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A theoretical assignment of the fundamental absorption bands in the infrared spectrum of *cis*–HCOOH following a normal coordinate analysis of the vibrations of the conformer

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ABSTRACT

The nine fundamental vibrational frequencies of *cis* – HCOOH which were identified in the infrared have, for the first time, been assigned on the basis of normal coordinate calculations. Significant differences between the assignments in this paper and previous assignments, especially in the 500 – 1100 cm^{-1} region are noted. The bands at 1760, 2207, 1108, 980, 661 and 503 cm^{-1} have all been reassigned.

INTRODUCTION

Even before Pettersson *et al* [1] published their recent work on the compound, Hisatsune and Heicklen [2] had assigned the infrared absorption bands of *cis* – HCOOH, apparently, on the basis of only two transient bands. And in more recent measurements and normal coordinate analyses [3] of the vibrational frequencies of formic acid, lack of experimental frequencies has continued to detract confidence from the results of such analyses. Availability of isotopic frequency, as in the work of Redington [4], does not help in the assignments of the vibrational frequencies of the *cis* – isomer, so long as that isomer could not be identified.

As Mika Pettersson et al remarked, the positive identification of *cis* – HCOOH has been difficult even at low temperatures until they carried out their measurements of the ir – spectra in solid Argon matrix. We have taken advantage of the availability of experimental vibrational frequencies from their work to revisit the normal coordinate analysis of the vibrational spectrum of *cis* – HCOOH. A full report of our analysis will be published later. Here we give the band assignments.

Force constants and experimental frequencies

The F –matrix for formic acid (HCOOH) breaks down into two blocks – the 7 x 7 block of $a^{/}$ symmetry and the 2 x 2 block of $a^{//}$ symmetry, with 28 matrix elements for the former and 3 matrix elements for the latter. This breakdown is, of course, under C_s point group symmetry. Furthermore, there is a total of 31 inde- pendent symmetry force constants required. Redington, in his calculations, used the full 28 independent symmetry force constants for the $a^{//}$ block and the 3 force constants for the $a^{//}$ block. However, these experimental frequencies are significantly different from those reported for the *cis* – isomer as is easily seen in Table 1. In our own calculations, two interaction force constants namely, that between ν (C = O) and ν (O – H), and another one between ν (C = O) and δ (C – O – H) were arbitrarily set to zero to give a total of 26 symmetry force constants in the a' block.

It has to be remembered that there can be no more than 9– fundamentals, and so the uniqueness of our force constants cannot be guaranteed. Isotopic substitution, although limited to four independent substitutions, gives sufficient frequency data to check the force constants.

As valuable as isotopic substitutions might be, Redington has pointed out some of its complications and suggested possible harmonic interactions, including resonance interactions, especially in the deuterated compounds. These interactions may render isotopic substitution within a harmonic approximation for the force field of limited value in checking force constants.

Assignments

Pettersson *et al* [1] observed the fundamental bands at 1108, 980, 661 and 503 cm^{-1} in lower frequency region although the 980cm^{-1} band was, in fact, not among the fundamental bands as they assigned it to an overtone mode as shown in Table 1. However, these are the bands we shall be concerned with in this

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Table 1: Assignments of the infrared bands of *cis* - HCOOH

Band Peak Positions[1] cm^{-1}	Assignment [2]	
	(a)	(b)
3168 (3569.4)	ν_1 (a'): ν (O – H)	ν_1 (a'): ν (O – H)
2899 (2937.8)	ν_2 (a') ν (C – H)	ν_2 (a') ν (C – H)
2760	$2\nu_4$ (a') or ν_3 (a') + ν_8 (a'')	ν_8 (a'') + $2\nu_9$ (a'')
2207	$2\nu_6$ (a')	ν_5 (a') + $2\nu_9$ (a'')
1808(1773.9)	ν_3 (a'): ν (C = O)	ν_3 (a') ν (C = O)
1396(1379.7)	ν_4 (a'): ρ (C – H)	ν_4 (a') ρ (C – H)
1244(1217.6)	ν_5 (a'): ν (C - O)	ν_5 (a'): CO – COH def
1108(1102.8)	ν_7 (a'): ν (C - O) + δ (C – O – H)	ν_6 (a'): COH – CO def
980	ν_9 (a''): τ (HCOOH)	$2\nu_9$ (a'')
661(625.9)	ν_8 (a''): ω (COO)	ν_7 (a'): OCO Scissors
503(637.6)	ν_6 (a'): δ (COO) + ν (C = O)	ν_9 (a''): τ COH

Note:
1. Figures in brackets are Redington's results and the others are those of Pettersson *et. al*.
2. (a) Are our assignments based on normal mode analysis of the results of Pettersson et al. and (b) are the published assignments in Pettersson et al. paper (1). ν: stretch; δ bend; ω: out of plane bending; ρ: rocking; τ torsion; π

paper. We have presented our own assignments alongside those in Pettersson's paper. As can be seen in the table, there is a complete revision of assignment from 1108 cm^{-1} to the 503 cm^{-1}-absorption band. Even the assignments of two bands at 2760 and 2207 cm^{-1} have been revised.

The revisions in the assignments that our normal coordinate analysis has suggested are, in general difficult to verify. However, our results agree with high level ab-initio calculations of the harmonic frequencies (5) for the ν_1 to ν_5 modes and disagree for the rest of the modes. These disagreements stand out most clearly in the assignments of the 980 cm^{-1} band. In the theoretical work referred to, this band is not even listed as one of the fundamentals. Moreover, our assignments predict a blue-shift of the torsional mode ν'_9 from the *trans*- to the *cis*-isomer whereas Pettersson *et al*'s assignment and the ab-initio calculations predict a red shift for the isomeric change. To complicate matters, for the higher frequency absorption where our normal coordinate analysis agree with the result of the ab-initio calculations, the agreement of the ab-initio calculated frequencies themselves with the experimental frequencies is not as good as that for the lower frequency results.

The comments above raise the issue of the sensitivity of the frequencies to the force constants used in the normal mode calculations for the *cis* – isomers. This is an open question at the moment.

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