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We shall conclude with a preliminary calculation of $[m_{\sigma h}]$ for a right-handed α helix,[2] with saturated side-chains. The configurations of these macromolecules are well suited to the present treatment, since the main absorbing system lies in a plane, parallel to the screw axis, and the vector e_σ has a favorable orientation. For simplicity, we confine our attention to the first strong system $(N \rightarrow V_1 \equiv \psi_0 \rightarrow \psi_\sigma)$ of the peptide group, whose maximum lies near 1850 A. We shall deal with these bands as if they were simple since, although they overlap the $n_0 \rightarrow \pi^*$ bands, they will only interact rather weakly with the latter. The oscillator strength of the $N \rightarrow V_1$ bands was found to be about $f = 0.237$.[16] The direction of the transition moment of this system has been investigated using flakes of myristamide $(C_{13}H_{27}CONH_2)$ by Peterson and Simpson,[17] who found that they were unable experimentally to distinguish between two possible orientations of the dipole. Translated in terms of the known geometry of a right-handed α helix, these two possibilities give

$$e_{\sigma t} e_{\sigma v} = -0.49, \ -0.23,$$

respectively. On theoretical grounds, the former is the more likely.[17] In both cases, the distance of the partial optic axis from the screw axis is about 1.6 A, which we take to be the value of ρ. $\Delta \nu_\sigma$ was estimated rather crudely to lie in the neighborhood of -1500 cm^{-1}. The calculations could be refined if the problem turns out to be of some practical importance. Taking an average value of -0.36 for $e_{\sigma t} e_{\sigma v}$, we now find that $[m_{\sigma h}]$, the partial rotation due to the specifically helical contribution of the first band, is of order $-150°$ at 5000 A. Between 5000 and 3000 A, owing to its abnormal frequency dependence, $[m_{\sigma h}]$ increases twice as fast as a partial rotation with the same band origin showing normal dispersion. We see that, even in the visible, $[m_{\sigma h}]$ should be important. Too little is known about such systems, however, to be able to tell what fraction of the observed rotation in the visible is attributable to this term.

In cases like desoxyribose nucleic acid,[3] where the absorbing groups are planar systems nearly normal to the screw axis, the term $e_{\sigma t} e_{\sigma v}$ will be very small. Moreover, its sign would be difficult to determine. No calculations are therefore offered for this helical system.

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The infrared spectrum of formic acid vapor at 150°C has been studied over the 1800–1250 cm^{-1} region. A vibrational assignment has been made for monomeric formic acid and the anomalous frequency shifts in the three deuterated isotopic acids explained on this assignment by considering vibrational interaction.

I. INTRODUCTION

THOUGH monomeric formic acid and its deuterium derivatives have been the subject of numerous infrared investigations[1-5] only two assignments of the vibrational frequencies have been attempted,[5,6] neither appearing to give a completely satisfactory explanation of all the available experimental data.

It is hoped, in this paper, to present a consistent assignment of the frequencies for the class A' vibrations of monomeric formic acid and to explain the observed frequency shifts in the deuterium substituted acids on this assignment.

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[1] L. G. Bonner and R. Hofstadter, J. Chem. Phys. 6, 531 (1938).
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[3] R. C. Herman and V. Z. Williams, J. Chem. Phys. 8, 447 (1940).
[4] V. Z. Williams, J. Chem. Phys. 15, 232, 243 (1947).
[5] W. J. Orville-Thomas, Discussions Faraday Soc. 9, 339 (1950).
[6] L. M. Sverdlov, Doklady Akad. Nauk S.S.S.R. 91, 503 (1953).

II. EXPERIMENTAL

As Williams' frequencies for monomeric formic acid were obtained with a grating spectrometer,[4] it is unlikely that they would be improved upon and, accordingly, the infrared spectrum of formic acid was only run over the 1800–1250 cm^{-1} region where the literature was doubtful.

Redistilled anhydrous formic acid, prepared by the action of dry hydrogen sulfide on recrystallized lead formate at 100°C, was examined in the vapor phase at 150°C using a 10 cm vapor path and a Beckman IR-2 spectrometer (used in conjunction with a Brown pen recorder) equipped with sodium chloride optics. Three bands were observed in the region under investigation at 1783, 1392, and 1332 cm^{-1} (see Fig. 1).

III. ASSIGNMENT OF THE FREQUENCIES FOR FORMIC ACID

The assignment proposed here for formic acid is given in Table I together with the assignments for the

TABLE I. Fundamental frequencies for HCOOH
and its deuterium derivatives.

		HCOOH	DCOOH	HCOOD	DCOOD
A'	ν_{O-H}	3567	3567	2632	2632
	ν_{C-H}	2943	2220	2948	2232
	$\nu_{C=O}$	1783[a]	...	1770	...
	δ_{HCO}	1392[a]	970	...	1040
	ν_{C-O}	1200	1206[c]	1178	1171
	δ_{COH}	1105	1143	972	945
	δ_{OCO}	658[b]	678[c]	667[d]	...
A''	δ_{C-H}	1033	...	1007	872
	δ_{O-H}	(232)[e]	...	...	...

[a] Reported here.
[b] Reported by Bonner and Hofstadter (reference 1).
[c] Reported by Herman and Williams (reference 3).
[d] Reported by Hofstadter (reference 2).
[e] Observed in the Raman spectrum by Bonner and Kirby-Smith (reference 12).

deuterated acids, Williams' grating values being used unless otherwise indicated.

Of the class A' vibrations, the O—H, C—H, and C=O stretching frequencies present no difficulty and can be assigned to bands at 3567, 2943, and 1783 cm^{-1}, respectively. The HCO bending mode is associated with the band at 1392 cm^{-1} by analogy with Fonteyne's assignment of a band at 1386 cm^{-1} in the formate ion to this mode,[7] and the assignment of a band at 1350 cm^{-1} in acetaldehyde[8] also to the HCO bending. The band at 658 cm^{-1} is assigned to the OCO bending vibration by analogy with the OCO bending frequencies in the formate[7] and acetate[9] ions at 775 and 658 cm^{-1}, respectively.

The remaining two A' vibrations, corresponding to the C—O stretching and COH bending, are essentially associated with the two bands at 1200 cm^{-1} and 1105 cm^{-1}, respectively, although the two vibrations may be interacting to a small extent. The higher frequency was associated with the C—O stretching for two reasons:

1. the homologous series of alkyl formates all have a band around 1185 cm^{-1} which apparently arises from the C—O stretching vibration of the formate group[10]

2. from a study of monomeric acetic acid and acetic acid-d, it is found[11] that the C—O stretching frequency occurs at 1279 and 1272 cm^{-1} in the two acids, respectively, while the COH bending frequency occurs at 1192 cm^{-1} in acetic acid. On the present assignment for formic acid, this change in corresponding frequencies in acetic acid is easily explained by an increased C—O force constant in the latter, due to the inductive effect of the methyl group, the effect of which is to increase the COH bending constant and hence increase the COH frequency.

[7] R. Fonteyne, Natuurw. Tijdschr. (Belg.) 25, 173 (1943).
[8] K. S. Pitzer and W. Weltner Jr., J. Am. Chem. Soc. 71, 2842 (1949).
[9] J. K. Wilmshurst, J. Chem. Phys. 23, 2463 (1955).
[10] H. W. Thompson and P. Torkington, J. Chem. Soc. 1945, 640.
[11] J. K. Wilmshurst (to be published).
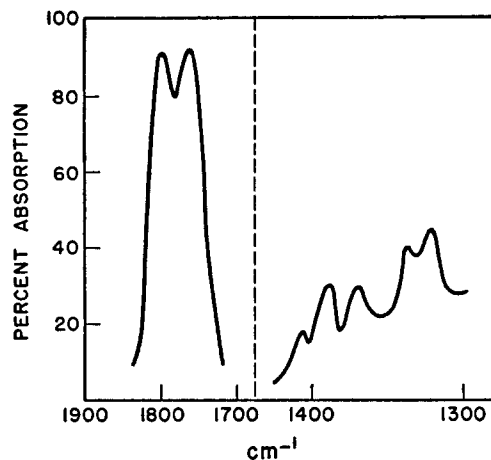
FIG. 1. The infrared spectrum of formic acid vapor in a 10 cm cell at 150°C over the 1850–1300 cm^{-1} region.

Of the class A'' vibrations, the band at 1033 cm^{-1} can be assigned immediately to the C—H bending vibration on analogy with sodium formate,[7] while the OH bending would be expected to occur at a low frequency ($\sim$250 cm^{-1}) and may possibly be associated with the Raman band[12] at 232 cm^{-1}.

The third band at 1332 cm^{-1} observed in the present experimental investigation is assigned to the overtone of ν_{OCO} ($2\times658=1316$ cm^{-1}).

IV. EXPLANATION OF THE FREQUENCY SHIFTS IN THE ISOTOPIC ACIDS

With the present assignment it is now possible to explain the observed frequency shifts in the isotopic acids and as an aid in doing this a line diagram (Fig. 2) has been drawn giving the observed bands for the four isotopic acids in the 1400–900 cm^{-1} region and the bands that would be expected if there was no interaction between vibrations.

It has already been mentioned that in HCOOH ν_{C-O} and δ_{COH} are considered to be interacting slightly, increasing the former and lowering the latter from their expected unperturbed frequencies by a few wave numbers. On deuteration of formic acid to give DCOOH both ν_{C-O} and δ_{COH} would be expected to remain constant or decrease very slightly, while δ_{HCO} would be expected to drop to $\sim$1040 cm^{-1} giving a frequency ratio of 1.34 (see δ_{HCO} for[7] HCO$_2^-$/DCO$_2^-$ 1.35; δ_{HCCl} for[13] HCCl$_3$/DCCl$_3$ 1.33). It is found, however, that both ν_{C-O} and δ_{COH} increase ($\Delta\nu=6$ cm^{-1} and 38 cm^{-1}, respectively), while δ_{HCO} has dropped well below the expected value to 970 cm^{-1}, giving a frequency ratio of 1.44($>\sqrt{2}$). This is explained by considering interaction between δ_{DCO} and δ_{COH}, the effect being to

[12] L. G. Bonner and J. S. Kirby-Smith, Phys. Rev. 57, 1078A (1940).
[13] G. Herzberg, Molecular Spectra and Molecular Structure (D. Van Nostrand Company, Inc., New York, 1945), Vol. 2, Table 86, p. 316.
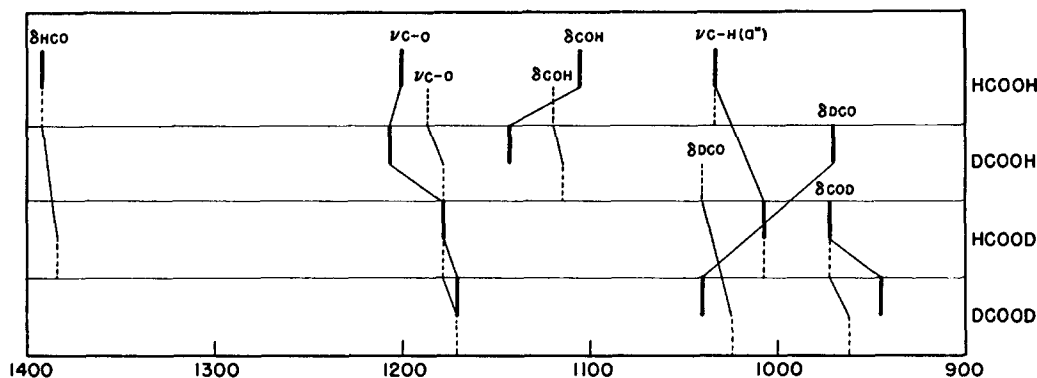
FIG. 2. A line diagram for formic acid and its three deuterium derivatives over the region 1400–900 cm⁻¹. The full lines are observed frequencies and the broken lines expected frequencies if there was no vibrational interaction.

lower the former and raise the latter frequency from their expected positions. The increased COH bending frequency now interacts a little more strongly with ν_{C-O} raising the latter frequency and causing δ_{COH} to drop again.

In HCOOD the effect of the COH bending vibration on the C−O stretching has been removed and both frequencies occur at their expected positions. Again, in DCOOD ν_{C-O} occurs at its expected position, while δ_{HCO} has dropped to 1040 cm⁻¹ and δ_{COD} decreased to 945 cm⁻¹. This decrease in δ_{COD} from HCOOD to DCOOD is a little larger than expected (27 cm⁻¹) and may indicate some small interactions between δ_{DCO} and δ_{COD}, which would not be unexpected.

V. COMPARISON OF THE PRESENT ASSIGNMENT WITH PREVIOUS ASSIGNMENTS

The present assignment for the class A' vibrations of HCOOH differs from that of Thomas[5] in the assignment of the HCO bending frequency,† and from that of Thomas[5] and Sverdlov[6] in the reversal of the assignment for ν_{C-O} and δ_{COH}. The A' assignments of DCOOH also differ from Sverdlov in the reversal of ν_{C-O} and δ_{COH}, but the assignments for HCOOD and DCOOD are essentially identical.

Thomas, who first suggested the interaction between ν_{C-O} and δ_{COH} in formic acid in a private communication, assumed the unperturbed positions of both ν_{C-O} and δ_{COH} to be at 1178 cm⁻¹, the position of ν_{C-O} in HCOOD, and the interaction to be such that ν_{C-O} decreased to 1105 cm⁻¹ and δ_{COH} increased to 1200 cm⁻¹. However, if the unperturbed position of ν_{C-O} is at 1178 cm⁻¹, then for any interaction between δ_{COH} and ν_{C-O} in formic acid to lower ν_{C-O} to 1105 cm⁻¹,

† Thomas assigned a frequency at 1033 cm⁻¹ in formic acid and 1069 cm⁻¹ in sodium formate to the A' HCO bending mode.

the COH bending frequency must increase to around 1250 cm⁻¹, in the case that both ν_{C-O} and δ_{COH} have identical unperturbed frequencies, or higher if their unperturbed frequencies are not identical. Actually δ_{COH} occurs at 1200 cm⁻¹. Again, if the band at 1105 cm⁻¹ in HCOOH was the perturbed position of ν_{C-O}, the perturbation arising from interaction with δ_{COH} which accordingly increases to 1200 cm⁻¹, then, the highest value the unperturbed C−O frequency can have is $\frac{1}{2}(1105+1200)=1153$ cm⁻¹, a value which does not lead to any satisfactory explanation of the observed frequency shifts in the isotopic acids. Thus, the present assignment for formic acid, allowing an easy explanation of the frequencies in the isotopic acids, is to be preferred to the assignments of Thomas and Sverdlov.

Another argument favoring the present assignment to that of Sverdlov is obtained by consideration of the relation between ν_{C-O} and δ_{COH} in formic and acetic acids. On the present assignment both ν_{C-O} and δ_{COH} increase by approximately the same amount in going from formic to acetic acid, whereas on Sverdlov's assignment, assuming identical unperturbed frequencies at 1178 cm⁻¹ for both ν_{C-O} and δ_{COH} in formic acid the former frequency increases by 101 cm⁻¹ while the latter frequency only increases by 14 cm⁻¹ which seems most unlikely.

Thus it appears that the present assignment gives a satisfactory explanation of all the experimental data for formic acid and its deuterium derivatives.