Acetamide Hemihydrochloride: a Case of False High Crystallographic Symmetry. Vibrational Spectra of the $^2H_0$ and *NN'O*-$^2H_5$ Derivatives

By **Ernest Spinner**, Medical Chemistry Group, John Curtin School of Medical Research, Australian National University, Canberra, Australia

The i.r. and Raman spectra of the title compounds have been examined. The i.r. spectrum remains highly anomalous after deuteriation. The centre of gravity of the very broad absorption due to hydroxy stretching is *ca.* 920 cm^{-1} for both OH and OD compound. This constancy in frequency is incompatible with a symmetrical O · · · H · · · O bond, and shows that the centrosymmetry found for the $(CH_3CONH_2)_2H^+$ complex by *X*-ray and neutron diffraction is not the true molecular symmetry. Several i.r.–Raman frequency coincidences are found. The stronger Raman bands of $(CH_3CONH_2)_2H^+$ all have counterparts in the Raman spectrum of solid CH_3CONH_2; prominent frequencies of $(CH_3CONH_2)_2H^+$ without good counterparts in CH_3CONH_2 have counterparts in the $CH_3C(OH)=N^+H_2$ spectrum, in agreement with structure (II) for the complex.

ACETAMIDE HEMIHYDROCHLORIDE was one of the first compounds found[1] to exhibit a highly anomalous i.r. spectrum with an intense very broad absorption centred at *ca.* 900 cm^{-1} which is interspersed with some deep transmission windows. It is also one of the earliest reported[2-4] to have an extremely short hydrogen bond, the O · · · O distance, $r(O \cdots O)$, being 2.418(11) Å. Numerous compounds with this type of spectrum, mainly hemi-salts[5-9] $RCO_2^- \cdot HOCOR\ M^+$ (M = metal), but also others,[10-13] have been studied by spectroscopy and by crystallography. Whether the very short apparently symmetrical OHO bonds in many of these compounds actually are symmetrical, and what the shape of the potential energy curve is, have often been matters of special interest. It is established, however, that such highly anomalous spectra (Hadži's[5] ' type ii ') are shown also by some compounds in which the hydrogen bonds are definitely neither symmetrical nor quasi-symmetrical.[10,14-16]

Both an *X*-ray[2,3] and a neutron[4] diffraction study (the latter at −150°) were carried out on $(CH_3CONH_2)_2$-HCl, but the published reports are very brief. The crystal has[2] the space group C^5_{2h} (No. 14; $P2_1/c$), with two $(CH_3CONH_2)_2HCl$ molecules in the unit cell of dimensions *a* 8.22 Å, *b* 8.33 Å, *c* 8.03 Å, β 134°. The Cl atoms and the points midway between closely neighbouring O atoms lie on crystallographic centres of inversion. According to the neutron diffraction results a H atom occupies each O · · · O midpoint. All other atoms lie in general positions. From the angles given it follows that the heavy-atom skeleton in the acetamidic moieties is planar, and so are the CNH_2 portions. No HOC or dihedral angles were recorded,[4] nor were data on intermolecular dispositions. Two N · · · Cl separations are given, 2.232 and 2.280 Å, but these are both extraordinarily low values and need to be treated with caution; the second closest N · · · Cl approach must be in excess of 3 Å if the structure is to fit the cell dimensions given by Hughes and Takei;[2] *cf.* also p. 398.

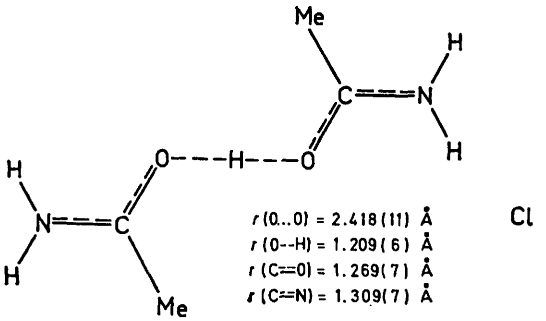
The i.r. spectrum of acetamide hemihydrobromide from 1 800 to 350 cm^{-1} has now been shown to be almost identical with that of the Cl salt, which implies very similar $(MeCONH_2)_2H^+$ geometries; there are also extensive similarities in the Raman spectra. Its structure[17] is only of medium precision, but important intermolecular information is given. The space group is again C^5_{2h} with two molecules in the unit cell, of volume 420 Å^3 (*cf.* 400 Å^3 for the Cl salt). The CCON skeletons lie in planes which subtend only a small angle with the *ac* plane. If the midpoint between O atoms is designated (0, 0, 0) one Br is at $(\frac{1}{2}, \frac{1}{2}, 0)$ [*cf.* the Cl atom shown in (I)], another at $(\frac{1}{2}, 0, \frac{1}{2})$. The molecular conformation in the Br (as in the Cl) salt is as shown in (I) and the long axis of the $(CH_3CONH_2)_2H^+$ complex points in a direction roughly from $(-\frac{1}{2}, 0, -\frac{1}{2})$ to $(+\frac{1}{2}, 0, +\frac{1}{2})$. The two close N · · · Br approaches are both 3.41(8) Å. Though none of the H atoms was located, the CNBr angles suggest[17] a linear NH · · · Br$^-$ hydrogen bond to the Br atom at $(\frac{1}{2}, 0, \frac{1}{2})$, and a nonlinear one to that at $(\frac{1}{2}, \frac{1}{2}, 0)$ [*cf.* the NH · · · Cl bond implied in (I)]. Intramolecular hydrogen bond dimensions are: $r(O \cdots O)$ = 2.48 Å (margin of error not given but presumably *ca.* 0.1 Å), ∠CO · · · O = 112.9° (1.1).

From the symmetry elements present[18] in space group C^5_{2h} it follows that all four N (likewise O, *etc.*) atoms within a unit cell are equivalent, and the $(CH_3CONH_2)_2H^+$ complexes are crystallographically centrosymmetric, in both Br and Cl salt.

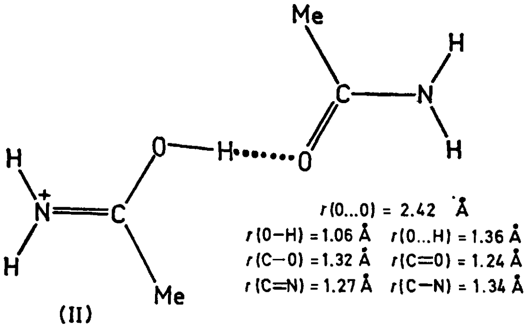
The diffraction results do not[4,17] establish whether this is a genuine molecular symmetry or whether it is the result of averaging over time and space. For a comparable case, potassium hydrogen maleate, with $r(O \cdots O)$ = 2.403 Å, the neutron diffraction data are accommodated equally satisfactorily[19] by a structure in which a proton is at the centre of the O · · · O bond (where its maximum in the diffraction pattern appears) and by one in which it is off-centre by 0.15 Å, *i.e.* with $r(O-H)$ = 1.05 and $r(O \cdots H)$ = 1.35 Å, and with randomness of the $_OH_O$ locations in the crystal. For a detailed discussion of this type of difficulty, see ref. 20.

The *a priori* possibilities for $(CH_3CONH_2)_2HCl$ are structures (I) and (II); (II) and its mirror image would need to be equally abundant in the crystal. {Coplanarity of Cl atom [indicated in (I) only roughly] and NH_2 group is *not* implied, nor is coplanarity of CNH_2 and CCNO skeleton.} The main dimensions that differ are listed beneath each; those for (I) are the neutron diffraction values,[4] those for (II) are expected (predicted) values. In (II) r(O–H) is expected to be 0.11 Å greater than in gaseous H_2O; *cf.* r(F–H) in the unsymmetrical F–H · · · F^- ion present in the *p*-toluidinium salt [21] and in gaseous HF: difference $+0.10_8$ Å. From a literature survey (ref. 22 and other data) most probable values were selected for r(C=O), r(C=N), r(C_{sp^2}–O), and r(C_{sp^2}–N) (variation from compound to compound *ca.* 0.02—0.03 Å).

The main object of this work was to study the structure of the $(CH_3CONH_2)_2H^+$ complex by comparison of OH and OD stretching frequency and by a search for frequency coincidences in i.r. and Raman spectrum. Other matters of interest were (a) the hydrogen bonding to Hal^- (now found to be of only moderate strength in both Cl^- and Br^- salt, in agreement with the N · · · Br distances reported [17]); (b) assignments for the transmission windows and deuteriation effects on them; (c) the O · · · O stretching band (not found).



(I)



(II)

EXPERIMENTAL AND RESULTS

Materials.—Acetamide hemihydrochloride sintered at 125° and had m.p. 131—133° (lit.,[23-25] sinters at 123°; m.p. 131°, 128—135°, 130—131°). Dissolution of $(CH_3CONH_2)_2$-HCl in D_2O and *rapid* evaporation to dryness *in vacuo* (K_2CO_3) gave the *NN′O*-$^2H_5$ derivative. Evaporation to dryness of a solution of specimen and KCl (200 mg) in D_2O, a procedure previously [15] found suitable for obtaining highly deuteriated discs, is not usable with this compound as hydrolysis occurs. The most highly deuteriated disc obtained (Figure 1) had a deuterium-content of *ca.* 90% as estimated from NH and ND (stretching) absorption intensity. Over 80 min (time for a complete spectral scan) the deuterium-content decreased slowly, but visibly. KCl for use in discs was dried *in vacuo* at 210°. Acetamide hemihydrobromide had m.p. 140—142°.

I.r. Spectra (4 000—200 cm^{-1}).—These were measured with a Perkin-Elmer model 621 dual grating spectrophotometer, fitted with a frequency marker accessory, and flushed with dried air. Both ordinary (complete) spectra and spectra with frequency scale expansion (scanned at *ca.* 5 cm^{-1} per min) were taken.

Raman Spectra (40—3 600 cm^{-1}).—These were measured with a JASCO model R-300 grating spectrophotometer fitted with a Coherent Radiation argon ion laser model CR-2SG. Specimens were in sealed glass capillary tubes. The wavelengths used for excitation were 4 880 and 5 145 Å, power range 380—560 mW at laser $\equiv$ 270—400 mW in sample compartment (specimens were chemically stable, over the long scanning times needed to take expanded spectra, at even higher powers). Strong source emission lines, in the range 0—1 100 cm^{-1} with 4 880 Å, and 3 000—3 600 cm^{-1} with 5 145 Å excitation, provided a check on the frequency [26] scale calibration; for inclusion in Figure 2 spectra were chosen so as to be free of these as far as possible; source lines still present are at 77, 266.3, 520.3, and 587.3 cm^{-1}. The nominal spectral slit widths in the caption to Figure 2 apply at 5 000 Å; mechanical (and not spectral) slit widths remained constant during scanning; Raman intensity $\propto$ (slit width) [3].

Spectra in Figure 2.—The specimen of $(CH_3CONH_2)_2HCl$ used consisted of small crystals, and appreciably different spectra were obtained by aligning and focusing on different points in the specimen tube. Crystal orientation effects gave rise to some major variations in relative intensities among neighbouring bands, while other bands which remained unresolved showed peak frequency variations of up to 3 cm^{-1}. Spectra (a) and (b) appear in Figure 2 because of the good resolution achieved, and even though they are not well averaged polycrystal spectra in respect of intensities. The $(CH_3COND_2)_2DCl$ was a powder, and gave a poorer spectrum, but the relative intensities are expected to be a good polycrystal average. It is stressed that in the ranges 60—200 cm^{-1} and 1 350—1 500 cm^{-1} there are no major differences between $^2H_0$ and $^2H_5$ derivative. In these regions spectra very like those in (d) and (e) were obtained several times with $(CH_3CONH_2)_2HCl$.

Range of Present Work and Comparison with Earlier Work.—Albert and Badger [1] reported the spectrum of $(CH_3CONH_2)_2HCl$ to be essentially the same in discs in KCl, KBr, and KI, and in mulls. Paraffin mull spectra showed poor band definition, now as in the earlier [1] work. The spectrum in KBr discs has now been found to be almost identical with that in KCl in the range 1 800—330 cm^{-1}, but at higher frequencies there are differences, in particular the NH stretching frequencies are higher in KBr. Double decomposition of sample with embedding medium [27] results in formation of acetamide hemihydrobromide; the spectrum attributed in ref. 1 to the Cl^- hemi-salt is actually that of the Br^- hemi-salt. This was confirmed with a specimen of genuine hemihydrobromide in KBr.

There are considerable discrepancies between an early photographic Raman spectrum [23] of solid $(CH_3CONH_2)_2HCl$ and that obtained now (there are no bands below 715 cm^{-1} in the old spectrum, and various frequencies differ). These are attributable not to orientation effects but to the difficulty of obtaining solid-state spectra by excitation with mercury lamps.

The Raman spectrum of solid α-acetamide [28] was remeasured. All major acetamide bands have obvious counterparts in the spectra of the hemi-HCl and the hemi-HBr derivatives, and the most intense hemi-salt bands can all be paired with acetamide bands. The more prominent $(CH_3CONH_2)_2HCl$ bands that (at least apparently) cannot are those at 3 011, 2 983, 1 716, 1 478, 1 285, 1 031, 765, and 232 cm^{-1}.

DISCUSSION

The most important finding is that the centre of gravity of the broad intense i.r. hydroxy stretching absorption remains unchanged on *O*-deuteriation, at *ca.* 920 cm^{-1} (Figure 1). Though a precise estimate is difficult, as this absorption is unsymmetrical for the $^2H_5$-hemi-salt, and there is a broad transmission window at 931 cm^{-1}, there is no doubt about the absence of that substantial downward shift of the hydroxy stretching frequency on *O*-deuteriation which would be found if $(CH_3CONH_2)_2HCl$ contained a symmetrical O · · · H · · · O bond as in (I) (see below).

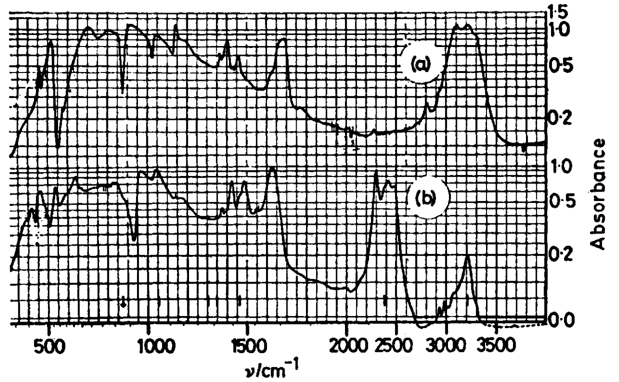


FIGURE 1 I.r. spectrum of (a) $(CH_3CONH_2)_2HCl$ (0.96 mg) in KCl (200 mg), (b) $(CH_3COND_2)_2DCl$, *ca.* 90% D (1.5 mg) in KCl (200 mg). In (b) the vertical bars denote that bands become more prominent as the D content decreases and are assignable to D_4 derivative(s); the vertical arrow denotes inverted band due to $CH_3C(OH)=N^+D_2·CH_3COND_2$; the dashed portion was reconstructed from a spectrum taken without a KCl disc in the reference beam

There is some further evidence that the $(CH_3CONH_2)_2H^+$ and $(CH_3COND_2)_2D^+$ complexes are not symmetrical, especially in the NH and ND stretching region.

NH and ND Stretching frequencies (cm^{-1}) in the solid Cl^- and Br^- salts of $(CH_3CONH_2)_2H^+$ ($^1H_5$) and $(CH_3COND_2)_2D^+$ ($^2H_5$) (discs in KCl and KBr, respectively)

	$^1H_5$·Cl		$^1H_5$·Br		α-$AcNH_2$ [b]	$^2H_5$·Cl	
Vibration [a]	I.r.	R	I.r.	R	R	I.r.	R
HNH *as st*	3 310	~3 315 3 290	3 315 3 290	~3 300	3 340	2 482	2 485
HN^+H *as st*	3 220	~3 215	3 243	~3 240		2 424	2 420
HNH *s st*	*m*? [c]	3 142	*m*?	3 165	3 157	*m*?	2 319
HN^+H *s st*	3 105	*m*?	3 131	*m*?		2 298	*m*?

[a] Assignment for structure (II) (see text); *s* = symmetric, *as* = antisymmetric, *st* = stretching. [b] Solid α-acetamide. [c] If present, masked by intense band close by.

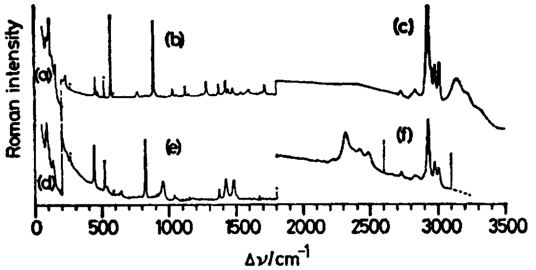


FIGURE 2 Raman spectrum of (a)—(c), $(CH_3CONH_2)_2HCl$ (small crystals), (d)—(f), $(CH_3COND_2)_2DCl$ (powder). Excitation wavelengths, power at laser, and nominal spectral slit widths were: (a) 5 145 Å, 380 mW, 2.4 cm^{-1}; (b) 5 145 Å, 380 mW, 2.8 cm^{-1}; (c) 4 880 Å, 525 mW, 4.0 cm^{-1}; (d) 5 145 Å, 540 mW, 2.4 cm^{-1}; (e) 5 145 Å, 500 mW, 4.0 cm^{-1}; (f) 4 880 Å, 550 mW, 4.0 cm^{-1}. Sensitivity was minimum except for (c) where it was doubled. Dashed portions were reconstructed from spectra run at lower sensitivity or with lowered zero suppression; × denotes laser line

According to the centrosymmetric model (I), 26 (' intramolecular ') vibrations within the complex are i.r.-allowed (the *u* combinations of the 21 vibrations within the acetamidic residues + two vibrations of these residues relative to one another + all three motions of the central H atom), and 25 are Raman- (R-)allowed (21 *g* combinations of motions within the residues + four motions of residues relative to one another, including O · · · O stretching). With a factor group symmetry of C_{2h} and two complexes in the unit cell (related by a glide plane), each i.r.-allowed intramolecular vibration is split into one A_u and one B_u, and each R-allowed one into one A_g and one B_g vibration (A = polarised in *ac* plane, B = polarised along *b*-axis). I.r.-allowed vibrations remain R-forbidden with model (I), and *vice versa*, but where the intramolecular coupling of acetamidic vibrations is only slight the i.r.- and R-allowed vibration frequencies may coincide for practical purposes.

With model (II) all intramolecular vibrations are (and, in the disordered crystal remain) i.r.- and R-allowed. Most will be essentially vibrations in one of the two moieties, CH_3CONH_2 and $CH_3C(OH)=NH_2^+$, but at times intramolecular coupling will be appreciable, *e.g.* that between C–C–N in-phase stretching in CH_3CONH_2 at [28-30] *ca.* 875 cm^{-1} and C–C–O in-phase stretching in $CH_3C(OH)=NH_2^+$ at [29,30] 886 cm^{-1}. The more intense Raman bands are expected to originate in the uncharged moiety as this is much more polarisable than the positively charged one (and, conceivably, from moiety *versus* moiety vibrations).

All vibrations in model (II) have obvious counterparts in (I); *e.g.* H–N–H and $H–N^+–H$ symmetric stretching in (II), and the in-phase (*g*) and out-of-phase (*u*) combination of $H–N^{\frac{1}{2}+}–H$ symmetric stretching in (I); C=O and

$C{=}N^+$ stretching in (II) and the *g* and *u* combinations of $O\overset{\cdots}{-}C\overset{\cdots}{-}N$ out-of-phase stretching in (I). For most frequencies satisfactory assignments are possible with either model. However, the NH stretching frequencies (in particular) are not at all satisfactorily assignable on the basis of structure (I), but are straightforward with (II). Therefore only the assignments based on structure (II) are listed, both in the Table and in the Supplementary Publication [SUP No. 22686 (5 pp.)],* in which the frequencies outside the NH stretching range are tabulated.

NH *and* ND *Stretching Region*.—The number of main bands, and the pattern of i.r.–R frequency coincidences, is the same for $^1H_5$ and $^2H_5$ species of Cl hemi-salt and for $^1H_5{\cdot}Br$ hemi-salt. Given structure (I), the coincidences mean that the intramolecular *g–u* splittings must be very *small* (at least for $H{-}N^{\frac{1}{2}+}{-}H$ antisymmetric stretching), yet the intermolecular *A–B* (correlation field) splittings have to be *large* (*ca.* 60—90 cm^{-1}) to account for (a) the number of bands being >2 i.r. + 2 R, (b) the separations among bands. This is a highly unlikely combination. Moreover, the behaviour of the i.r. NH stretching band system of $MeCONHD{\cdot}MeCOND_2{\cdot}DCl$, when present (in varying concentration) as an isotopic impurity in $(MeCOND_2)_2DCl$, is incompatible with a large NHD–NHD correlation field splitting, and, by implication, with large NH_2–NH_2 or ND_2–ND_2 *A–B* splittings.

As the content of labile protium is raised from 10 to 20%, the inflection at 3 130—3 110 cm^{-1} [due to NH_2 groups, and barely visible in Figure 1(b)] gradually becomes more prominent, but the main system, *viz.* a peak at 3 209 cm^{-1} and inflections at *ca.* 3 310 and *ca.* 3 065 cm^{-1}, is merely intensified and otherwise largely unchanged in shape. Even with an isotopic composition of 25% H–75% D to 30% H–70% D the broadening of the peak at 3 209 cm^{-1} is not great and the relative prominence of the shoulder at 3 310 cm^{-1} remains unchanged. Over this isotopic composition range the content of NHD groups with NHD neighbours increases greatly, and the absence of appreciable spectral effects around 3 209 and 3 310 cm^{-1} shows that NHD–NHD interactions, inter- *and* intra-molecular, are quite small. (For typical changes in the spectrum with concentration of isotopic contaminant in cases where correlation field splitting *is* appreciable, see HCl–DCl and DCl–HCl data.[31])

All NH stretching frequencies observed are above 3 050 cm^{-1}, which is consistent with only moderately strong $NH \cdots Cl$ hydrogen bonding [$r(N \cdots Cl)$ probably *ca.* 3.2 Å, and certainly $\nless$3 Å unless the $NH \cdots Cl$ system is far from linear].

The 3 050—1 350 cm^{-1} *Range*.—The following i.r.–R frequency coincidences ($\nu_{\text{i.r.}}$ first) are observed: $(MeCONH_2)_2H^+$, *ca.* 3 017—3 013, 2 980—2 982, 2 930—2 934, *ca.* 1 690—1 688, possibly 1 431—1 426; $(MeCOND_2)_2D^+$, 3 010—3 011, 2 981—2 980, 2 933—2 932, 1 486—1 481, 1 424—1 422, 1 376—1 374 cm^{-1}. From the above discussion it is clear that such coincidences need to be treated with caution; nevertheless the majority of them are probably genuine.

Throughout the spectrum, prominent $(CH_3CONH_2)_2$-HCl frequencies with no good counterparts in the CH_3CONH_2 spectrum have counterparts in the $CH_3CONH_2{\cdot}HCl$ spectrum.[29,30]

The 1 350—400 cm^{-1} *Region*.—In the (spectroscopically especially interesting) region of the hydroxy absorption continuum, comparison between i.r. and Raman spectrum is more complicated. If a state of discrete energy lies within a continuum, and the discrete state interacts with the continuum state, the resultant absorption curve may have a variety of shapes, depending on the slope of the continuum absorption, relative intensity of continuum and discrete absorption, and on the intrinsic breadth of the latter.[32-34] The unperturbed frequency of the discrete state may coincide with the ' transmission window ' (or ' anti-resonance ') frequency, or may lie anywhere between this absorption minimum and the adjacent absorption maximum. Continua with anti-resonance dips (albeit not very deep ones) have been observed in inelastic scattering spectra, *e.g.*[35] for the excitation of ^{238}U nuclei by collision with neutrons with energies in the 1 meV region. In principle a Raman scattering curve, too, might show broad bands with inverted bands appearing as dips. In practice this has not been observed either in the present spectra or in the Raman spectra of other compounds with ' highly anomalous ' i.r. spectra, presumably because O–H stretching bands have only low Raman intensities.

Where vibrations that interact with O–H (or O–D) stretching have appreciable Raman intensity, the resultant Raman curve cannot be expected to bear a simple relation to the absorption curve. In the light of the above, only the following are considered to be genuine i.r.–R coincidences: for $(CH_3CONH_2)_2H^+$, i.r. 1 027 cm^{-1} minimum *cum* 1 047 cm^{-1} maximum—R 1 031 cm^{-1} (probably in-plane bending of methyl H in cation), and for $(CH_3COND_2)_2D^+$, i.r. 931 cm^{-1} minimum *cum* 966 cm^{-1} maximum—R 956 cm^{-1}, tentatively assigned to mixed cationic C–C–O in-phase stretching–OD in-plane bending (Coriolis coupling between OD bending and OD stretching is expected).

The only very prominent window shown by the $^2H_5$ complex is that at 931 cm^{-1}. *O*-Deuteriation reduces the number of windows (see Figure 1) as usual. The window at 553 cm^{-1} which practically reaches the base line, like similar ones in various other highly anomalous OH spectra (see *e.g.* ref. 15), is assigned to a vibration in which the O atom moves with large amplitude along the O–H axis, *i.e.* CCO bending.

$O \cdots O$ *Stretching*.—None of the stronger bands observed, Raman or i.r., is assignable to this vibration. R 233 cm^{-1}, weak for $(CH_3CONH_2)_2HCl$ present as an inflection for the $^2H_5$ derivative, and absent from the CH_3CONH_2 spectrum, is an unlikely $\nu(O \cdots O)$, not being clearly in evidence for $(CH_3CONH_2)_2HBr$. The

---

* For details of Supplementary Publications, see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1979, Index issue.

naively ' predicted ' ν(O · · · O) with r(O · · · O) = 2.42 Å and a molecular weight of *ca.* 60 for the hydrogen-bonded moieties is *ca.* 350 cm^{-1} (see Novak's [7] Table 5).

Vibrations of $(MeCONH_2)_2HCl$ and $(MeCOND_2)_2DCl$ below 200 cm^{-1} are expected to be residue *versus* residue bending, lattice vibrations, and methyl torsions.

ν(OD) : ν(OH) *Ratios, the Potential Energy Curve for* O–H *Stretching and the Energy Hypersurface.*—Curves for strongly hydrogen-bonded systems, crystallographically symmetrical ones in particular, have been discussed extensively and many (simplified) quantitative treatments of double-minimum potentials have appeared.[5,6,8,36–44]

Normally an X–H stretching frequency is reduced on deuteriation by almost $1/2^{\frac{1}{2}}$; for a simple harmonic pure antisymmetric stretching motion of linear symmetric OHO, ν(ODO) : ν(OHO) = 0.718. Given that in the compounds of interest OH stretching is largely pure except near the window frequencies, such a ratio should be found whenever the O · · · H · · · O system is symmetrical [*e.g.* with (I)], though small deviations may occur, as the centres of gravity of the very broad bands are not necessarily accurate positions of the genuine ν(OH) or ν(OD). For several hemi-salts with highly anomalous spectra, *e.g.*[9,45] $KH(CF_3CO_2)_2$, $KH(CCl_3CO_2)_2$, and $RbH(CCl_3CO_2)_2$, a *prima facie* case has been presented for the presence of a genuinely symmetrical O · · · H · · · O bond (with a symmetric single-minimum potential); these do have ν(OD) : ν(OH) in the range 0.71—0.74 and thus satisfy the above requirement.

Large deviations from 0.71_8 are obtainable only if OH stretching is somehow highly anharmonic, or if deuteriation changes the crystal structure. ν(OD) : ν(OH) Ratios near 1.0 have been reported repeatedly [7,9,15] for ' type *B* ' salts and other compounds with unsymmetrical equilibrium configurations. The majority have r(O · · · O) somewhat too long and ν(OH) too high to be wholly relevant in the present context, but in some r(O · · · O) is extremely short (⩽2.48 Å) and ν(OH) extremely low (1 200—600 cm^{-1}): *e.g.*[9a] $BaC_2O_4{\cdot}H_2C_2O_4{\cdot}2H_2O$ has ν(OD) : ν(OH) *ca.* 1, ν(OH) 1 000 cm^{-1}, and the hydrogen bond with r(O · · · O) 2.45 Å joins the distinctly different [46] moieties $H_2C_2O_4$ and $C_2O_4^-$; leucine hemihydrochloride has ν(OD) : ν(OH) *ca.* 0.94, ν(OH) 850 cm^{-1}, r(O–H) 1.06(9) Å and [47] r(H · · · O) 1.37(9) Å ∠O–H · · · O 175°, *i.e.* r(O · · · O) = 2.43 Å.

Thus acetamide hemihydrochloride is notable in being a ' type *A* ' salt [6] (O · · · O bond necessarily symmetrical crystallographically), with r(O · · · O) as low as 2.42 Å and yet having a very high ν(OD) : ν(OH).

Somorjai and Hornig's result,[37] that a ν(OD) : ν(OH) of *ca.* 1 is obtainable with a *simple* symmetric double-minimum potential for OH stretching if the $v = 1$ level and the energy barrier coincide, has been disputed [38,39] (v = vibrational quantum number). A quite anomalously high ν(OD) : ν(OH) is obtainable, however, if [15] (1) the potential energy curve for hydroxy stretching is flattish over a sufficiently prolonged range of r(O–H) [the term ' flattish ' embraces the possibility of a shallow second minimum around r(O–H) *ca.* 1.36 Å], (2) the $v = 1$ level for OH stretching falls within that flattish portion while that for OD stretching is just below it (see Figure 6 in ref. 15, also Figure 3, potential V_{11}, in ref. 37, which already shows a bunching together of OH energy levels at an only short flattish portion). For a solid with an extremely short r(O · · · O) and a symmetric single-minimum potential for O · · · H stretching [as in (I)] a combination of conditions (1) and (2) is not physically realistic.[15]

A ν(OD) : ν(OH) ratio as high as $1._0$ in effect rules out structure (I) for acetamide hemihydrochloride.

An isolated complex (II) has two equivalent minima in its potential energy hypersurface, but it needs to be stressed that the potential energy curve for O–H stretching *alone* is not of the symmetrical double-minimum type. The conversion of (II) into its mirror image entails, *in addition* to the stretching of the O–H bond by *ca.* 0.30 Å: in the (initially) cationic moiety, compression of the C–O and lengthening of the C=N$^+$ bond, in the neutral moiety, lengthening of the C=O, and compression of the C–N bond (all by amounts *ca.* 60—100% in excess of zero-point vibration amplitudes). Thus the hypersurface in which an isolated (II) has two symmetrically placed equivalent minima (' wells ') is at least five-dimensional.

In the disordered crystal the position is more complicated yet, as the conversion of (II) into its mirror image moves the positive charge from the left- to the right-hand nitrogen atom. This is liable to change the repulsions among the charges. At any time, only a minority of complexes (II) will have the + and − charges around them distributed symmetrically with respect to inversion about the O · · · O midpoint (*i.e.* with + · · · + repulsions *not* minimised). For the majority, the distribution of surrounding charges, and hence the molecular energy hypersurface, is unsymmetrical, with the two well depths unequal (favourable charge dispositions being preferred).

The multimensionality of the system strengthens Somorjai and Hornig's selection rule for unsymmetrical systems:[37] ' left well ' ⟶ ' left well ' and ' right well ' ⟶ ' right well ' only, and no ' well to well ' transitions; the line joining the two minima does not (nearly) lie within any of the planes within which one single vibrational co-ordinate changes. Residence (or lingering ' [40]) times in the individual wells are lengthened and the splitting of the energy levels is reduced. It is thus not surprising that splittings of acetamidic bands analogous to those which Wood [43] predicted, but did not observe, for the complex $(pyridine)_2H^+$ with a double minimum are not in evidence for $(CH_3CONH_2)_2H^+$. Whether there is any interconversion splitting of ν(O–H) one cannot say; the great breadth of the band swamps what splitting there may be.

Mr. D. T. Light and Mr. S. Brown are thanked for technical assistance.

[7/2283 *Received, 29th December*, 1977]

REFERENCES

[1] N. Albert and R. M. Badger, *J. Chem. Phys.*, 1958, **29**, 1193.

[2] E. W. Hughes and W. J. Takei, *Structure Reports*, 1955, **19**, 509.

[3] W. J. Takei, Thesis, California Institute of Technology, 1958, quoted in refs. 1 and 4.

[4] S. W. Peterson and J. E. Worsham, Annual Report of Chemistry Division, Oak Ridge National Laboratory, for year to 20 June 1959, p. 69.

[5] D. Hadži, *Pure Appl. Chem.*, 1965, **11**, 435; *Chimia*, 1972, **26**, 7.

[6] J. C. Speakman, in M.T.P. International Review of Science, Phys. Chem. Ser. I, Vol. 11, 'Chemical Crystallography,' ed. J. M. Robertson, Butterworths, London, 1972, pp. 1—31.

[7] A. Novak, *Structure and Bonding*, 1974, **18**, 177.

[8] J. A. Ibers, *Ann. Rev. Phys. Chem.*, 1965, **16**, 384; G. C. Pimentel and A. L. McClellan, *ibid.*, 1971, **22**, 347.

[9] (*a*) D. Hadži and B. Orel, *J. Mol. Structure*, 1973, **18**, 227; (*b*) D. Hadži, B. Orel, and A. Novak, *Spectrochim. Acta*, 1973, **29A**, 1745.

[10] D. Hadži, *J. Chem. Soc.*, 1962, 5128.

[11] H. H. Mills, and J. C. Speakman, *Proc. Chem. Soc.*, 1963, 216.

[12] A. S. Gilbert and N. Sheppard, *Chem. Comm.*, 1971, 337; *J.C.S. Faraday II*, 1973, **69**, 1628.

[13] J. O. Lundgren and I. Olovsson, *Acta Cryst.*, 1967, **23**, 966.

[14] L. Golic, D. Hadži, and F. Lazarini, *Chem. Comm.*, 1971, 860.

[15] E. Spinner, *Austral. J. Chem.*, 1974, **27**, 1149.

[16] F. Takusagawa and A. Shimada, *Acta Cryst.*, 1976, **32B**, 1925.

[17] J. Wiemann, Mme. Gillier-Pandraud, N. Thoai, and C. Beauté, *Bull. Soc. chim. France*, 1969, 2147.

[18] W. G. Fateley, *Appl. Spectroscopy*, 1973, **27**, 395.

[19] S. W. Peterson and H. A. Levy, *J. Chem. Phys.*, 1958, **29**, 948; (*cf.* S. F. Darlow and W. Cochran, *Acta Cryst.*, 1961, **14**, 1250).

[20] B. L. McGaw and J. A. Ibers, *J. Chem. Phys.*, 1963, **39**, 2677.

[21] J. M. Williams and L. F. Schneemeyer, *J. Amer. Chem. Soc.*, 1973, **95**, 5780.

[22] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 866; W. A. Denne and R. W. H. Small, *ibid.*, 1971, **27B**, 1094; I. N. Hsu and B. M. Craven, *ibid.*, 1974, **30**, 974; M. Kimura and M. Aoki, *Bull. Chem. Soc. Japan*, 1953, **26**, 429; C. C. Costain and J. M. Dowling, *J. Chem. Phys.*, 1960, **32**, 158; E. Hirota, R. Sugisaki, C. J. Nielsen, and G. O. Sorensen, *J. Mol. Spectroscopy*, 1974, **49**, 251; J. E. Worsham, H. A. Levy, and S. W. Peterson, *Acta Cryst.*, 1957, **10**, 319; W. Cochran, *ibid.*, 1953, **6**, 260; G. M. Brown and R. E. Marsh, *ibid.*, 1963, **16**, 191; L. L. Merritt and E. Lanterman, *ibid.*, 1952, **5**, 811; J. Bernstein, *J.C.S. Perkin II*, 1972, 946.

[23] L. Kahovec and K. Knollmüller, *Z. Phys. Chem. B*, 1942, **51**, 49.

[24] J. B. Polya and P. L. Tardrew, *J. Chem. Soc.*, 1948, 1081.

[25] R. E. Buckles, R. C. Johnson, and W. J. Probst, *J. Org. Chem.*, 1957, **22**, 55.

[26] L. Minnhagen, *Arkiv f. Fysik*, 1963, **25**, 203.

[27] D. M. Drew and J. T. v. Gemert, *Appl. Spectroscopy*, 1971, **25**, 465; J. W. Milne, *Spectrochim. Acta*, 1976, **32A**, 1347.

[28] K. W. F. Kohlrausch, 'Ramanspektren,' Becker and Erler, Leipzig, 1943, p. 275; S. S. Raskin and A. V. Setchkarev, *Doklady Akad. Nauk S.S.S.R.*, 1959, **128**, 67.

[29] W. Kutzelnigg and R. Mecke, *Spectrochim. Acta*, 1962, **18**, 549.

[30] E. Spinner, *Spectrochim. Acta*, 1959, **15**, 95; *Austral. J. Chem.*, 1966, **19**, 2153.

[31] D. F. Hornig and G. L. Hiebert, *J. Chem. Phys.*, 1957, **27**, 752.

[32] U. Fano, *Nuovo Cimento*, 1935, **12**, 156; *Phys. Rev.*, 1961, **124**, 1866.

[33] J. C. Evans, *Spectrochim. Acta*, 1960, **16**, 994; 1962, **18**, 507.

[34] J. C. Phillips, *Phys. Rev. Letters*, 1964, **12**, 447; J. Jortner and G. C. Morris, *J. Chem. Phys.*, 1969, **51**, 3689.

[35] M. A. Preston, 'Physics of the Nucleus,' Addison–Wesley, Reading, Mass., 1962, p. 503.

[36] N. Sheppard, in 'Hydrogen Bonding,' ed. D. Hadži, Pergamon, London, 1959, pp. 85—105.

[37] R. L. Somorjai and D. F. Hornig, *J. Chem. Phys.*, 1962, **36**, 1980.

[38] J. Laane, *J. Chem. Phys.*, 1971, **55**, 2514.

[39] R. W. Redding, *J. Chem. Phys.*, 1972, **57**, 3729.

[40] J. Brickmann and H. Zimmermann, *J. Chem. Phys.*, 1969, **50**, 1608.

[41] R. E. Rundle, *J. Physique*, 1964, **25**, 487.

[42] T. R. Singh and J. L. Wood, *J. Chem. Phys.*, 1969, **50**, 3572.

[43] J. L. Wood, *J. Mol. Structure*, 1972, **13**, 141; 1973, **16**, 349; 1973, **17**, 307.

[44] R. Janoschek, E. G. Weidemann, H. Pfeiffer, and G. Zundel, *J. Amer. Chem. Soc.*, 1972, **94**, 2387; R. Janoschek, E. G. Weidemann, and G. Zundel, *J.C.S. Faraday II*, 1973, **69**, 505.

[45] A. L. Macdonald, J. C. Speakman, and D. Hadži, *J.C.S. Perkin II*, 1972, 825; J. Stepisnik and D. Hadži, *J. Mol. Structure*, 1972, **13**, 307; P. J. Miller, R. A. Butler, and E. R. Lippincott, *J. Chem. Phys.*, 1972, **57**, 5451.

[46] Y. Dusausoy, J. Protas, J. C. Martin, G. Watelle, *Acta Cryst.*, 1970, **26B**, 1567.

[47] L. Golič and W. Hamilton, *Acta Cryst.*, 1972, **28B**, 1265.