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Vibrational spectrum and frequency assignments for 2,2-diaminohexafluoropropane

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Abstract—The infrared spectra of gaseous 2,2-diaminohexafluoropropane and its N-perdeuterated derivative have been studied in the range 4000–200 cm^{-1}. A supplementary study of the Raman spectra of the liquids including polarization measurements has been carried out. By comparing the spectra with those of similar molecules it has been possible to suggest an assignment for the frequencies of the normal vibrations of $(CF_3)_2C(NH_2)_2$ observed in the cited range.

INTRODUCTION

LINEAR organic molecules in which two NH_2 groups are bonded to the same carbon atom are exceedingly rare and tend to be quite unstable. However, recently the synthesis of a diaminomethane derivative, 2,2-diaminohexafluoropropane, $(CF_3)_2C(NH_2)_2$, has been described [1]. This diamine can be distilled at normal pressure without decomposition and the borane chemistry of the compound is presently being investigated in our laboratories. Therefore, it seemed desirable to obtain a reasonable interpretation of the vibrational spectrum of 2,2-diaminohexafluoropropane. The present work reports on a study of the Raman and infrared spectrum of the compound and of its *N*-perdeuterated derivative, $(CF_3)_2C(ND_2)_2$, and an assignment of fundamentals is proposed.

EXPERIMENTAL SECTION

Preparative procedures

2,2-Diaminohexafluoropropane was obtained by bubbling hexafluoroisopropylidenimine [1], $(CF_3)_2CNH$, into anhydrous liquid ammonia. Excess of ammonia was evaporated and, after standing overnight, the remaining liquid was distilled to give a nearly quantitative yield of the desired product, b.p. 87–92° (lit.: 91–91.5°). A spectroscopically pure material, b.p. 91°, was obtained by two redistillations. The N-perdeuterated compound was obtained in an analogous procedure utilizing $(CF_3)_2CND$ and ND_3 as starting materials.

Recording of spectra

The gas phase infrared spectra of $(CF_3)_2C(NH_2)_2$ and $(CF_3)_2C(ND_2)_2$ were obtained in the 4000–660 cm^{-1} range with a Perkin–Elmer Model 21 double-beam spectrophotometer, using a 10 cm gas cell equipped with sodium chloride windows, and in the 4000–200 cm^{-1} range with a Perkin–Elmer Model 621 double-beam spectrophotometer, using a 5 cm gas cell equipped with cesium iodide windows. The spectra were obtained at the vapor pressure of each compound at ambient temperature. Infrared spectra were also recorded on the neat liquids. However, the resolution of the liquid phase spectra was inferior to that of the gas phase spectra. This feature may result from intermolecular association which is indicated by the observed minor frequency shifts particularly of those bands involving motions of the NH_2 groups (see Table 1). The gas phase infrared spectrum of $(CF_3)_2C(NH_2)_2$ is illustrated in Fig. 1. Raman spectra of the neat liquids were obtained through the courtesy of Dr. E. B. Bradley, Department of Electrical

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[1] W. J. MIDDLETON and C. G. KRESPAN, *J. Org. Chem.* **30**, 1398 (1965).

Engineering, University of Kentucky, with a Perkin–Elmer LR-1 Raman spectrometer using a 5 mW Spectrophysics He–Ne laser as the exciting device. In all cases the frequencies listed reflect an average of several recordings.

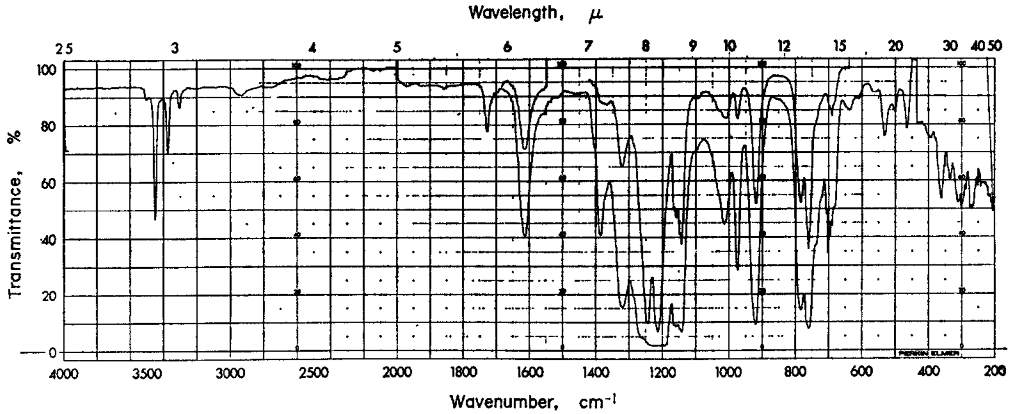

Fig. 1. Infrared spectrum of $(CF_3)_2C(NH_2)_2$, gas phase.

Structural Model

A determination of the structure of $(CF_3)_2C(NH_2)_2$ is not presently available and, hence, a complete normal coordinate analysis of the molecule is not feasible at this time. The spectrum of hexafluoroisopropylidenimine, $(CF_3)_2CNH$, is adequately described assuming a C_{2v} model [3]. However, such a symmetry would be inadequate for the $(CF_3)_2C(NH_2)_2$ molecule: Of the two possible C_{2v} conformations (see Fig. 2) one presents a situation which should provide for large intermolecular interactions. Such an event is not borne out by the relatively high vapor pressure of the compound nor by the observed spectral data. The second C_{2v} arrangement presents an electrostatically unfavorable situation. Hence, reasonable choice for a model of the $(CF_3)_2C(NH_2)_2$ molecule would be either C_s or C_2 symmetry (see Fig. 2)

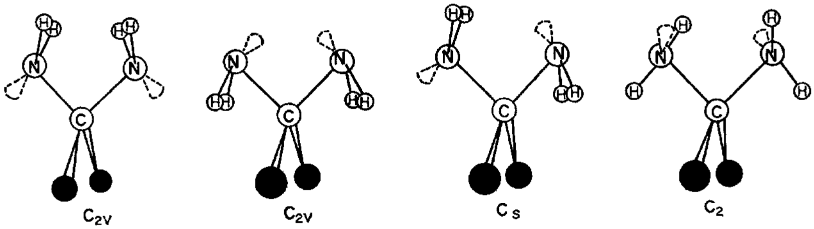

Fig. 2. Possible molecular conformations of $(CF_3)_2C(NH_2)_2$.

but no ready choice can be made on the basis of the present spectroscopic data. A total of 39 fundamentals will be expected for a C_s model of 2,2-diaminohexafluoropropane, 21 of which should be totally symmetric and hence polarized in the Raman spectrum; for a C_2 model one should expect 20 polarized fundamentals. However,

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[2] F. A. Miller and F. E. Kiviat, *Spectrochim. Acta* **25A,** 1577 (1969).

[3] K. Niedenzu and co-workers, unpublished data.

only nine polarized Raman lines were observed and several Raman lines and infrared bands are observed without counterparts. This observation would contradict both C_s and C_2 symmetry though the noted bands appear in the region of CF vibrations and additional absorptions may be camouflaged by the high intensities of the CF frequencies. From a chemical point of view the weak basic properties of $(CF_3)_2C(NH_2)_2$ and its ready loss of ammonia [3] would seem to favor C_2 symmetry which is assumed as the basis for the following discussion.

ASSIGNMENT OF FUNDAMENTALS

In the 4000–200 cm^{-1} region of the spectrum of $(CF_3)_2C(NH_2)_2$, thirty-eight infrared bands were observed, twenty-one of which have Raman counterparts (Table 1). There are four additional Raman bands for which no infrared counterparts could be observed. Nine of the Raman bands are polarized and can be assigned as symmetric modes. On the basis of these observations and of experimental data on $(CF_3)_2C(ND_2)_2$ and hexafluoroisopropylidenimine [2, 3], assignments of most of the fundamentals of the 2,2-diaminohexafluoropropane can be proposed. The suggested assignments are summarized in Table 2. In making these assignments it should be emphasized that the spectra exhibit only one absorption in regions where more than one fundamental might be expected, probably due to accidental degeneracy.

NH_2 *vibrations*

The NH stretching modes of $(CF_3)_2C(NH_2)_2$ are assigned to bands near 3452 and 3378 cm^{-1}, with Raman counterparts at 3420 and 3340 cm^{-1}. The Raman line at 3340 cm^{-1} is distinctly polarized, and thus can be identified as the symmetric mode. In the spectrum of the N-perdeuterated compound, the corresponding ND vibrations are observed at 2580 and 2465 cm^{-1} respectively.

The NH_2 scissoring deformations have been assigned to bands in the 1600 cm^{-1} region for both the CH_3NH_2 [4] and $NH_2CH_2CH_2NH_2$ [5] molecules. In the spectrum of $(CF_3)_2C(NH_2)_2$ two bands appear in this same region, one in the infrared at 1614 cm^{-1} with a Raman counterpart at about 1620 cm^{-1}; an additional depolarized Raman line is observed at 1640 cm^{-1}; it has no infrared counterpart. The degree of polarization and exact position of the line at 1620 cm^{-1} could not be determined due to the broadness of the 1640 cm^{-1} band. In the N-deuterated compound the corresponding frequencies are shifted to 1260 and 1370 cm^{-1} respectively. This observation is in agreement with the expected shift for isotopic labeling and thereby supports the suggested assignments.

The assignment of the NH_2 twisting motion presents some difficulty. GRAY and LORD [4] assign this mode to the band at 1416 cm^{-1} in the spectrum of CH_3NH_2 while SABATINI and CALIFANO [5] propose assignment of the twisting NH_2 mode of ethylenediamine to a band at 1249 cm^{-1}. The infrared spectrum of $(CF_3)_2C(NH_2)_2$ exhibits a medium to strong absorption at 1386 cm^{-1}, with no band in this region in the N-deuterated compound. The N-deuterated compound, however, exhibits a band of the same intensity and shape as the above 1386 cm^{-1} absorption at 1040 cm^{-1}. This observation indicates a shift of the same magnitude as the previously

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[4] A. P. GRAY and R. C. LORD, *J. Chem. Phys.* **26**, 690 (1957).

[5] A. SABATINI and S. CALIFANO, *Spectrochim. Acta* **16**, 677 (1960).

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Table 1. Infrared and Raman spectra of $(CF_3)_2C(NH_2)_2$ and $(CF_3)_2C(N_2D)_2$*

$(CF_3)_2C(NH_2)_2$			$(CF_3)_2C(ND_2)_2$	
Raman (liq.)	I.r. (gas)	I.r. (liquid)	Raman (liq.)	I.r. (gas)
	3508 vw			
3420 w, dp	3452 ms	3420 m		3458 vw
3340 m, p	3378 mw	3325 m, b		3410 vw
	3306 w			
	2946 vw			
	2755 vvw			
				2580 ms
				2521 mw
			2422 m	
	1972 vw			1952 vw
1720 vw, p	1729 mw			
1640 1620 w, dp	1614 ms	1612 m		1624 vw
				1466 m
1367 vw, p	1386 m	1379 mw	1370 vw	
1314 w, dp	1320 ms	1320 w	1315 w	1319 s
1270 sh, dp			1275 vw	
				1262 ms
1240 mw, p 1200 sh, sp	1242 1212 vs	1218 vs, b		1238 1219 vs
	1149 m			1170 m
	1160 ms		1145 vw	1162 m
1142 w, dp	1142 m	1145 s, b		
	1092 vw			1110 w
				1040 s
1030 sh, dp	1031 sh		1030 w	1026 ms
1010 m, p	1016 mw	1015 m		1018 sh
	975 m		945 vw	935 mw
929 w, dp	920 s	930 s, b		
				888 mw
			860 mw	864 vw
				840 vw
			822 w	818 vw
	785 s			
763 vs, p	761 s	765 m	758 vs	766 m
			715 vw	728 s
704 vw	704 m	705 m		672 vw
				648 w
645 mw, p	638 vw	645 mw	617 m	613 vw
616 m, dp	610 vw	617 w	590 sh	596 vw
564 vw	550 vw	563 w	570 w	564 sh
530 mw, p	543 mw	531 mw		531 vw
	501 vw		510 m	508 vw
			485 sh	
470 vw	466 mw	471 m	458 w	453 mw
	396 vw		438 w	
370 sh, dp	361 mw	370 w	370 sh	
	341 sh	341 w	343 sh	350 w
	336 w			
330 s, p	326 w	325 w	322 ms	324 mw
	312 w			304 vw
290 w, dp	300 w		280 vw	291 w
	270 w			260 w
245 vw, dp				

* Frequencies in cm^{-1}; w = weak, m = medium, s = strong, v = very, p = polarized, dp = depolarized, sh = shoulder, b = broad.

cited modes involving the NH/ND pair and thus substantiates the suggested assignments (see Table 2).

The NH_2 out-of-plane deformations can be identified as the only remaining frequencies with a NH/ND shift of over 1.20. These were observed at 1031 and

Table 2. Assignment of the fundamentals of $(CF_3)_2C(NH_2)_2$

Description of modes	Frequencies (cm^{-1}) $(CF_3)_2C(NH_2)_2$	$(CF_3)_2C(ND_2)_2$	ν_H/ν_D*
NH stretch (asym)	3452	2580	1.34
NH stretch (sym)	3340	2422	1.37
NH_2 scissor (asym)	1640	1370	1.20
NH_2 scissor (sym)	1614	1262	1.30
NH_2 twist	1386	1040	1.31
CF_3 stretch (asym)	1320	1319	1.00
CF_3 stretch (asym)	1270	1275	1.00
CF_3 stretch (sym)	1242	1238	1.00
CF_3 stretch (asym)	1212	1219	1.00
CF_3 stretch (asym)	1165	1162	1.00
CF_3 stretch (asym)	1149	1170	0.98
CN stretch (asym)	1142	1026	1.11
NH_2 wag	1031	864	1.20
CN stretch (sym)	1016	935	1.09
CC stretch (asym)	975	888	1.10
NH_2 wag	920	721	1.26
CF_3 deformation	785	766	1.03
CC stretch (sym)	761	728	1.05
CF_3 deformation	704	665	1.05
CF_3 deformation	638	613	1.04
CF_3 deformation	610	596	1.02
CF_3 deformation	543	531	1.02
CF_3 deformation	530	510	1.04
CCF_3 rock	501	508	0.98
NCN deformation	466	453	1.02
CCN deformation	361	350	1.03
CCC deformation (sym)	330	322	1.02
CF_3 rock	300	291	1.03
CF_3 rock	270	260	1.04

* ν_H/ν_D represents the ratio of N-hydrogenated modes to corresponding modes in the N-perdeuterated derivative.

920 cm^{-1} respectively with counterparts in the N-deuterated compound at 864 and 721 cm^{-1}. These assignments are supported by those suggested for the corresponding modes of ethylenediamine [5] which are reported at 951 and 920 cm^{-1}.

CF_3 *vibrations*

CF_3 stretching modes are assigned to infrared bands at 1320, 1242, 1212, 1165, and 1149 cm^{-1} and a Raman line at 1270 cm^{-1}. These assignments are made by comparison with the spectra of $(CF_3)_2CO$, $(CF_3)_2CNH$, and $(CF_3)_2CNCH_3$ and are readily identified [6, 2, 3]. The corresponding vibrations in the spectrum of the N-deuterated compound are observed at virtually identical frequencies and are easily distinguishable due to their great intensities with respect to other frequencies. The CF_3 valence angle deformational modes are assigned on a similar basis; they correspond closely with the data obtained on the above similar molecules [2, 3, 6] and are assigned to the infrared bands at 785, 704, 638, 610, and 543 cm^{-1} and to the Raman line at 530 cm^{-1} (see Table 2).

CN *vibrations*

The two expected C—N stretching modes can be identified at 1142 and 1016 cm^{-1}; the latter band is polarized in the Raman and hence can be attributed to the symmetric vibration. C—N stretching vibrations are assigned to absorptions at 1104 and

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[6] C. V. Berney, *Spectrochim. Acta* **21,** 1809 (1965).

1065 cm^{-1} for ethylenediamine [5], being consistent with the proposed assignments. Moreover, no corresponding absorptions are observed in the spectrum of hexafluoroacetone. The NCN deformation and the CCN deformation are also assigned by comparing the present data with the spectrum of hexafluoroacetone: the infrared bands at 466 and 361 cm^{-1} respectively have no counterparts in the spectrum of the latter [6].

CC *vibrations*

The CC antisymmetric and symmetric stretching modes are identified in the infrared spectrum of $(CF_3)_2C(NH_2)_2$ at 975 and 761 cm^{-1} respectively. These assignments are substantiated by comparison with the spectra of similar molecules [2, 3, 6] and also by the degree of polarization of the corresponding Raman lines.

The CCC symmetric deformation can be assigned to the infrared band at 326 cm^{-1}. It has a strong, polarized counterpart in the Raman spectrum of the compound at 330 cm^{-1}. This observation corroborates the proposed assignment for the polarized 336 cm^{-1} line to this same mode in the spectrum of $(CF_3)_2CNH$ molecule [2, 3].

CONCLUSION

With the exception of the 1729 cm^{-1} frequency, all medium or stronger vibrations have been assigned to fundamentals of the $(CF_3)_2C(NH_2)_2$ molecule. The one unassigned frequency is too high to be considered as a NH_2 deformation. Hence, a reasonable assignment for this absorption appears to be a combination of NH_2 wag at 920 cm^{-1} and CF_3 deformation at 785 cm^{-1} (see Table 2).

It is noteworthy that the CF modes are virtually unaffected by the substituent on the center carbon. Apparently, the CF vibrations do not mix with the $(CF_3)_2C$ substituent modes since the fluorine atoms are at least two carbons removed from the substituent. On that basis the present assignments can be utilized to interpret spectral features of more complex derivatives containing the basic $(CF_3)_2C$ skeleton.

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