frac{1}{2}$ –1 ml ethyl bromide was treated in a 50 ml pyrex glass ampulla. Occasional shaking proved to be very important for the magnitude of the yield which was 25–30 % of theory based on ethyl bromide. This amount of purified material was obtained after a crude distillation *in vacuo* from solid reaction products and subsequent gaschromatographical separation on a dry silica-gel column (length 150 mm, diameter 10 mm, temperature 82°C). The infrared spectrum of (I) (gas-phase) was identical with the spectrum published by Nielsen *et al.*³ Its boiling point was correct (–32°C).

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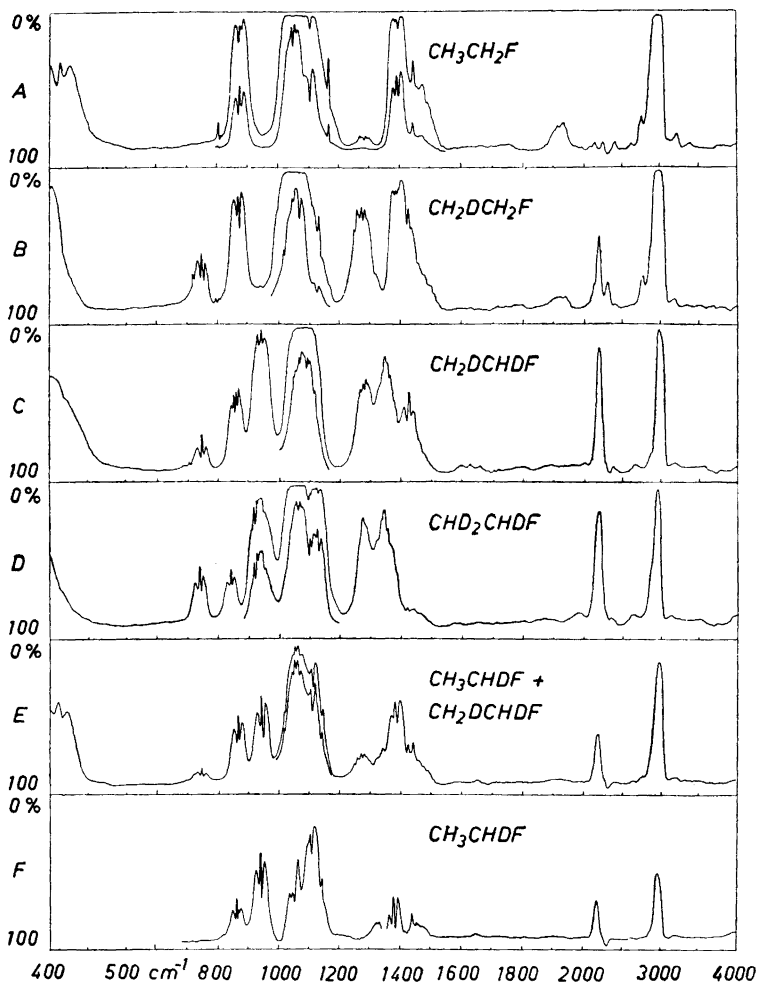
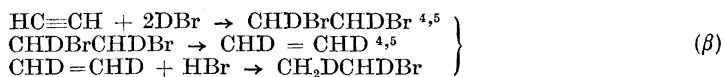
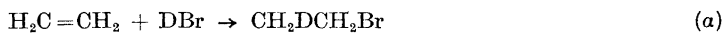


Fig. 1. Infrared spectra of gaseous ethyl fluoride (A) and deuterated species (B)–(F) at room temperature. Pressure 150 mm unless otherwise stated. The spectrum (F) is the spectrum of the mixture $\text{CH}_3\text{CHDF} + \text{CH}_2\text{DCH}_2\text{F}$ ($p = 75$ mm), run against $\text{CH}_2\text{DCH}_2\text{F}$ ($p = 37$ mm) in a reference cell (length 10 cm).
 Ordinate: percent transmission at 10 cm path length.
 Abscissa: wave numbers in cm^{-1} .

(II')–(V') were prepared by the reactions:



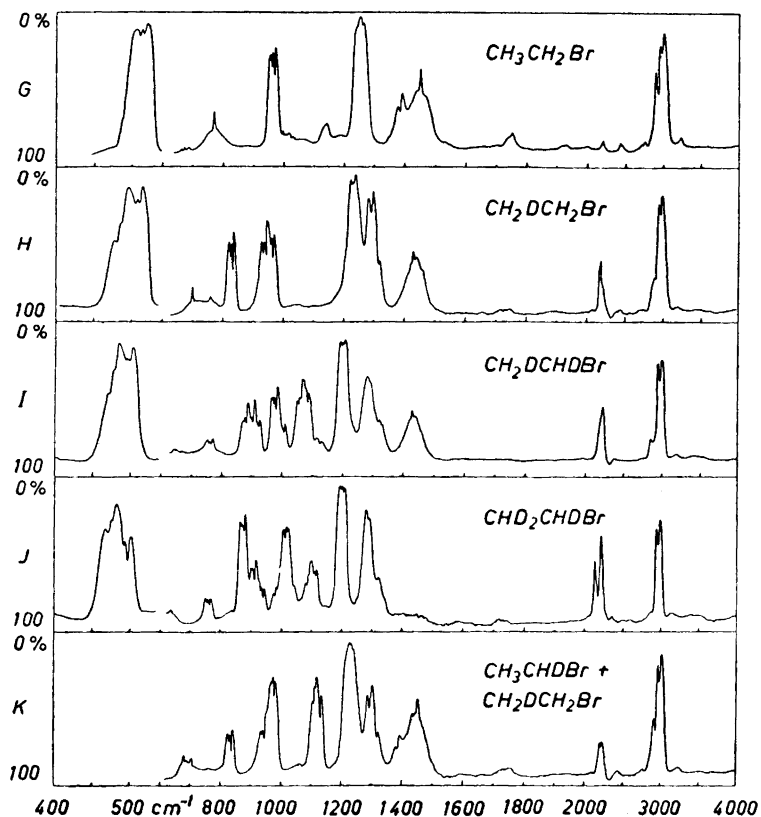
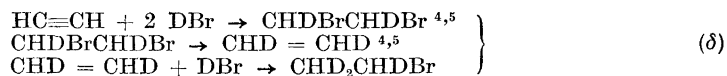
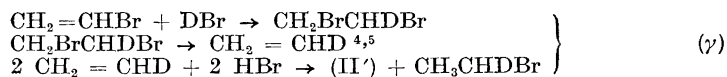


Fig. 2. Infrared spectra of gaseous ethyl bromide (G) and deuterated species (H)–(K) at room temperature. Pressure 70 mm Hg unless otherwise stated. The spectrum (K) is the spectrum of the mixture $\text{CH}_3\text{CHDBr} + \text{CH}_2\text{DCH}_2\text{Br}$. Because of a mishap, (K) was not run in the 400–600 cm^{-1} region.

Ordinate and abscissa as in Fig. 1.

(III') was only obtained as a 50 % mixture with (II'):



The yield at the processes (a)–(d) was 90 %. As shown by the infrared absorption spectra no undesired exchange took place. In all cases (including ethylene) the addition of HBr (DBr) took place under ultraviolet irradiation.

B. *Infrared spectra.* Infrared spectra of (I), (II), (III), (IV) and (V) in the gas phase were recorded on a Perkin-Elmer 21 double beam instrument at room temperature.

Table 1. Raman data^a and infrared spectra of ethyl bromide and four deuterated species (liquids). Temperature 25°C. Infrared spectra were recorded in the 400—1 500 cm⁻¹ region. Cell thickness 0.03 mm. In parenthesis, optical density at peak. The accuracy of the infrared measurements is ± 2 cm⁻¹.

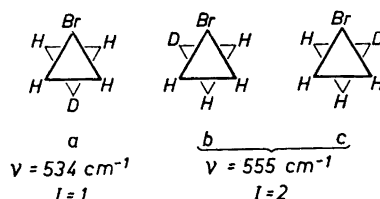
CH ₃ CH ₂ Br (I')		CH ₂ DCH ₂ Br (II')		CH ₃ CHDBr (III')		CH ₂ DCHDBr (VI')	CHD ₂ CHDBr (V')
Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Infrared
—	290.4(6)	—	280.8(5)	—	290.6(5)	—	523(>1)
562(>1)	560.4(10)	—	287.0(3)	548(>1)	549.0(10)	526(0.62)	542(0.70)
765(0.80)	—	534(0.75)	536.7(7)	673(0.50)	678.4(½)	543(>1)	605(0.25)
954(>1)	959.3(2)	555(>1)	557.5(10)	802(0.18)	807.7(½)	640(0.41)	625(0.26)
—	1 022 (½)	699(0.50)	703.8(½)	966(>1)	971 (2)	671(0.28)	636(0.28)
1 060(0.15)	1 062.0(3)	758(0.35)	—	1 048(0.22)	1 054 (3)	758(0.34)	753(0.34)
1 120(0.15)	—	822(>1)	826.4(2)	1 090(0.40)	—	792(0.12)	817(0.11)
1 238(>1)	1 241.5(2)	—	896.8(½)	1 110(>1)	1 117 (2)	821(0.13)	863(>1)
1 250(>1)	1 250 (½)	—	912.0(½)	1 210(>1)	1 214.0(3)	874(0.86)	901(0.80)
—	1 255 (1)	930(>1)	935.2(2)	—	1 311 (½)	894(0.44)	929(0.36)
—	1 348.5(½)	957(>1)	960.8(1.5)	1 375(0.70)	1 378 (1)	914(0.92)	955(0.13)
1 375(>1)	1 378.5(1)	1 025(0.12)	1 031.0(1.5)	1 440(>1)	1 443.7(2)	966(>1)	978(0.29)
1 442(>1)	1 443.3(2)	1 042(0.13)	1 046.4(1)	—	1 453 (1)	1 002(0.69)	1 008(0.98)
1 447(>1)	1 453 (1)	1 112(0.18)	—	—	—	1 052(>1)	1 027(0.32)
		1 182(0.36)	1 181 (½)			1 078(>1)	1 080(0.54)
		—	1 189 (½)			1 112(0.34)	1 102(0.54)
		1 227(>1)	1 231.2(3)			1 194(>1)	1 136(0.13)
		—	1 247 (½)			1 275(>1)	1 192(>1)
		—	1 260 (0.6)			1 312(0.62)	1 232(0.22)
		1 282(>1)	1 286.3(2)			1 422(0.84)	1 276(>1)
		1 307(0.86)	1 309.9(0.8)			1 438(0.59)	1 307(0.41)
		—	1 347 (½)			—	1 327(0.23)
		1 423(0.86)	1 424.5(1)				
		—	1 437 (½)				
		1 442(0.90)	1 444.5(2)				
		—	1 453 (1)				
Number of rotational isomers:							
1		2		1		3	3
Number of diff. bands in I.R. and Raman							
14 (theory 13)		26 (theory 26)		13 (theory 13)		20* (theory 39)	22* (theory 39)

* Not comparable with the numbers 14, 26 and 13 since no Raman data are available.

A cell thickness of 10 cm was applied throughout. Due to the usual band-spread in the spectra of gases a reliable normal vibration analysis on this basis is not possible. Since the spectra of (I)—(V) in the liquid phase were not obtained we shall refrain from extending Nielsen's work³ on ethyl fluoride, but the spectra are nevertheless given because of their documentary value (Fig. 1).

Infrared spectra of the bromides (I'), (II'), (II' + III'), (IV') and (V') in the liquid phase at room temperature were also taken. The absorption line frequencies are given in Table 1. We have attempted to subtract the lines originating from (II') in the spectrum of (II' + III'). For sake of comparison we have included the Raman observations made

Fig. 3. Rotational isomers (a), (b) and (c) of $\text{CH}_2\text{DCH}_2\text{Br}$. Since (b) and (c) are mirror images they are spectroscopically indistinguishable. ν = frequency, I = relative intensity of observed bands.



by Langseth and Bak⁶. These are, *e. g.*, of special value in the identification of the (III')-lines since Langseth and Bak prepared (III') by the different process



giving a sample not contaminated with $\text{CH}_2\text{DCH}_2\text{Br}$.

DISCUSSION

The default that no Raman data have been published for (IV') and (V') may tentatively be removed by the argument supported by columns 1—6 of Table 1, that the *total* number of different lines observed, either in the infrared or in the Raman spectrum, is approximately equal to the number of observed lines + $4n$ when n is the number of rotational isomers. Estimated in this way, the number of different bands from (IV') or (V') would be, respectively, $20 + 12 = 32$ and $22 + 12 = 34$. This is probably an upper limit so that for both (IV') and (V') we are so far from the number of theoretically observable lines, 39, that it is hard to avoid the conclusion that two of the rotational isomers have many coinciding bands. In fact we believe that these isomers can be pointed out.

In the spectrum of (II') (Table 1. Two rotational isomers in a 1:2 ratio) it is seen that the rotational isomers absorb near 540 cm^{-1} (C—Br stretching frequencies). Fig. 3 illustrates the situation.

Now, the three spectroscopically distinguishable isomers (IV') are, in fact, deuterium derivatives of the species in Fig. 3.

According to the Rayleigh rule, which it is legitimate to apply here because of the relatively isolated position of the C—Br band in question (*cf.* Table 1),

$$\begin{aligned} \nu (e \text{ and } f) &\leq 534\text{ cm}^{-1} \\ \nu (g \text{ and } h) &\leq 555\text{ cm}^{-1} \\ \nu (i \text{ and } j) &\leq 555\text{ cm}^{-1}. \end{aligned}$$

Now, two lines were observed at 526 and 543 cm^{-1} , their intensity ratio being about 1:2. The only solution is that

$$\begin{aligned} \nu (e \text{ and } f) &= 526\text{ cm}^{-1} \\ \nu (g \text{ and } h) &\sim \nu (i \text{ and } j) = 543\text{ cm}^{-1}. \end{aligned}$$

Therefore, the C—Br stretching frequencies coincide for the isomers (g , h) and (i , j).

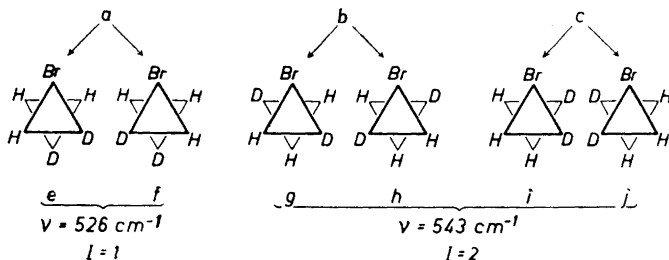


Fig. 4. Rotational isomers of CH_2DCHDBr . Since (e) and (f), (g) and (h), (i) and (j) are mirror images there are only three spectroscopically distinguishable isomers.

We can argue in a similar way considering (V') as a deuterium derivative of (IV'). Selecting (e), (g), and (i) as suitable representatives we get the isomers (k), (l), (m), (n), (o) and (p) (Fig. 5).

According to the Rayleigh rule:

$$\nu(k) \leq 526 \text{ cm}^{-1}, \nu(o) \leq 543 \text{ cm}^{-1}. \quad \text{Since } (k) \equiv (o), \nu(o) \leq 526 \text{ cm}^{-1}$$

$$\nu(l) \leq 526 \text{ cm}^{-1}, \nu(n) \leq 543 \text{ cm}^{-1}. \quad \text{Since } (l) \equiv (n), \nu(n) \leq 526 \text{ cm}^{-1}.$$

Also

$$\nu(m) \leq 543 \text{ cm}^{-1}, \nu(p) \leq 543 \text{ cm}^{-1}.$$

Again, two lines were observed at 542 and 523 cm^{-1} with an intensity ratio of 1:2. The only solution is that

$$\nu(k) \sim \nu(l) = 523 \text{ cm}^{-1}$$

$$\nu(m) = 542 \text{ cm}^{-1}.$$

It follows from the low number of observed lines in the spectra of (IV') and (V') that some coincidence of spectral lines must take place. Since the C—Br stretching frequencies coincide in the spectra of the rotational isomers (g) and (i), respectively (k) and (l), the remaining parts of these spectra may also be very similar.

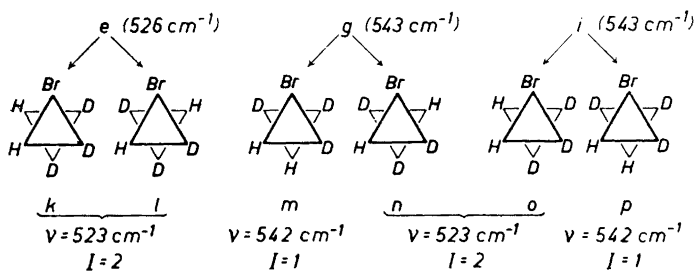


Fig. 5. Rotational isomers of CHD_2CHDBr . Here (k) \equiv (o), (m) \equiv (p), and (l) \equiv (n).

Table 2. Comparison between infrared absorption frequencies of the C—Br stretching vibration of CH_2DCHDBr (IV') and CHD_2CHDBr (V') in the liquid and gaseous states. Frequencies in cm^{-1} . In parenthesis, relative intensity.

	CH_2DCHDBr			CHD_2CHDBr		
Liquid	526(1)		543(2)	523(2)		542(1)
Vapour	538.8(1)	556.6(1)	559.2(1)	536.0(1)	536.0(1)	554.7(1)

This postulated closer similarity is in harmony with the fact that (*k*) and (*l*) are identical molecules with respect to the grouping about one carbon atom and mirror images with respect to the grouping about the second carbon atom whereas no such simple relationship exists between (*k*) and (*m*).

In order to see whether the C—Br stretching frequencies of the rotational isomers (*g*) and (*i*), respectively (*k*) and (*l*), are at all separated, spectra of (IV') and (V') in the gas phase were run, using a Beckman IR3 spectrograph with a somewhat higher resolution than the Perkin-Elmer instrument. The path length was 10 cm and the pressure 150 mm Hg. In Table 2 the results are summarized and compared with the data for the liquid state.

As seen from Table 2, three distinct Q-branches were observed only in the case of the rotational isomers (*e*), (*g*) and (*i*) with the common formula CH_2DCHDBr .

Acknowledgement. We are grateful to Dr. F. A. Andersen for taking the spectra on the Beckman instrument. One of us (S.D.) wants to express her thanks for a Danish Government scholarship.

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Received September 17, 1958.