HAMA-SD 77-1021

Aust. J. Chem., 1977, **30**, 2591–6

The Effect of Pressure on the Infrared Spectrum of Ammonium Formate: HCO_2NH_4, DCO_2NH_4, HCO_2ND_4, DCO_2ND_4. An Unusual Intermolecular Coupling of Non-identical Vibrations in Phase II

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Abstract

The infrared spectra of the title compounds have been measured over the pressure range 0–42 kbar at 25°C. The phase change at *c.* 12 kbar is accompanied by an increase in the NH stretching frequencies and other well-defined spectral changes. Vibrational coupling in phase II of HCO_2NH_4 between CH in-plane bending in HCO_2^- and a bending motion in NH_4^+, and its counterpart for DCO_2ND_4, account for some unusual frequency changes arising from isotopic substitution in the counter ion. The spectral changes suggest that during the phase change I → II the NH···O hydrogen bonds are weakened and the cations move to positions in close proximity beside the CH bonds.

Introduction

A systematic study by Bridgman[1] showed that solid ammonium formate forms a new modification 'phase II' at high pressure. At 25°C the transition occurs at *c.* 11·8 kbar. A third modification ('phase III') was found[1] only at 75°C and higher temperatures. In later work[2] the I → II transition was found to be accompanied by an entropy change of -9 J mol^{-1} K^{-1} and by a large contraction in volume, viz. by 10·9%. The infrared spectral changes, for HCO_2NH_4, too, were measured[2] but not analysed or reported in detail.

Donaldson *et al.*[3] reported the infrared bands of HCO_2NH_4 (in phase I) which they attributed to the formate moiety. On the strength of spectral resemblances they suggested that it has the same type of crystal structure as sodium formate, the space group of which is known[4] to be C_{2h}^6 (No. 15, $C2/c$), with four molecules in the unit cell (two in the primitive unit cell). However, an X-ray diffraction study[5] of ammonium formate has, since, shown that the space group is actually C_s^2 (No. 7, Pc); there are two molecules in the unit cell (≡ primitive unit cell).

All the atoms lie in general positions. The molecular environments around the two formate oxygen atoms are similar, but not identical. All four NH_4^+ hydrogens form hydrogen bonds, but their lengths differ. The N–O separations, in Å, are: for H1, 2·885; H2, 2·818; H3, 2·808; H4, 2·867. The hydrogen atoms were not located,

[1] Bridgman, P. W., *Proc. Am. Acad. Arts Sci.*, 1938, **72**, 227.
[2] Hamann, S. D., Linton, M., and Pistorius, C. W. F. T., *High Temp.—High Pressures*, 1973, **5**, 575.
[3] Donaldson, J. D., Knifton, J. F., and Ross, S. D., *Spectrochim. Acta*, 1964, **20**, 847.
[4] Zachariasen, W. H., *J. Am. Chem. Soc.*, 1940, **62**, 1011.
[5] Nahringbauer, I., *Acta Crystallogr., Sect. B*, 1968, **24**, 565.

and the NHO angles are thus not available directly. However, the disposition of oxygen atoms around the nitrogen atom approaches a tetrahedral one; four of the six ONO angles are in the range 110–115°. It appears highly probable that the N–H···O constellations, other than that involving H 1, do not depart far from linearity.

Thus, within the crystal environment in phase I, neither the ammonium nor the formate ions possess symmetry elements (other than *I*). The crystal structure of phase II is not known.

In studies of pressure effects on the infrared spectra of the alkali metal formates[6] deuteration greatly aided spectral analysis. To obtain similar clarification of the (necessarily more complicated) spectrum of ammonium formate, *C*- and *N*-deuterated salts have now been studied.

Experimental

Materials

The HCO_2NH_4 was a recrystallized commercial product. DCO_2NH_4 was obtained by quantitative neutralization of DCO_2D (Merck AG, Darmstadt, 99% D) with ammonia in 1 : 9 water–methanol and evaporation to dryness. Treatment with D_2O gave the ND_4^+ salts.

Infrared Spectra

These were measured at pressures of 0, 14, 28 and 42 kbar, with a diamond-anvil high-pressure cell placed in a Perkin–Elmer 521 spectrophotometer as described previously.[2] Two epoxy resin seals attached to the cell protected the (powder) specimens from atmospheric moisture. Frequencies (and frequency shifts on change in pressure) were normally reproducible to within 2 cm^{-1}. No correction was made for instrumental frequency calibration error.[6]

Results and Discussion

The infrared frequencies observed for phases I and II are listed in Table 1. The effect of raising the pressure on the phase II frequencies is also indicated, qualitatively. For the phase I frequencies these effects are usually hard to observe, as the phase change occurs at a low pressure, and a range of pressures is always present within the cell. At 14 kbar the amount of conversion I → II (estimated roughly from the peak intensity of the CD in-plane bending band of DCO_2NH_4) was around 85%. On release of the pressure from 42 kbar to zero the original spectra (with a little loss of band definition) were regenerated; i.e. reconversion to phase I is complete.

For the NH_4 salts band assignments are now straightforward. The nomenclature for the vibrations is that used previously.[6,7] For the *N*-deuterated salts some assignments are uncertain, as three isotopic species were present in appreciable amount. The compositions, estimated roughly, were around 57% ND_4 salt, 34% ND_3H salt and 8% ND_2H_2 salt, corresponding to around 90% overall deuteration.

The Formate Ion Frequencies

No crystal splittings of bands were observed for phase I (in agreement with an earlier report;[3] some of our frequencies, though, differ markedly from those reported[3]). Correlation field splitting into doublets undoubtedly occurs with a space group of C_s^2 and two molecules in the unit cell, but is evidently too small to be seen (in the present

[6] Hamann, S. D., and Spinner, E., *Aust. J. Chem.*, 1977, **30**, 957.
[7] Spinner, E., *J. Chem. Soc. B*, 1967, 879.

spectra). In phase II there is evidence of splitting of the intense and broad carboxylate stretching bands at 1600–1700 cm^{-1} ('CO *st I*') but the other bands remain unsplit.

Table 1. The infrared spectra of HCO_2NH_4, DCO_2NH_4, HCO_2ND_4, and DCO_2ND_4 in phases I and II (3500–2650 cm^{-1}; 1800–630 cm^{-1})

Wavenumbers in cm^{-1}. no, No band observed. Data for phase II apply to pressure of 14 kbar; effect of increase in pressure on frequency: +, raised; (+), slightly raised; *O*, unaffected; (−), slightly lowered. Nomenclature for vibrations as in ref. 6

Vibration	HCO_2NH_4		DCO_2NH_4		HCO_2ND_4		DCO_2ND_4	
	I	II	I	II	I	II	I	II
OCO *sciss*	774	749 (+)	768	742 (+)	774	749 (+)	765	742 (+)
CH (or CD) *op be*	1070	no?	914	908 (+)	[A]	[A]	913	910 (+)
CH (or CD) *ip be*	1370	1478 (+)[B]	1014	1067 (+)	1370	1449 *O*	1014	1059 *O*
CO st II	1347	1349 +	1321	1324 +	1351	1354 +	1323	1329 +
CO st I[C]	1605	1598 +	1605	1600 +	1605	1605 (+)	1610	1610 +
		1632 +[D]		1625 +[D]		1630 +[D]		1625 +[D]
		1685 +[D]		1680 +[D]		1685 +[D]		1685 +[D]
2 × (CH *ip be*)	2712	[A]	[E]	[E]	2712	2915[F]	[E]	[E]
CH st	2810[D]	2798 +	[E]	[E]	2806	2797 +	[E]	[E]
NH (or ND) *be* III[G]	1426	1420 *O*	1423	1424 *O*	1072	1078 *O*[D]	1075	1073 (−)
NH (or ND) *be* II[G]	1454	*c.* 1420[B]	1453	1447 *O*[D]	1098	1088 +	1098	1100 +
NH (or ND) *be* I[G]	1697	[A]	1699	[A]	1270[F]	no	1264[F]	no?
NH st IV[C]	2870	2880 +	2870	2885 +	[E]	[E]	[E]	[E]
NH st III[C]	3010	3015 ?	3005	3015 ?	[E]	[E]	[E]	[E]
NH st II[C]	3075	3085 +	3075	3090 +	[E]	[E]	[E]	[E]
NH st I[C]	3190	3190 *O*	3190	3190 (+)	[E]	[E]	[E]	[E]
ND_3H^+: ND *be* II[H]					1146	1143 *O*[I]	1149	1143 (+)[I]
ND_3H^+: ND *be* I[H]					1215[F]	1236 *O*[F]	1216[F]	1236 +[F]
ND_3H^+: NH *st*					3060[C]	3115 +	3070[C]	3120 (+)
Others			3440[J]		2925[C,K]		2824[L]	2846 +[L]

[A] Band masked by other absorption. [B] Attributed to mixed anionic CH *ip be*/cationic NH *be II* vibrations; see text. [C] Bands broad or very broad; frequencies are approximate. [D] Inflexion; frequency approximate. [E] Diamond cell absorption obscures CD *st* and most of ND *st* regions. [F] Assignment uncertain. [G] *be I* is in-phase double scissoring; *be II* and *be III* are out-of-phase scissoring motions. [H] For the isotopic contaminant ND_3H^+, ND *be I* is probably symmetric bending, and ND *be II* asymmetric bending. [I] Poorly resolved double band. [J] CO *st II*+CD *st* combination band; DCO_2ND_4 also shows this. [K] CO *st I*+CO *st II* combination band. [L] Unassigned.

The phase change lowers the frequencies of CH stretching ('CH *st*'), OCO scissoring ('OCO *sciss*') and out-of-plane bending ('*op be*') but the lower carboxylate stretching frequency ('CO *st II*') is raised, and those of CH and CD in-plane bending ('*ip be*') are raised strongly.

The 'effective Goldschmidt radius' of the ammonium ion in ammonium formate in phase I is 1·4–1·5 Å,* to be compared with radii[8a] of 1·33 Å for K^+ and 1·49 Å for Rb^+. It seems reasonable therefore to compare ammonium formate with the potassium and rubidium salts. In fact, some of the above frequency changes (e.g. that for CH *st*)

* A van der Waals radius of 1·40 Å for oxygen[8b] has been subtracted from the experimental N···O separations[5] (2·81–2·89 Å).

[8] Pauling, L., 'The Nature of the Chemical Bond' 3rd Edn (*a*) p. 518; (*b*) p. 260 (Cornell University Press: Ithaca, New York, 1960).

closely resemble those previously found[6] for the I → II transformation in HCO_2K and DCO_2K; others (e.g. that for OCO *sciss*) resemble those found for HCO_2Rb and DCO_2Rb. It does not appear safe to make deductions concerning the packing of the formate moieties in phase II, more especially as phase II probably has not the same structure for the potassium and the rubidium salt.

In phase II the CH *ip be* frequency appears to be 29 cm^{-1} higher in the NH_4 than in the ND_4 salt. This is a remarkably large difference. For CD *ip be*, too, there is a difference, in the same direction, but smaller, viz. 8 cm^{-1}. In phase I the CH and CD *ip be* frequencies, like the others, are practically unaffected by the isotopic composition of the counter cation. This anomaly in phase II will be discussed more fully below.

The Ammonium Ion Frequencies

In an environment of tetrahedral, cubic, or spherical symmetry, the nine fundamental vibrations of the NH_4^+ ion, of point group T_d, divide[9] into all-in-phase NH stretching (ν_1, species a_1), in-phase double-scissoring (ν_2, e) which is doubly degenerate and out-of-phase NH stretching (ν_3, f_2) and out-of-phase NH double-scissoring (ν_4, f_2) which are both triply degenerate. Only the triply degenerate vibrations are allowed in the infrared spectrum.

In the unsymmetrical environment present in ammonium formate in phase I the degeneracies are all split, at least formally; all-in-phase NH stretching and in-phase double-scissoring are allowed in the infrared, but their absorption intensities are still expected to be low. Vibrational coupling between the two cations in the unit cell doubles the number of frequencies, and, with a factor group of C_s, all are allowed in the infrared (for cations as for anions).

In phase I, the NH_4^+ absorption is complex in the NH *st* region, with probably four separate intense bands (the great band breadths make for some poor band definition). In the in-phase double-scissoring region there is only one, weak, band ('NH *be I*'), but in the out-of-phase scissoring region there are two bands for both NH_4^+ and ND_4^+ ('*be II*' and '*be III*').

The phase change I → II displaces the intensity maximum of the NH *st* system from *c.* 3010 cm^{-1} to *c.* 3090 cm^{-1}; the lower- (though not the upper-) frequency edge of the system, and some individual component bands, are displaced to higher frequencies. The phase change probably does not reduce the complexity of this system (the element of doubt arising from poor band definition, and the presence in all spectra of bands due to some of the unwanted phase).

Of special interest here is the NH *st* absorption which is due to the residual protium in the *N*-deuterated salts. It is simple, originating mostly from the ND_3H^+ ions present (in *c.* 32–36%); only weak wings, due to the small amounts of $ND_2H_2^+$ present, appear in addition to the main, now *un*split, NH *st* band. This is still fairly broad in phase I, but much narrower in phase II (half-bandwidth *c.* 60–70 cm^{-1}; see Fig. 1). This narrowing implies that the four NH bonds in NH_4^+ do not differ greatly in phase II, in respect of the factors that determine the NH *st* frequency. (The band-broadening which results from intermolecular coupling of the NH *st* vibrations

[9] Herzberg, G., 'Molecular Spectra and Molecular Structure, Vol. II. Infrared and Raman Spectra of Polyatomic Molecules' p. 306 (Van Nostrand: New York 1945).

should be small for ND_3H^+ ions that are 'isotopically diluted' with ND_4^+ ions, in phase I as well as II.)

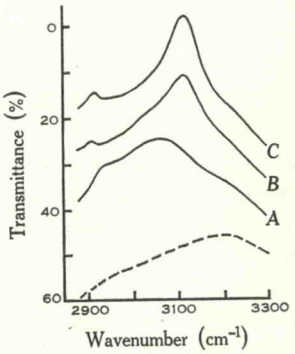


Fig. 1. Pressure-induced changes in the NH stretching band of residual HCO_2ND_3H (*c.* 34%) in HCO_2ND_4 at 25°C. The dashed curve represents the background absorption of the diamond cell. Curve *A* is for phase I at atmospheric pressure and curves *B* and *C* are for phase II at pressures of 14 and 42 kbar, respectively. For the sake of clarity, curve *B* has been shifted vertically by 10%, and curve *C* by 20%, on the transmittance scale.

The phase transition raises the NH *st* frequency of ND_3H^+ by *c.* 50 cm^{-1}. This suggests that the N^+–H···O hydrogen bonds are, on average, somewhat weaker in phase II than in phase I (this may be surmised already from the spectra of the NH_4 salts, but only tentatively, because of the complexity of their NH *st* absorptions; concerning similar complications encountered with other NH_4^+ salts, see Oxton *et al.*[10]).

Corroborative evidence from ND *st* bands, unfortunately, is not available, because these are obscured by diamond absorption bands (ref.[6], Fig. 3*b*).

The effect of the phase change on the out-of-phase scissoring frequencies is not the same in the four salts. For HCO_2NH_4 the two bands (NH *be II* and NH *be III*) are replaced by a single band. For DCO_2NH_4 the two bands become largely merged, but there is a clear inflexion on the high-frequency side, at *c.* 1447 cm^{-1}, which persists over the pressure range 14 kbar to 42 kbar; i.e. the splitting is diminished in phase II but is still present. This applies also to the ND *be* bands of HCO_2ND_4 (an inflexion, now on the low-frequency side, at *c.* 1088 cm^{-1}, persists). For DCO_2ND_4, by contrast, the splitting between the frequencies of ND *be I* and ND *be II* is *greater* in phase II than in phase I (by *c.* 4 cm^{-1} if the 0 kbar and 14 kbar spectra are compared, *c.* 11 cm^{-1} if comparison is made with the 42 kbar spectrum).

These variations result from the fact that, in phase II, the NH and ND *be II* frequencies are affected by the isotopic composition of the counter anion. In phase I, by contrast, these frequencies (*c.* 1454 cm^{-1} in NH_4^+ and *c.* 1098 cm^{-1} in ND_4^+) are practically the same in HCO_2^- and DCO_2^- salt, i.e. in phase I they behave normally (as do the other ammonium frequencies, in phases I and II).

Cause of the Anomalous Dependences of Frequencies on Isotopic Composition of Counter Ion

The anomalies are found for CH and CD in-plane bending and one of the ammonium out-of-phase scissoring vibrations, in NH_4^+ and ND_4^+, in phase II only.

The simplest explanation is intermolecular coupling in phase II between non-identical vibrations, which is appreciable only when their intrinsic frequencies are similar; viz., in HCO_2NH_4, between CH *ip be*, of intrinsic frequency *c.* 1449 cm^{-1}

[10] Oxton, I. A., Knop, O., and Falk, M., *Can. J. Chem.*, 1975, **53**, 2675.

(as in HCO_2ND_4), and NH *be II*, with intrinsic frequency *c.* 1447 cm^{-1} (as in DCO_2NH_4), to give composite vibrations at 1478 cm^{-1} and *c.* 1420 cm^{-1}; and in DCO_2ND_4 between CD *ip be*, intrinsic frequency *c.* 1067 cm^{-1} (as in DCO_2NH_4), and ND *be II*, intrinsic frequency *c.* 1088 cm^{-1} (as in HCO_2ND_4), to give resultant vibrations at 1100 cm^{-1} and 1057 cm^{-1}. In the 'mixed' salts, DCO_2NH_4 and HCO_2ND_4, the (unperturbed) frequencies concerned are well separated, and coupling is inappreciable.

This explanation implies a close spatial proximity of cation by the side of the CH (or CD) bond in phase II; otherwise coupling would still be insubstantial even when the frequencies concerned coincide. The low absorption intensities of the bands concerned, throughout, imply only a weak coupling between the vibrations by dipolar interaction.

An alternative explanation might be sought on the basis of the steric secondary isotope effect of deuterium. There is good (kinetic) evidence[11] that under conditions of strong steric crowding a deuterium is appreciably smaller than a protium atom. Thus, in phase II ND_4^+ could be appreciably smaller than NH_4^+, and the effective CH (and CD) in-plane bending force constant (and hence the frequencies) could therefore be higher in the NH_4 than in the ND_4 salt. However, only the anomalies in the CH and CD *ip be* frequencies are to be explained in this way; those in the NH and ND *be II* frequencies remain unexplained. The steric secondary isotope effect of deuterium appears to be of no more than minor importance in ammonium formate in phase II.

Changes in Relative Dispositions of Ions During the Phase Change

All the spectral results are consistent with the suggestion that the transformation from I to II entails a loss of approximate linearity of the N^+–H···O bonds, and/or an increase in the average N–O separation, while NH bonds move into close proximity at the sides of the CH bonds.

Acknowledgments

We thank Messrs K. G. Carey and D. T. Light for technical assistance.

Manuscript received 30 March 1977

[11] Melander, L., and Carter, R. E., *J. Am. Chem. Soc.*, 1964, **86**, 295; Sherrod, S. A., and Boekelheide, V., *J. Am. Chem. Soc.*, 1972, **94**, 5513; and other work cited in these papers.