following the appearance of developed 2,4-dinitrodiphenyl ether at the appropriate wavelength. In the case of the other halogen derivatives kinetic experiments (second-order conditions) were carried out in the presence of an excess of free phenol, concentration of which ranged from 7×10^{-2} to 3.0×10^{-1} M. The same experimental procedure describe by Liotta and Karelits[10] was adopted.

Reaction of 2,4-Dinitrobromobenzene with N_3^-. Kinetic experiments were carried out exactly following the experimental procedure described by Parker.[13]

Reactions of 2,4-Dinitrofluorobenzene with Piperidine. Kinetic runs were carried out by following the appearance of the substitution product at appropriate wavelength. Pseudo-first-order conditions in the presence of an appropriate excess of the corresponding ammonium salt were adopted.

All experimental rate constants reported from the work represent averaged values of 3–4 single determinations.

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(21) Electronic properties of nucleofugic groups can show a strong influence[24] on α_x parameter of eq 3, when they markedly influence the magnitude of a positive charge at reaction center.[26] Since in the 2,4-dinitrobenzene series this positive charge is mainly induced by the presence of nitro groups in ortho and para positions with respect to the electrophilic atom, the above assumption seems to be correct. This assumption is also supported by the finding that when the electron-withdrawing character only of the nucleofugic group is being varied in a sequence of 2,4-dinitrophenyl *z*'-phenyl ethers, the Hammett's values for the more basic MeO^- and the less basic MeS^- are almost the same.

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Selective Deuteration in Neutron-Scattering Spectroscopy: Formic Acid and Deuterated Derivatives

C. V. Berney*[1a] and J. W. White[1b]

Contribution from the Department of Nuclear Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and the Institut Laue-Langevin, Grenoble, France. *Received March 28, 1977*

Abstract: The usefulness of selective deuteration as a technique for clarifying vibrational assignments in hydrogenous molecules is demonstrated by contrasting the inelastic neutron-scattering spectra of solid formic acid (HCOOH) and the deuterated derivatives HCOOD and DCOOH. Since the intensity of observed peaks depends on the vibrational motion of ^{1}H nuclei, deuteration at a given site virtually eliminates corresponding spectral features, permitting their unambiguous assignment. In particular, an intense peak around 250 cm^{-1} in the HCOOH and HCOOD spectra is greatly weakened in the DCOOH spectrum, indicating C–H involvement. The peak is thus assigned as a librational motion about an axis approximating the molecular A axis. Other features are discussed, and detailed assignments are made in accordance with previous infrared and Raman measurements and with normal-coordinate calculations.

Introduction

Inelastic neutron scattering (INS) spectroscopy is a uniquely useful tool for studying the vibrations of hydrogen-containing molecules due to the fact that the proton has an incoherent neutron-scattering cross section larger than that of any other nucleus, and an order of magnitude larger than most.[2] The intensity of a given vibrational peak in an INS spectrum is proportional to the sum over all nuclei of the scattering cross section times the square of the vibrational amplitude. The combined effects of light mass and high cross section for ^{1}H mean that hydrogen motions will dominate the spectrum, producing intense peaks for vibrational modes directly involving ^{1}H nuclei. If deuterium is substituted for hydrogen at a specific site in the molecule, the corresponding vibrations will be greatly reduced in intensity; thus selective deuteration in neutron scattering offers a means of unambiguously assigning hydrogen vibrations.[3,4] Formic acid (HCOOH) has two chemically distinct hydrogen sites—the aldehydic (C–H) and the carboxylic (O–H)—and so is one of the simplest compounds on which selective deuteration may be practiced. For that reason, and because of the intrinsic interest of the dynamics of hydrogen-bonded systems, we have undertaken an INS study of solid formic acid and the deuterated species HCOOD and DCOOH.

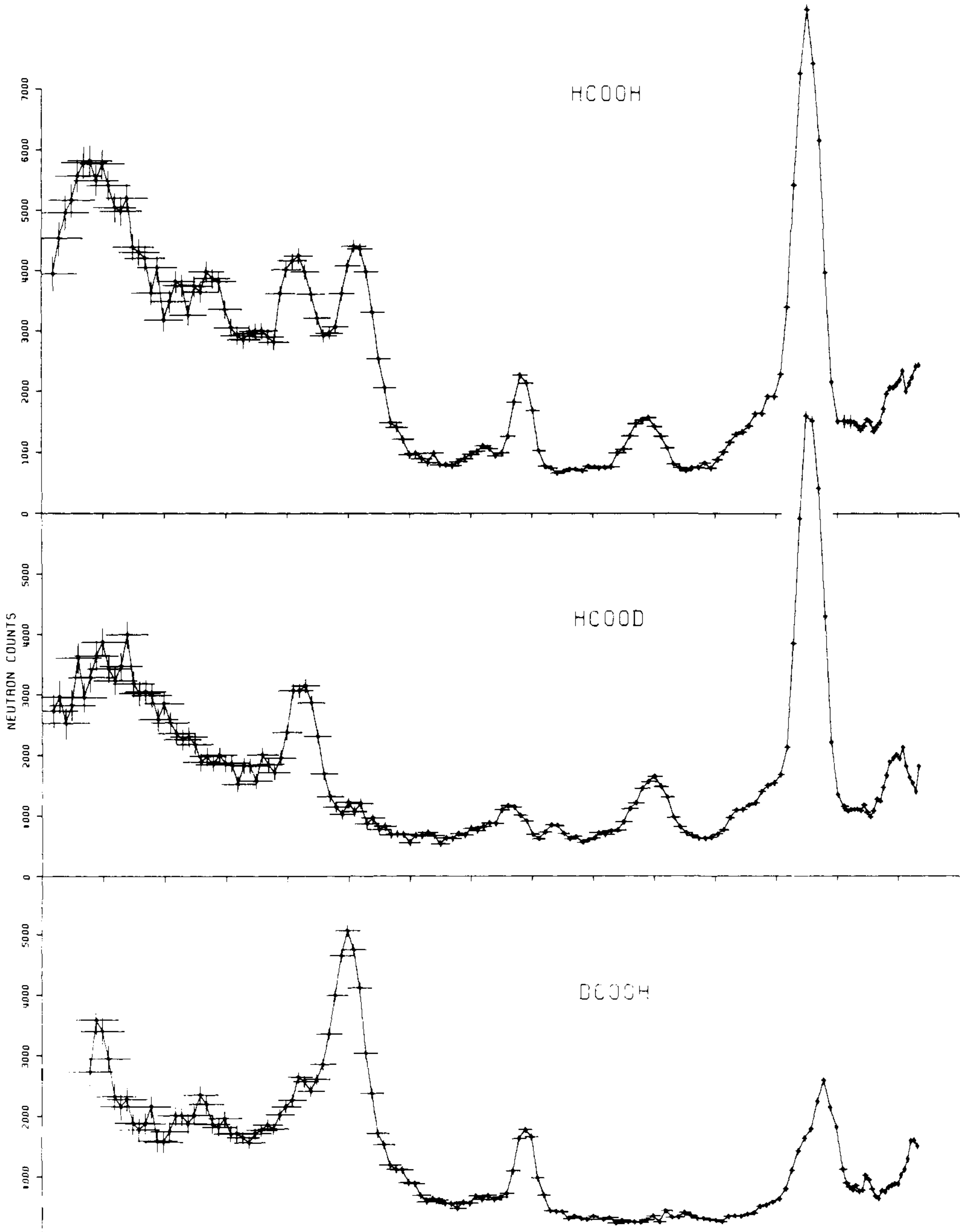

Figure 1. Neutron-scattering spectra of HCOOH, HCOOD, and DCOOH (~77 K). Vertical bars represent one standard deviation above and below the data point; horizontal bars represent spectrometer resolution. The ordinate corresponds to scattered neutron counts per 10^6 monitor counts.

Experimental Section

The spectra were taken on the beryllium-filter spectrometer at the PLUTO reactor at Harwell,[5] the same instrument used in Collins and Haywood's study of carboxylic acids.[6] Samples of HCOOH, HCOOD, and DCOOH were obtained from commercial sources; specified isotopic purity for the deuterated samples was 98%. They were vacuum-distilled from anhydrous $CuSO_4$ directly into quartz sample cells about 6 × 6 cm with a sample thickness of 1 mm. The cells were sealed off after filling, so the samples had no contact with air. The solid was obtained by cooling the liquid to ~77 K; thus, the β form of the solid[7] was obtained. This form has an orthorhombic unit cell, space group *Pna*, with four monomers arranged in two hydrogen-bonded chains.[8] The incoming neutron beam was made monochromatic by reflection from the (511), (311), and (111) planes of a single crystal of aluminum. The energy-transfer regions covered by these planes are 1500–600, 600–190, and 190–66 cm^{-1}, respectively.

Results

Figure 1 shows strikingly the extent to which the INS spectrum of HCOOH can be regarded as the sum of the spectra due to HCOOD and DCOOH—that is, the extent to which the major peaks may be attributed to specific vibrations involving the chemically distinct ^1H nuclei. Conversely, the selective deuteration employed gives direct visual evidence of whether a given peak is due to motion of the C-H or O-H portion of the molecule. In particular, it is obvious that vibrations around 1100 and 250 cm^{-1} involve the C-H bond, while the feature around 1000 cm^{-1} is due to O-H motion.

Infrared[9,11] and Raman spectra,[10] and normal coordinate calculations,[11] are available for the β form of crystalline formic acid and deuterated derivatives. These results were used in the interpretation of the INS spectra given below.

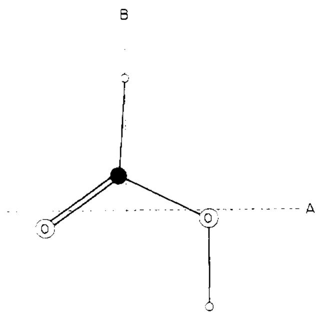

Figure 2. Formic acid monomer with inertial axes A and B (the C axis is perpendicular to the molecular plane).

1500–1300 cm^{-1}. This region suffers from experimental difficulties due to the small Bragg angle of the monochromator and the low neutron flux at this energy. The first condition leads to poor resolution (HWHM = 30–40 cm^{-1}) and the second to relatively poor statistics. In addition, multiphonon effects tend to build up the background at higher frequencies. The infrared studies[9] and normal-coordinate calculations[9,11] indicate that the C–H and O–H deformations occur in this region, giving rise to the relatively intense peaks around 1400 and 1360 cm^{-1}.

1300–1100 cm^{-1}. The peak occurring around 1230–1240 cm^{-1} in HCOOH and DCOOH (but missing in HCOOD) may be attributed[9,11] to modes involving a high proportion of C–O stretching. The acid proton is secondarily involved, being carried along with the motion of the carboxyl O atom. This leads to peaks which are observable, but not so intense as those in which the proton is primarily involved. It is well known that normal modes in carboxylic acids involve considerable mixing of the O–H deformation and the C–O stretch. The fact that the peaks around 1400 cm^{-1} are more intense than those around 1240 cm^{-1} gives direct evidence that the higher-frequency modes involve a greater proportion of O–H deformation.

1100–900 cm^{-1}. In this region the HCOOH spectrum displays two major peaks at 1080 and 991 cm^{-1}; they are easily assigned[9,11] as the out-of-plane C–H deformation and the O–H torsion. The virtual elimination of one of these peaks in each of the deuterated compounds illustrates the power of this technique in verifying assignments.

900–600 cm^{-1}. A peak of medium intensity occurs just above 700 cm^{-1} in the spectra of HCOOH and DCOOH. From previous work[9,11] it can be assigned as the O=C–O deformation (the scissors mode). As in the case of the C–O stretch around 1240 cm^{-1}, the acid proton is secondarily involved. The aldehydic proton is secondarily involved as well, since the carbon moves during the deformation, so the feature is not entirely absent from the HCOOD spectrum.

Table I. Neutron-Scattering Spectra of Formic Acid and Deuterated Derivatives, Giving Energy Transfer Values (cm^{-1}) and Intensities of Observed Peaks. Normal Modes Numbered as in Mikawa, Brasch, and Jakobsen[9]

HCOOH	HCOOD	DCOOH	Assignments
~1420 m	~1400 m		ν_4,ν_{14} (C–H def)
1360 m	1360 m	1411 mw	ν_5,ν_{15} (O–H def)
~1230 m		1241 w	ν_6,ν_{16} (C–O str)
1080 s	1075 s	1080 vw	ν_{21},ν_{26} (C–H out-of-plane def)
991 s		1001 s	ν_{22},ν_{27} (O–H torsion)
718 m	740 mw	709 m	ν_7,ν_{17} (O=C–O def)
	663 w		
510 m	500 m		$2\nu_{28}$ (overtone of libration)
251 vs	246 vs	260 sh	ν_{28} (~A-axis libration)
		220 ms	ν_8 (~C-axis libration)
151 w	156 vw	151 w	ν_{19} (O . . . H str)
113 w	103 w		ν_{24} (out-of-plane libration)
92 w	92 w		
		73 w	ν_{29} (out-of-plane libration)

600–66 cm^{-1}. The previous studies[9,11] indicate that the O=C–O deformation is the lowest-lying of the internal modes, so all remaining features must be due to lattice modes. For descriptive purposes, these can be divided into translations and librations. The division is rigorous if the crystal structure has a center of symmetry; however, under space group *Pna* the description is approximate. In HCOOH and HCOOD this region (indeed, the entire spectrum) is dominated by an intense feature around 250 cm^{-1}. The corresponding peak in the DCOOH spectrum is reduced in intensity by a factor of 3. There are several phonon branches in this region (Mikawa et al.[9] observed infrared peaks at 271 and 232 cm^{-1} in HCOOH, Blumenfeld and Fast[10] observed Raman peaks at 261 and 247 cm^{-1}), but the fact that the INS intensity is so sensitive to deuteration on the carbon atom implies that most of the scattering is due to a large-amplitude motion of the aldehydic hydrogen, as would occur for libration about an axis such as the inertial axis A (Figure 2). Mikawa et al.[9] have provided diagrams of the normal modes they calculated, and their $\nu_{28}(a_2)$ has the proper form. Tubino and Zerbi[11] calculate zone-center frequencies of 271, 259, and 247 cm^{-1} for ν_{28} in HCOOH, HCOOD, and DCOOH. (These frequencies are not strictly comparable with the energy-transfer values of INS peaks since the latter represent integrations over the Brillouin zone). The in-plane libration ν_8 (with rotation about an axis approximating the C axis of the monomer) may also make a contribution in this region—this would allow us to assign the shoulder around 260 cm^{-1} in the DCOOH spectrum to ν_{28}, and the sharp peak at 220 cm^{-1} to ν_8.

A weak feature around 150 cm^{-1} is better developed in HCOOH and DCOOH than in HCOOD, and may thus be tentatively assigned as $\nu_{19}(b_2)$, the hydrogen-bond stretch. The calculated[9] zone-center frequencies for this mode are 170–177 cm^{-1}. In addition, a complex feature occurs around 100 cm^{-1} in HCOOH and HCOOD, but is missing in DCOOH, implying a large component of C–H motion. The normal-mode calculations[9,11] place three phonon branches in this frequency region (ν_9,ν_{24},ν_{29}); of these possibilities, $\nu_{24}(b_1)$ has the required C–H involvement. In this low-frequency region it may be that interchain modes and interactions become important. They were not included in the simplified (single-chain) model used in the calculations.[9,11] We are currently engaged in efforts to apply Born-von-Kármán techniques to the full unit cell, and to calculate predicted neutron-scattering spectra directly from potential-function models for the solid.

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