SHORT COMMUNICATIONS

Far Infrared Spectrum of Gaseous Formic Acid

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Since the first report of Bonner and Kirby-Smith[1] on a Raman line of formic acid, low frequency vibrations of the acid have not been studied till recently. However, it is interesting to investigate the vibrational bands in relation to the anomalous band features of OH groups due to hydrogen bonding found in both near infrared and infrared regions[2]. Sato and Nagakura explained their results by the motion of the proton in the double minimum potential. Oshida, Ooshika and Miyasaka[3] also explained these phenomena theoretically by the same model, and predicted appearance of new bands in the far infrared region. However, though Pitzer et al.[4] observed two bands of gaseous formic acid at 237 cm^{-1} and 160 cm^{-1}, they ascribed[5] them to the intermolecular vibrations between the two monomers making up formic acid dimer by hydrogen bonding.

In the course of studies[6] on chemisorption of gaseous formic acid HCOOH to the silver surface, the present authors also found two bands independently[7]. In connection to this measurement they extended their research over the region 85$\sim$300 cm^{-1} not only on formic acid HCOOH but also on formic acid-d HCOOD, and found some new knowledge, the essential point of

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[1] L. Bonner and J. B. Kirby-Smith, *Phys. Rev.*, **57**, 1078 (1940).

[2] Y. Sato and S. Nagakura, *Sci. of Light*, **4**, 120 (1955); *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **76**, 1007 (1955): Y. Sato, ibid., **79**, 358, 1384 (1958).

[3] I. Oshida, Y. Ooshika and R. Miyasaka, *J. Phys. Soc. Japan*, **10**, 849 (1955).

[4] R. C. Millikan and K. S. Pitzer, *J. Am. Chem. Soc.*, **80**, 3515 (1958).

[5] T. Miyazawa and K. S. Pitzer, ibid., **81**, 74 (1959).

[6] K. Hirota, K. Kuwata and Y. Nakai, This Bulletin, **31**, 861 (1958).

[7] K. Hirota and Y. Nakai, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 700 (1959).

which will be reported.

Formic acid of chemically pure grade (Edogawa Kagaku Kogyo Co.) was repeatedly vacuum-distillated, crystallized, and dehydrated with unhydrous copper sulfate. Formic acid-d was prepared by the reaction of sodium formate, whose degree of purity was the same as formic acid, with sulfuric acid-d D_2SO_4 (36%). Method of purification was the same as described on formic acid. It was confirmed that formic acid-d thus obtained does not include H_2O and HCOOH so much as can be detected by use of the NMR method (Apparatus: Varian V 4300 B).

The spectrometer made by Yoshinaga et al.[8], Engineering Faculty of Osaka University, was used. During the measurement, the apparatus was kept constant at 21°C, while the pressure of the acid in the measuring cell was about 30 mmHg. Gratings, light sources, reststrahlen filter and width of slits were changed according to the spectrum range as shown in Table I.

TABLE I

Wave number (cm^{-1})	Light source	Reststrahlen filter	Slit width (mm.)
300～190	Pt-source	NaCl	0.36
190～155	Hg lamp	NaCl	0.50
160～130	〃	KCl	0.47
140～105	〃	KBr	0.68
110～ 85	〃	KBr	1.30

The experimental results are shown in Figs. 1 and 2 and in Table II, where the data of Pitzer[4] and Simova[9] are compared for the sake of discussion. However, Simova's values seem to be of less confidence, because they were estimated from the combination bands of a Raman line.

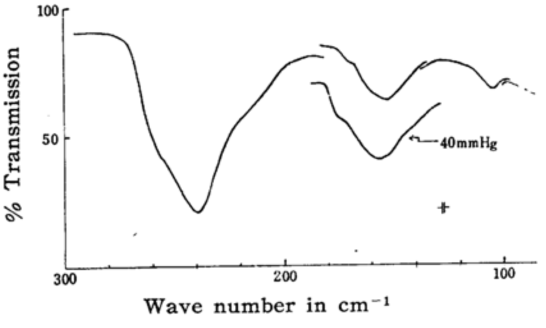

Fig. 1. Far infrared spectrum of HCOOH Pressure 30 mmHg; Temp. 21°C.

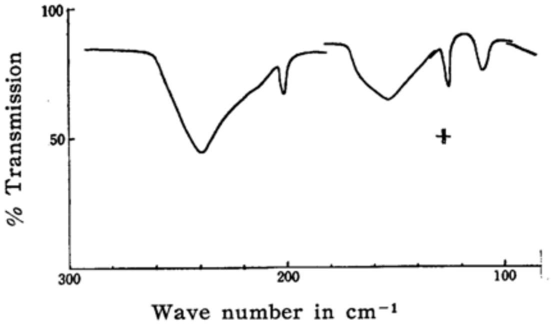

Fig. 2. Far infrared spectrum of HCOOD Pressure 30 mmHg; Temp. 21°C.

TABLE II. FAR INFRARED BANDS OF FORMIC ACID (cm^{-1})

The present work		Pitzer HCOOH	Simova HCOOH	Other researchers HCOOH
HCOOH	HCOOH			
ca. 270 (sh.)				
240±5 (vs)	240±5 (vs)	237	230	232[a]
	202 (m)		200	
175 (sh.)			170	
155 (s)	155 (s)	160		
			145	
	126 (m)			
109 (m)	111 (m)			110[b]

a) Cf. G. Herzberg, "Infrared and Raman Spectra", D. Van Nostrand Co., New York (1945).

b) L. M. Sverklow, *Izv. AN. USSR*, **17**, 567 (1953).

The important point obtained from the present data is as follows. Strong bands are observed at 240 cm^{-1} and 155 cm^{-1} in both acids, but it is noteworthy that their feature differs markedly; i.e., (a) in case of HCOOH the 240 cm^{-1} band is broad and begins at 278 cm^{-1}, making a sharp contrast with the beginning at ca. 258 cm^{-1} in case of HCOOD, and (b) small bands can be detected at ca. 270 cm^{-1} and 175 cm^{-1} as shoulders of the 240 cm^{-1} and 155 cm^{-1} bands, respectively, in case of HCOOH. These shoulders become conspicuous if the pressure of formic acid is increased to ca. 40 mmHg as shown in Fig. 1. The second point to be mentioned is appearance of sharp bands at 202 cm^{-1} and 126 cm^{-1} in case of HCOOD. Besides, a new band is observed at ca. 110 cm^{-1} in both acids. Their nature, however, will not be discussed in the present note*),

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[8] Y. Yoshinaga, S. Fujita, S. Minami, A. Mitsuishi, R. A. Oetjen and Y. Yamada, *J. Opt. Soc. Am.*, **48**, 311 (1958).

[9] P. Simova, *Izv. Bulgar. Akad. Nauk. Otdel. Fiz. Mat. i Tekh., ser. Fiz.*, **2**, 107 (1951).

*) Their frequency is too high if they are the lowest infrared active band predicted by Miyazawa and Pitzer.

except to mention that a Raman line has been observed in the neighborhood of this band (110 cm^{-1}).

The strong and broad bands at 240 cm^{-1} and 155 cm^{-1} seem to correspond to those at 238 cm^{-1} and 160 cm^{-1} observed by Pitzer et al. and can be assigned to the bands produced by the intermolecular vibration between the two monomers making up formic acid dimer as already done by Miyazawa and Pitzer. They may be two higher frequency bands of the three infrared active ones which are expected from the symmetry of the dimer (C_{2h}). It is necessary, therefore, to introduce another cause in order to explain the appearance of two bands of the similar form at 270 cm^{-1} and 175 cm^{-1} in case of HCOOH. Taking the fact into consideration that the ratio of their wave number to that of the sharp bands at 202 cm^{-1} and 126 cm^{-1} in case of HCOOD nearly equals $\sqrt{2}$, respectively, it may presumably be reasonable to assign them to the bands due to the motion of the proton in the double minimum potential, as proposed several years ago[2,3,10].

In conclusion, the present authors express their sincere thanks to Professor H. Yoshinaga and the members of his laboratory (Dr. S. Fujita, Dr. Y. Yamada and Dr. A. Mitsuishi) without whose assistance the present research could not be carried out, and they are much indebted to Professor S. Nagakura of the University of Tokyo and also to Associate Professor S. Seki of Osaka University for helpful discussion of the problem here considered.

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[10] *Discussions Faraday Soc.*, **9**, 210–212 (1950).