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Note on the Infra-Red Absorption Spectra of the Vapors of DCOOH and DCOOD

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In order to complete the set of infra-red spectra of the deuterated formic acids begun by Bonner and Hofstadter[1] (HCOOH) and Hofstadter[2] (HCOOD), the dimer and monomer spectra of the vapors of DCOOH and DCOOD have been obtained in the region 1 to 15μ. We hoped that sufficiently regular shifts in band positions would appear from one spectrum to the next so that approximate calculations would enable us to make assignments of bands whose frequencies lie below 1700 cm^{-1}.

Heavy formic acid (DCOOD) was prepared by the thermal decomposition of anhydrous deuterated oxalic acid [$(COOD)_2$] in vacuum at about 180°C. The deuterated oxalic acid was obtained by exchanging anhydrous oxalic acid (Kahlbaum) with 99.6 percent D_2O and was dehydrated by heating under vacuum. The

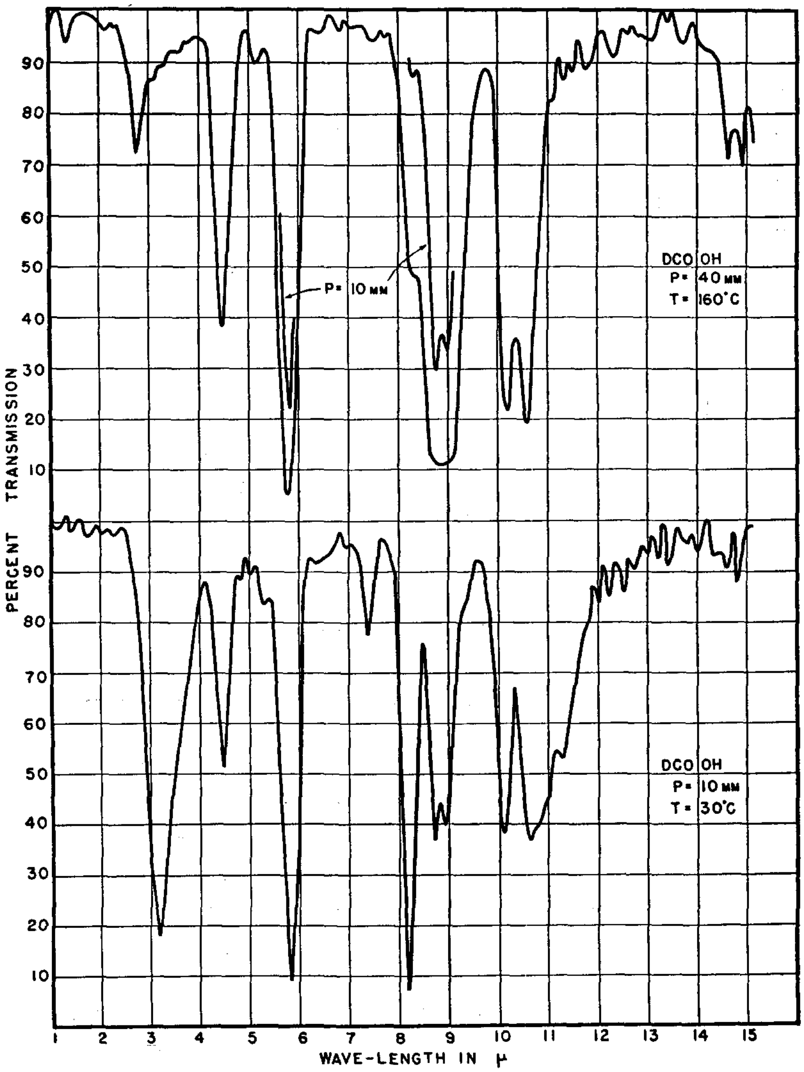

Fig. 1. Absorption spectrum of DCOOH. Cell length 22 cm.

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[1] L. G. Bonner and R. Hofstadter, J. Chem. Phys. 6, 531 (1938).

[2] R. Hofstadter, J. Chem. Phys. 6, 540 (1938).

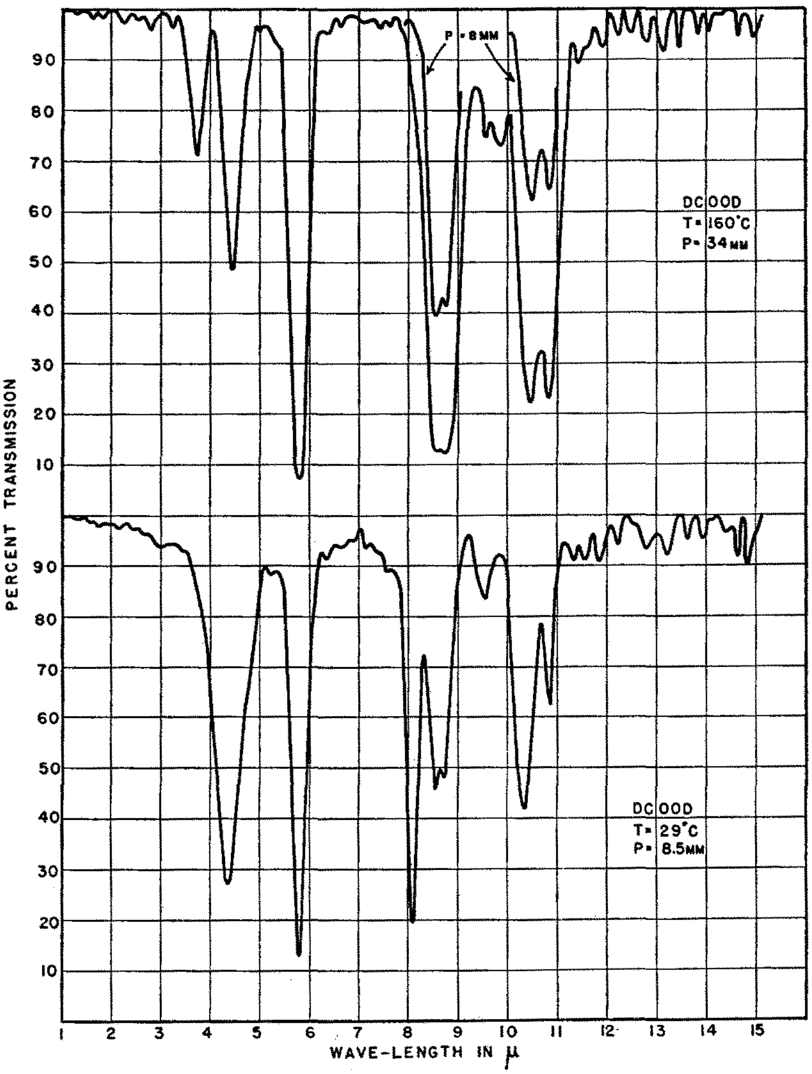

FIG. 2. Absorption spectrum of DCOOD. Cell length 22 cm.

DCOOD was purified by several vacuum distillations after pumping off the CO_2. The DCOOH was prepared by exchanging the DCOOD several times with H_2O. Anhydrous copper sulfate was used to dehydrate the acid between exchanges.

TABLE I.

DCOOD				DCOOH			
DIMER		MONOMER		DIMER		MONOMER	
2325 cm^{-1}	ν(ODO)	2680 cm^{-1}	ν(OD)	3175 cm^{-1}	ν(OHO)	3633 cm^{-1}	ν(OH)
	ν(CD)	2265	ν(CD)	2248	ν(CD)	2250	ν(CD)
1719	ν(C=O)	1730	ν(C=O)	1730	ν(C=O)	1730	ν(C=O)
1243		1178		1358		1206	
1178		1143		1224		1146	
1150		1052		1150		1114	
1052		1015		1121		982	
974		957		990		946	
927		926		944*		678	
				887			

* Broad.

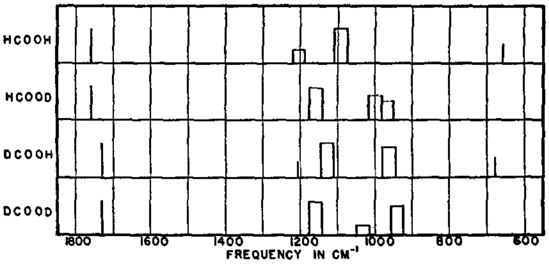

FIG. 3. Line graph for the monomers of formic acid. Heights of lines indicate intensities approximately.

A preliminary experiment was performed on the thermal decomposition of light oxalic acid in vacuum at about 180°C. The resultant HCOOH was tested for water content by comparison of vapor pressure measurements with those made by Coolidge[3] for formic acid-water mixtures. Further, the infra-red spectrum of the light acid showed no absorption band in the region of 1600 cm^{-1} where water absorbs strongly. These tests showed that there was less than 3 percent of H_2O present. The high yield of formic acid obtained substantiates the work of Wobbe and Noyes[4] on the thermal decomposition of oxalic acid. Unfortunately, it was not possible to determine the extent of the deuteration of the formic acids by means of the mass spectrograph. However, the spectra themselves indicate that the CD, OD, and OH groups are at least 95 percent pure. The experimental technique was the same as that employed in previous investigations.[5]

The monomer and dimer spectra of DCOOH and DCOOD are shown in Figs. 1 and 2. Parts of the monomer spectra of HCOOH and HCOOD were restudied and a few corrections and additions are made. In the spectrum of HCOOH $\nu(C=O)$ is found at 1760 cm^{-1}, the double band listed at 1093 has minima at 1111 and 1075 cm^{-1}, and there is also a true monomer doublet with minima at 1221 and 1190 cm^{-1}. In the monomer spectrum of HCOOD the following minima were redetermined: 1178, 1142, and 1018 cm^{-1}. Fig. 3 shows the positions of all the bands below 1800 cm^{-1} in the spectra of the four isotopic monomer forms of formic acid. Table I gives the positions and some assignments for the bands in the monomer and dimer spectra of DCOOH and DCOOD.

We are unable to give a consistent interpretation of the bands whose frequencies lie below 1700 cm^{-1}. The apparently irregular shifts that occur in the spectra upon deuterium substitution seem to indicate either accidental degeneracies or strong interactions which are different for the different molecules. The simple triatomic calculation suggested by Bonner and Hofstadter is certainly inadequate to explain the spectra.

It is interesting that practically all the bands in the monomer spectra below 1700 cm^{-1} show a doublet structure with a separation of about 34 cm^{-1} which is roughly the separation to be inferred from the spectrum of the $3\nu(OH)$ band in formic acid at 10,203A studied by Bauer and Badger.[6] It seems difficult to understand why these bands seem to show a persistent doublet structure since any vibrational mode which has an appreciable change in dipole moment parallel to the least moment of inertia axis should exhibit a strong qQ branch. It would seem worth while to study the fundamental bands of the various formic acids under higher resolution.

We wish to express our appreciation to the Research Department of the Calco Chemical Division of American Cyanamid Company for the interest shown in this work.

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[3] A. S. Coolidge, J. Am. Chem. Soc. **50**, 2166 (1928).

[4] D. E. Wobbe and W. A. Noyes, Jr., J. Am. Chem. Soc. **48**, 2856 (1926).

[5] R. C. Herman and R. Hofstadter, J. Chem. Phys. **6**, 534 (1938).

[6] S. H. Bauer and R. M. Badger, J. Chem. Phys. **5**, 852 (1937).