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Infrared Investigation of Acetic Acid and Acetic Acid-d Vapors and a Vibrational Assignment for the Monomeric Acids

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The infrared spectra of acetic acid and acetic acid-d, as vapors at 150°C, have been obtained from 2–25μ and an assignment of the fundamental vibrational frequencies made for the monomeric acids, with the exception of the two low lying type A'' torsional frequencies. Infrared spectra of the two acids, in the vapor phase, have also been obtained over the 5–15μ region at 25°, 65°, 105°, and 150° and the effect of temperature on some of the frequencies discussed.

INTRODUCTION

THE study of the infrared spectrum of acetic acid is complicated by the fact that, even in the vapor phase, acetic acid is a mixture of two species, monomers and dimers, the latter being formed by very strong hydrogen bonding between two monomeric molecules to yield a cyclic structure.[1] From studies of the effect of temperature on the degree of this association in acetic acid,[2] it is found that at 150°C the vapor is nearly completely monomeric and, hence, in order to obtain the infrared spectrum of the monomeric acid with the minimum interference from the dimeric form, it is necessary to study the vapor at this temperature.

This has been done by Gillette and Daniels,[3] who investigated the effect of temperature on the infrared spectrum of acetic acid vapor by obtaining the spectrum from 2–10 μ at 25° and 144°C, and by Herman and Hofstadter,[4] who obtained the infrared spectrum over the NaCl region of acetic acid and acetic acid-d vapors at 25° and 144°C, in an investigation upon the strength of the hydrogen bonds in the dimeric acid.

Using the infrared results of Herman and Hofstadter,[4] for acetic acid vapor at 144°C and the Raman results of Angus, Leckie, and Wilson[5] for liquid acetic acid, Sverdlov[6] has attempted a complete vibrational assignment for the monomeric acid. However, since acetic acid associates so readily and with the formation of such strong hydrogen bonds, it is extremely unlikely that any frequencies observed in the Raman investigation of the liquid, arising from the carboxyl group, would be related to the corresponding frequencies for the monomeric acid, and, consequently, Sverdlov's use of the Raman data in his assignment for the monomeric acid is dubious.

In this investigation, the infrared spectra of acetic acid and acetic acid-d vapors at 150°C have been rein-

vestigated and extended to cover the region from 2–25 μ. Making use of the vibrational assignments previously reported for sodium acetate,[7] a vibrational assignment of all the fundamentals, with the exception of the two type A'' torsional modes, has been made for the two acids. The effect of temperature on the infrared spectra of the vapors of the two acids, in the 5–15 μ region, has also been studied and confirms the assignments of Hadži and Sheppard[8] for the characteristic frequencies of the carboxyl group in the dimeric acids.

EXPERIMENTAL

The infrared spectra of acetic acid and acetic acid-d in the vapor-phase at 150°C were obtained from 2–15μ using a Beckman IR–2 spectrometer (in conjunction with a Brown recorder) equipped with LiF and NaCl optics and from 15–25 μ using a Perkin-Elmer model 21 spectrometer (with electronic recording) equipped with KBr optics. The sample path, in all cases, was 9 cm, and the spectra are shown in Fig. 1.

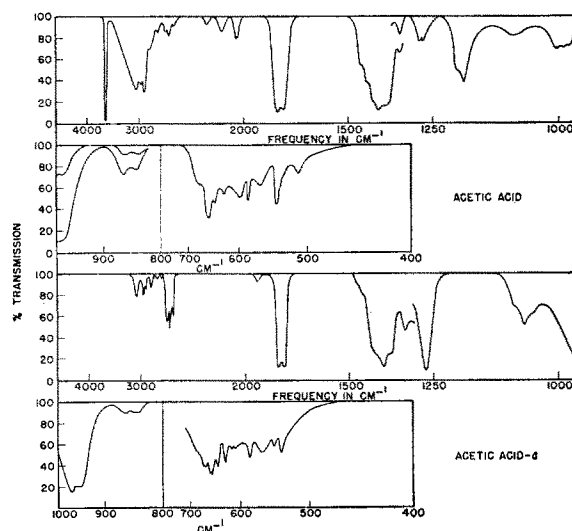The acetic acid used in the present investigation was

Fig. 1. The infrared spectra of acetic acid and acetic acid-d vapors at 150°C.

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[1] J. Karle and L. O. Brockway, J. Am. Chem. Soc. **66**, 574 (1944).
[2] M. D. Taylor, *ibid*. **73**, 315 (1951).
[3] R. H. Gillette and F. Daniels, *ibid*. **58**, 1139 (1936).
[4] R. C. Herman and R. Hofstadter, J. Chem. Phys. **6**, 534 (1938).
[5] Angus, Leckie, and Wilson, Proc. Roy. Soc. (London) **A155**, 183 (1936).
[6] L. M. Sverdlov, Izvest. Akad. Nauk. S.S.S.R. **17**, 567 (1953).
[7] J. K. Wilmshurst, J. Chem. Phys. **23**, 2463 (1955).
[8] D. Hadži and N. Sheppard, Proc. Roy. Soc. (London) **A216**, 247 (1953).

TABLE I. Fundamental frequencies for CH_3COOH and CH_3COOD.

		CH_3COOH	CH_3COOD	CH_3COO^-
O—H stretch	ν_1	3577	2640	
CH₃ unsym. stretch	ν_2	2997	2957	3006
CH₃ sym. stretch	ν_3	2961	2929	2941
C=O stretch	ν_4	1799	1792	
CH₃ unsym. bend	ν_5	1401	1387	1407
CH₃ sym. bend	ν_6	1340	1323	1341
A' C—O stretch	ν_7	1279	1272	
COH bend	ν_8	1192	959	
CH₃ rock	ν_9	990	~995[a]	1014
C—C stretch	ν_{10}	846	837	923
OCO bend	ν_{11}	654	654	
CO₂ rock	ν_{12}	536	536	
	τcalc 0.530	τobs 0.558		
CH₃ unsym. stretch	ν_{13}	3048	3058	3006
A'' CH₃ unsym. bend	ν_{14}	1445	1464	1438
CH₃ rock	ν_{15}	1068	1057	1046
CO₂ rock	ν_{16}	582	582	

[a] Occurs as an inflexion on the side of the strong 959 band.

distilled from chromic acid, again from sodium bisulfate, and finally redistilled, only the middle fraction in each case being accepted.

The acetic acid-d was prepared by distilling redistilled acetyl chloride into 99.95% heavy water and carefully fractionating the product.

ASSIGNMENT OF THE FREQUENCIES

Acetic acid has, at most, one plane of symmetry, namely the plane containing the carboxyl group and, hence, of the eighteen fundamental frequencies, twelve must be symmetric and six unsymmetric with respect to this plane. The experimental information allows a complete assignment of all the type A' frequencies and a partial assignment of the type A'' frequencies, as shown in Table I.

The assignments for the methyl group vibrations follow, without hesitation, from the corresponding assignments in sodium acetate,[7] which are given in column 3 of Table I for comparison, the only difference being the increased splitting in the frequencies that represent a degenerate mode in methyl chloride. The C—C stretching vibration is associated with the band at 846 cm⁻¹ (837 cm⁻¹ in acetic acid-d) the frequency being lower than that in the acetate ion in agreement with the expected decrease of the contributor type

$$H^+CH_2=C\begin{matrix} O^- \\ \\ OH \end{matrix}$$
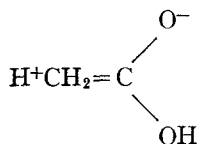
to the resonance hybrid.

The bands at 3577 and 1799 cm⁻¹ in acetic acid, becoming 2640 and 1792 cm⁻¹ respectively in acetic acid-d, can be safely assigned to the O—H and C=O stretchings respectively. By analogy with formic acid,[9] the

[9] J. K. Wilmshurst, J. Chem. Phys. **25**, 478 (1956).

band at 654 cm⁻¹ is assigned to the OCO bending mode, while by analogy with sodium acetate[7] the bands at 536 and 582 cm⁻¹ are assigned to the A' and A'' rocking vibrations of the carboxyl group respectively.

Of the remaining fundamentals, that at 1279 cm⁻¹, becoming 1272 cm⁻¹ in acetic acid-d, is assigned to the C—O stretching mode, in agreement with the observation of a strong band at 1245 cm⁻¹ in the spectra of a series of alkyl acetates due to the OC↔OR stretching,[10] while that at 1192 cm⁻¹, becoming 959 cm⁻¹ in acetic acid-d, is assigned to the inplane COH bending vibration, giving a frequency ratio of 1.24.

The two A'' torsional modes, corresponding to torsion about the C—C and C—O bonds, would both be expected to have very low frequencies (<400 cm⁻¹) and were not observed.

Application of the Teller Redlich ratio rule to the type A' vibrations gives satisfactory agreement between the observed and calculated ratios. All of the remaining observed frequencies can be assigned in terms of these fundamentals to overtone or combination bands as shown in Table II.

THE DIMERIC ACIDS

The infrared spectra of acetic acid and acetic acid-d as vapors at 25°, 65°, 105°, and 150°C over the 5–15 μ region are given in Figs. 2 and 3, respectively, the spectra at 25°C corresponding essentially to the dimeric form of the acids, that at 150°C to the monomeric form, and those at 65° and 105°C to mixtures of the two species in the dimer/monomer ratio of approximately 2:1 and 1:2 respectively.

The formation of the cyclic dimer from the monomeric acid molecules would be expected to affect essentially the frequencies associated with the COOH group and, to a lesser extent, the C—C stretching frequency, while the frequencies associated with the methyl group would remain appreciably constant. Thus, the effect of a temperature change on the spectrum of acetic acid or acetic acid-d vapor should only cause a

TABLE II. Overtone and combination frequencies.

Assignment	CH_3COOH calc	obs	CH_3COOD calc	obs
$\nu_7+\nu_{11}$	1933	1931	1926	1923
$\nu_8+\nu_{10}$	2038	2045	1796	...
$2\times\nu_{15}$	2136	2155	2114	...
$\nu_8+\nu_9$	2182	2212	~1954	...
$\nu_7+\nu_9$	2269	2283	~2267	...
$\nu_6+\nu_8$	2532	2513	2282	...
$\nu_5+\nu_8$	2593	2577	2346	...
$\nu_4+\nu_{10}$	2645	2632	2629	2624
$\nu_5+\nu_7$	2680	2668	2659	2654
$\nu_5+\nu_6$	2741	...	2710	2723
$2\times\nu_5$	2802	...	2774	2778
$\nu_6+\nu_{14}$	2846	...	2851	2855
$2\times\nu_{14}$	2890	2878	2928	(2929)

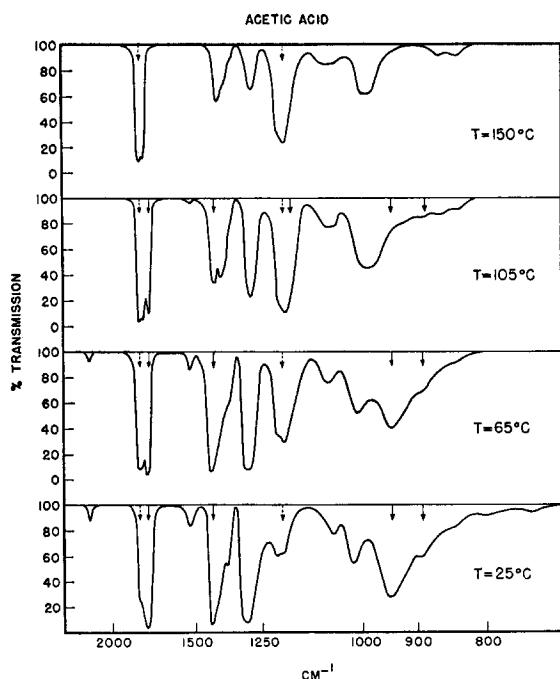[10] H. W. Thompson and P. Torkington, J. Chem. Soc. 640 (1945).

FIG. 2. The infrared spectra of acetic acid vapor at the temperatures shown. Full arrows indicate dimeric bands, broken arrows monomeric bands.
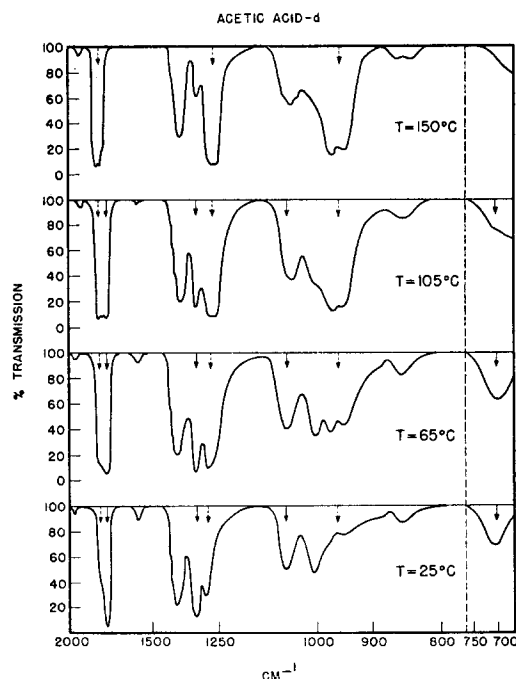

FIG. 3. The infrared spectra of acetic acid-d vapor at the temperatures shown. Full arrows indicate dimeric bands, broken arrows monomeric bands.

major effect in those frequencies associated with the carboxyl group and C—C stretching. Five frequencies in the 1800–700 cm^{-1} region of acetic acid dimer, and four in acetic acid-d dimer are observed to be temperature dependent.

In acetic acid, very strong bands at 1752, 1434, 946, and 1299 cm^{-1} gradually weaken as the temperature is increased, the first three disappearing completely at 150°C, while the latter becomes a medium-strong band at 1279 cm^{-1} in the monomeric acid. This 1279 cm^{-1} band is assumed to be a real band in the monomeric spectrum, since it is unlikely that, if the type B$_{3u}$ C=O band (assuming point group V_h for the dimer), normally the strongest in the spectrum, has completely disappeared, any other dimer bands would remain even as weak bands, let alone as a medium-strong band. Further, the change in frequency of this band in going from the dimer to the monomer is certainly outside the experimental error, and also confirms its "reality" in the monomer spectrum. A fifth band in acetic acid dimer at 895 cm^{-1} also disappears at elevated temperatures.

In acetic acid-d, very strong bands at 1731 and 1329 cm^{-1} and moderately strong bands at 1067 and 703 cm^{-1}, decrease in intensity with increasing tempera-

ture and can therefore be assigned to the dimer, the best assignment, consistent with these results, being that of Hadži and Sheppard,[8] when assuming point group V_h for the dimer, the bands at 1731 and 1329 cm^{-1} are assigned to the type B$_{3u}$ and B$_{2u}$ C—O stretchings respectively, and the bands at 1067 and 703 cm^{-1} are assigned to the inplane and out of plane OD bendings respectively.

Corresponding assignments follow in acetic acid dimer, with the exception of the type B$_{2u}$ C—O stretching and the inplane OH bending modes. Both of these vibrations should give rise to bands in the 1300–1400 cm^{-1} region, but, due to coupling, the frequencies are displaced to 1299 and 1434 cm^{-1}. The remaining band in acetic acid dimer at 895 cm^{-1} is assigned to type B$_{2u}$ C—C stretching vibration, coincident with the type Ag mode[11] as may be expected.

ACKNOWLEDGMENTS

[11] J. T. Edsall, J. Chem. Phys. 5, 508 (1937).