Vibrational Spectroscopy of Compounds with Very Short Hydrogen Bonds. The Aqueous Bisformate Ion. Comparison with Two Solid Salts, and Some Comments on Broad OH Absorption Continua

Ernest Spinner

Medical Chemistry Group, Australian National University, Canberra, A. C. T. 2601, Australia

The infrared and Raman spectra of aqueous bisformate ions $(HCO_2)_2H^-$, $(HCO_2)_2D^-$, $(DCO_2)H^-$, $(DCO_2)_2D^-$, and of the isotopic mixture $(HCO_2)(DCO_2)H^-$ are reported. For hydroxyl stretching $\nu_{OH} \approx \nu_{OD} \approx 1400$ cm^{-1} (*cf. ca.* 1100 cm^{-1} in the solid Na$^+$ and *ca.* 1400 cm^{-1} in the K$^+$ salt). All the bands expected for a formate ion moiety and most of those expected for a formic acid moiety appear in both the infrared and the Raman spectrum (as for the solid Na$^+$ salt). Essentially unmodified formate ion is complexed with appreciably modified formic acid and the complex does not possess the centrosymmetric C_{2h} structure predicted for it by a recent *ab initio* molecular orbitals calculation, nor a centrosymmetric OHO bond.

The strong dependence of the infrared spectrum of the bisformate ion on molecular environment demonstrates the high variabilities of the potential energy curves that make up the potential energy hypersurface, which are also the cause of the continuum character of the OH band. That is to be attributed to fluctuations in the irregular, highly anharmonic, O—H and H...O stretching motion from largely normal-mode to rather 'abnormal'-mode type, with attendant frequency fluctuations. The short duration of the photonic excitation process relative to these fluctuations needs to be taken into account.

INTRODUCTION

This work is concerned with what have come to be known as »Hadži's type ii« spectra[1]. The special characteristics of these are: very broad intense O—H stretching bands, normally centred in the range 1200 cm^{-1} to 600 cm^{-1}, often plateau-like, and often showing inverted bands[2,3] (sometimes called »transmission windows« or »antiresonances«[4]). Of special interest are the structures[5] of the compounds that show them, their potential energy curves[6,7] or hypersurfaces,[8] the reason for the great breadth of the absorption, and assignments for the inverted bands. The correlations between XH··Y hydrogen bond lengths and the frequences of X—H and H··Y stretching, also of XHY bending, have been reviewed extensively[9]; type ii spectra are associated with extremely short hydrogen bonds, i. e. $r(O_H··O) \leqslant 2.48$ Å.

✲ Festschrift of Professor Dušan Hadži.

Crystallographically these may be symmetrical as in Speakman's[5] »type A« salts or more or less unsymmetrical (»type B«). For type A salts there is always the problem[10] whether the symmetry is genuine, as in O—H—O, which has a (symmetrical) single-minimum potential, or false (statistical), concealing a double-minimum potential.[8b] Other evidence is then required. Non-crystallographic evidence for the presence of O—H—O bonds has been produced[11,12] for e. g. $NaH(CH_3CO_2)_2$, $KH(CF_3CO_2)_2$, $KH(CCl_3CO_2)_2$, and RbH $(CCl_3CO_2)_2$. For these the ratio of the stretching frequencies ν_{ODO}/ν_{OHO} is in the vicinity of 0.72, which it must be with credible O—H—O structures. By contrast a ν_{OD}/ν_{OH} ratio of unity or higher is evidence of an unsymmetrical hydrogen bond in the equilibrium configuration, or of a major structural difference between OH and OD compound.

Bisformate is the simplest possible biscarboxylate ion, and the present study of it will address itself to most of the above-mentioned interesting facets. In crystalline[13] $KH(HCO_2)_2$ the distance $r(O \cdot \cdot O)$ is 2.44_7 Å i. e. extremely short; hydrogen atoms were not located in that work. The OCO/OCO dihedral angle is 110^0, i. e. the complex is far from planar. The HCO_2 moieties are similar but not identical, the bond distances (in Å) being: C_IO 1.220, C_IOH 1.257, $C_{II}O$ 1.240, $C_{II}OH$ 1.251. The infrared spectra[12] of $KH(HCO_2)_2$ and $KD(HCO_2)_2$ show extremely broad OH and OD stretching bands that obliterate many features and were not easy to interpret. They were remeasured here and will be discussed later.

According to recent ab initio calculations[14] the most stable form of the $(HCO_2)_2H^-$ ion, in vacuo, has the centrosymmetric C_{2h} structure and conformation I. Conformation III is not quite so stable, and the symmetrical structures I and III are considerably more stable than the unsymmetrical ones II and IV. The bisformate ion in the K^+ salt, it was argued, is a distorted version of I, the cations being the cause of the distortion.
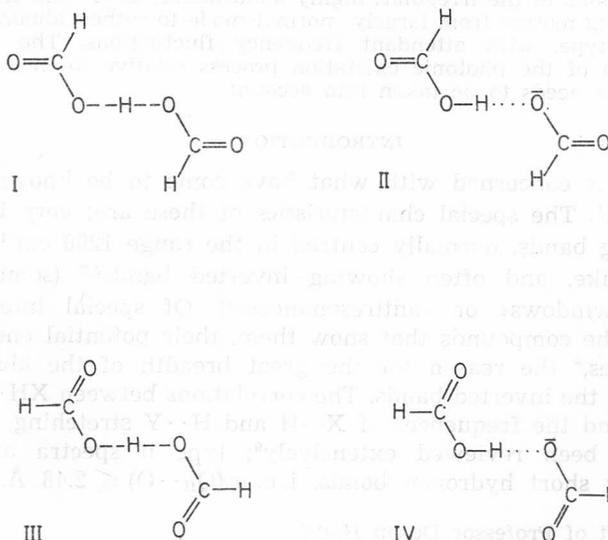
For further tests of the predictions of Emsley et al.[14] it is obviously desirable to have data for other environments around the $(HCO_2)_2H^-$ ion. The complexes I and III would both have relatively simple vibrational spectra, obeying the law of mutual exlusion for infrared and Raman bands because of the presence of a centre of symmetry.

It turns that the vibration spectrum of the bisformate ion does not at all conform to the above prediction in aqueous medium, and likewise in the solid Na^+ salt. The latter will be reported on in detail elsewhere[15], but some features will be referred to in the comparisons later. Its crystal structure is not known, but is obviously different from that of the K^+ salt. It is stressed that the forces and constraints that might stop a bisformate ion from assuming its intrinsically preferred structure are much weaker in solution than in a crystal.

EXPERIMENTAL

Materials

Solid sodium hydrogen bisformates were made[16] from equimolar amounts of the appropriate sodium formate and formic acid. The starting materials were purified HCO_2Na and HCO_2H, DCO_2Na (Wilmad, or Merck, Sharp and Dohme, Canada) and DCO_2D (Merck, Darmstadt). The deuterated compounds were chemically pure as supplied and had isotopic purities higher than 98 atom % D.

Aqueous solutions were sometimes made from the solids and sometimes direct from the three components. The standard concentration used was one molar equivalent of bisformate in three of water, but for the parent perprotio compound infrared spectra were obtained also for $NaH(HCO_2)_2 \cdot 6H_2O$ and $NaH(HCO_2)_2 \cdot 12H_2O$. The isotopically mixed solution examined had the components HCO_2H, DCO_2Na and H_2O in mole ratio $1:1:4$. Whenever required, a manipulator box flushed with dried air was used; powdered sodium bisformate is very hygroscopic and deliquesces at humidities around 60%. $NaH(DCO_2)_2$ was obtained by exposure of $NaD(DCO_2)_2$ to the atmosphere prior to dissolution, but the D was not exchanged completely, hence DOH bands at 2635 cm^{-1} and 1443 cm^{-1} are visible in Figure 1d.

Spectra

Infrared spectra were measured with a Perkin-Elmer model 621 dual grating spectrophotometer, flushed with dried air and fitted with a frequency marker accessory. Aqueous solutions were examined as films, normally between thallium bromide-iodide plates. Raman spectra were taken with a Japan Spectroscopic Company JASCO model R300 grating spectrophotometer fitted with a Coherent Radiation CR-4 argon ion laser. Samples in sealed capillary tubes were irradiated at 488 nm, power in cell compartment ca. 380 mW. Spectral slit widths were about 2 cm^{-1}.

RESULTS AND DISCUSSION

Table I lists the infrared and Raman frequencies of concentrated aqueous sodium hydrogen bisformate, Figure 1 depicts infrared and Figure 2 some Raman spectra. For comparison purposes, Table II lists frequencies for $HCO_2H \cdot 3H_2O$ and for solid $NaH(HCO_2)_2$, and Figure 2 the Raman spectrum of solid $NaD(DCO_2)_2$, and the infrared spectrum of solid $NaH(DCO_2)_2$.

Extent of Complexing

For $HCO_2H \cdot 3H_2O$ (see Figure 1c), after subtraction of the H_2O absorption, the peak of the OH stretching band, of here probably mainly $(HCO_2H)_2$, is around 3150 cm^{-1}. Upon addition of one molar equivalent of HCO_2Na to this solution (see Figure 1b), the band at 3150 cm^{-1} essentially disappears (leaving little besides a broadened water band in the region 3100 cm^{-1} to 3650 cm^{-1}),

TABLE I

Vibration Frequencies of Aqueous Bisformate Ion (cm⁻¹)ᵃ

Vibration Frequencies of Aqueous Bisformate Ion $(cm^{-1})^a$

Assignmentᵇ	$(HCO_2)_2H^-$ IR	R	$(HCO_2)_2D^-$ IR	R	$(DCO_2)_2H^-$ IR	R	$(DCO_2)_2D^-$ IR	R
A combᶜ	2940		2940		2906		2902	
N CH *st*	2926	2936	2928	2935	2196	2193	2200	2200
A CH *st*	2828	2835	2824	2830	2126	2129	2121	2127
A 2CH *ip be*	2734	2743	d	2745	2030	2030	2028	2035
	2525	2525						
A 2CH *op be*		2122		2124		1820		1821
N 2CH *op be*					1780	1782	1777	
N C=O*st*	1715	1715	1707	1707	1689	1690	1685	1684
A CO *st I*	1596		1598		1588		1584	1584
N CH *ip be*	(1398)				1008ᶠ		996	999
A CH *ip be*	1387	(1393)ᵍ	1386	(1393)ᵍ	1025	1024	1024	1025
A CO *st II*	1353	1353	1352	1355	1326	1328	1327	1330
N C—O *st*	1224	(1230)	1253	1256	1231	1236	1253	1250
N CH *op be*	1050		1053		894	892	894	
A CH *op be*		1066		1066	912	909	913	916
A OCO *scis*	767	766	733	722	757	753	764	764
N OCO *scis*	702	707	(675)	690	693	693	(680)	681
N OH *ip be*	ʰ		(1053)		ʰ		1069	1075
N OH *ip be*	ʰ			(659)				(650)
N OH *st*ᵈ	1400		1400		1350		1350	

ᵃ IR = Infrared, R = Raman. Bracketed values are of reduced precision. ᵇ A = anionic formate, N = neutral formic acid; *st* = stretching, *be* = bending, *ip* = in-plane, *op* = out of plane; *scis* = scissoring. Nomenclature for formate ion vibrations as in ref. 20. For CH read CD where appropriate. ᶜ Combination CO *st I* + CO *st II*. ᵈ Band centre estimates, ± 50 cm⁻¹. ᵉ Masked by D₂O absorption. ᶠ Very broadened (presumably by interaction with OH continuum; cf. inverted band near 1000 cm⁻¹ in Figure 2d.). ᵍ Merged band. ʰ Cannot be picked out; presumably quite board.

TABLE II

Vibration Frequencies of Solid Sodium Hydrogen Bisformate and of Aqueous Formic Acid CHO₂H · 3H₃O (cm⁻¹)ᵃ

Assignmentᵇ	NaH(HCO₂)₂[15] IR	R	HCO₂H IR	DCO₂H IR
A combᶜ	2949			
N CH *st*	2902	2902	2936	2238
A CH *st*	2778	2780		
A 2CH *ip be*	2697	2699		
			2720	2700
			2576	2575
N 2CD *op be*				1776
N C=O *st*	1755	—	1726	1695
A CO *st I*	1626	1640, 1669		
N CH *ip be*	1400	1396	1398ᵈ	1004ᵈ
A CH *ip be*	1373	1374		
A CO *st II*	1366	1367		
N C—O *st*	1316	1324	1206	1220
N CH *op be*			1070ᵉ	887ᵉ
A CH *op be*	1066	1067		
A OCO *scis*	768	767		
N OCO *scis*	730		693	688
N OH *ip be*			(1400)	1399
N OH *op be*			950	945
N OH *st*	1100		(3150)	(3150)

Footnotes ᵃ to ᶜ as for Table I. ᵈ Sharp bands; for HCO₂H this band is telescoped on top of the broader band around 1400 cm⁻¹. ᵉ Partly inverted band.
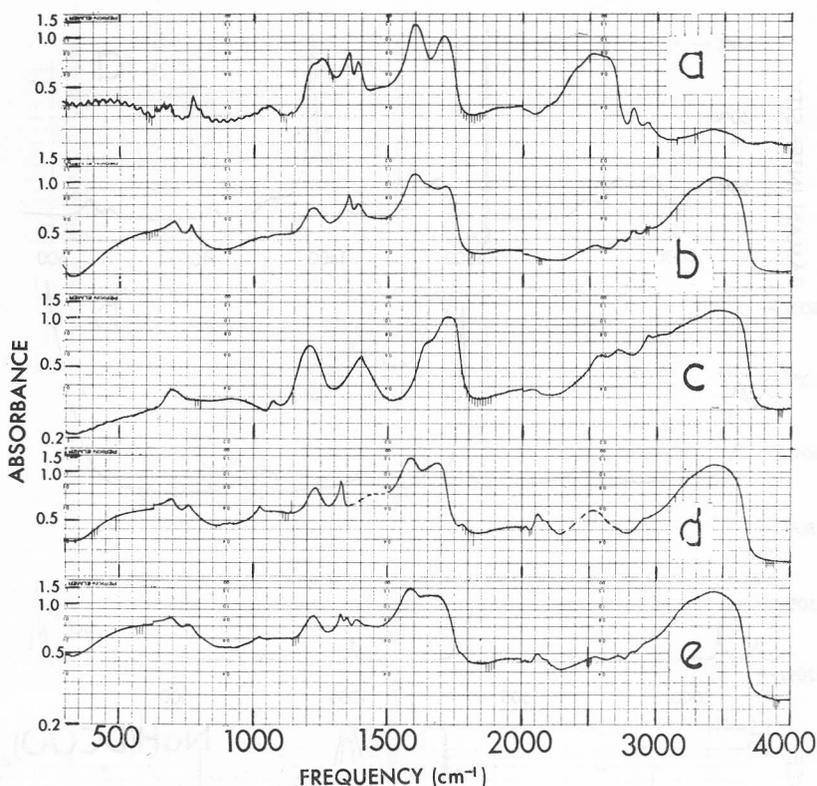
Figure 1. Infrared spectra of aqueous solutions (scale change at 2000 cm⁻¹; filter or grating change steps sometimes appear at 3142, 2000, 1142 and 630 cm⁻¹; in spectrum a interference fringes are present below 1000 cm⁻¹), a: $NaD(HCO_2)_2 \cdot 3D_2O$; b: $NaH(HCO_2)_2 \cdot 3H_2O$; c: $HCO_2H \cdot 3H_2O$; d: $NaH(DCO_2)_2 \cdot 3H_2O$; e: $NaH \cdot HCO_2 \cdot DCO_2 \cdot 4H_2O$.

and in its place there is now a very broad band centred around 1400 cm⁻¹. Evidently there is very little uncomplexed formic acid in this solution, and the spectrum 1b is essentially uncontaminated by the spectra of the uncomplexed components.

This conclusion is confirmed by a comparison between the spectra of $HCO_2H \cdot 12H_2O$ and $HCO_2Na \cdot HCO_2H \cdot 12H_2O$. The latter, unlike the former, still shows a rising background in the range 900 cm⁻¹ to 1050 cm⁻¹, and quite an appreciable *very broad* background absorption centred around 1400 cm⁻¹, but *not* the *narrow* HCO_2H band at 1400 cm⁻¹; also, around 1712 cm⁻¹ and 1220 cm⁻¹ there are differences between the peak frequencies in these two spectra of ca. 8 cm⁻¹. I. e. there is still extensive complexing between HCO_2^- and HCO_2H at this concentration; the equilibrium constant for this association is here certainly higher than the values in the range $0.25 \times M^{-1}$ to $1 \times M^{-1}$ estimated by earlier workers[17] for more dilute solutions, using a variety of conditions and making various assumptions. No quantitative estimate of K_{assoc} is practicable from the infrared data; $HCO_2H \cdot 12H_2O$ contains a considerable amount of $(HCO_2H)_1$.

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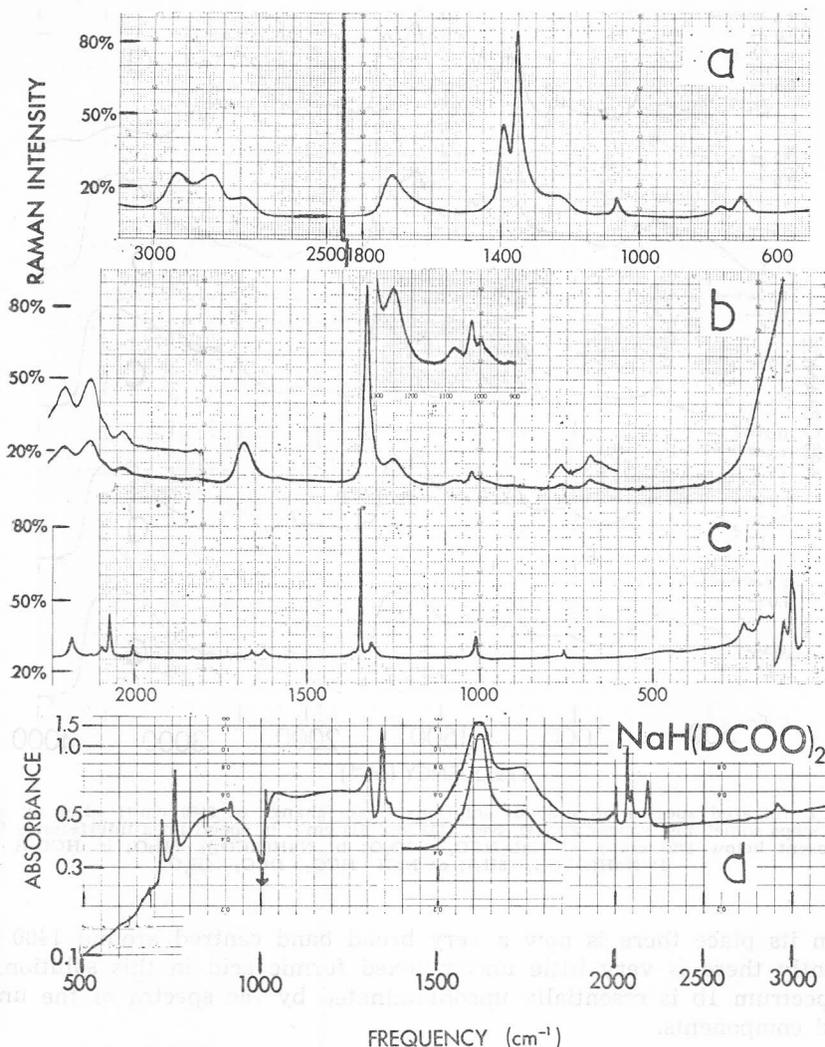
Figure 2. a: Raman spectrum of NaH(HCO₂)₂ · 3H₂O (solution); b: Raman spectrum of NaD(DCO₂)₂ · 3D₂O (solution); c: Raman spectrum of solid NaD(DCO₂)₂; d: Infrared spectrum of solid NaH(DCO₂)₂ in KBr disc — arrow indicates inverted band due to CD in-plane bending in DCO₂H moiety.

On dilution from $NaH(HCO_2)_2 \cdot 3H_2O$ to $NaH(HCO_2)_2 \cdot 6H_2O$ several bands become narrower and some frequencies change a little. Possibly a little dissociation occurs at $1:6$ dilution (the HCO_2^- bands are sharper than their counterparts for $(HCO_2)_2H^-$), but there could also be a concentration effect on the amount(s) of minor conformation(s) of the complex ion present.

Main Features of Infrared Spectra

The spectrum of $(HCO_2)_2D^-$ (Figure 1a) still shows the broad background band centred around ca. 1400 cm⁻¹ (or higher). Relative to the D_2O band at

2530 cm^{-1}, its intensity is about the same as that of the 1400 cm^{-1} background in Figure 1b relative to the H$_2$O band around 3435 cm^{-1}. These backgrounds have to be attributed to hydroxyl stretching within the complex; although these centres of gravity can be estimated only roughly, the ratio ν_{OD}/ν_{OH} is obviously close to 1.0.

The bisformate spectra in Figure 1 are obviously not of Hadži type ii, ν_{OH} being a little too high, while the intensity of the broad band is too low; but they border on type ii, and there is no doubt that r (O$_H\cdots$O) in the complex must still be very short (somewhere around 2.50 Å).

About half the bands in Figure 1b are counterparts of bands in Figure 1c (sometimes a little displaced, broadened or weakened), the remainder are very close to bands observed for aqueous HCO$_2$Na. *All* bands observed for aqueous HCO$_2$Na are present in spectra 1b and 2a. With the exception of the OH stretching and bending bands of HCO$_2$H, and perhaps out-of-plane CH bending, all HCO$_2$H bands in Figure 1c are seen also in Figure 1b.

The Chemical Nature of the Aqueous Bisformate Ion

For the complex ions I and III, which both have point group symmetry C$_{2h}$, the 21 internal vibrations divide as follows:

7A$_g$ (5 within the formate moieties, 1 O—H—O symmetric stretching, and 1 moiety versus moiety in-plane bending);

2B$_g$ (out-of-plane bending, 1 within the formate moieties, 1 moiety versus moiety);

8A$_u$ (5 within the formate moieties, 1 moiety versus moiety in-plane bending, 1 O—H—O antisymmetric stretching, 1 OHO in-plane bending);

4B$_u$ (1 within the formate moieties, 1 OHO out-of-plane bending, 2 moiety versus moiety out-of-plane bending including 1 torsion).

The six moiety versus moiety vibrations, including O—H—O symmetric stretching are expected below 550 cm^{-1}, leaving fifteen above, viz. (5A$_g$ + 1B$_g$) Raman-active and (8A$_u$ + 1B$_u$) infrared-active fundamentals. Put more concretely, for the centrosymmetric structures one expects one Raman and one infrared band for C—H stretching, and likewise for the other vibrations with the formate moieties.

Actually the infrared spectra clearly show two bands for at least four of the formate moiety vibrations, and most of them appear also in the Raman spectrum. For (DCO$_2$)$_2$D$^-$ all twelve formate moiety fundamentals appear in the infrared, and eleven of them also in the Raman spectrum; OD in- and out-of-plane bending appear in both. Thus the aqueous bisformate ion does not possess (or nearly possess) C$_{2h}$ symmetry, and structures I and II are ruled out.

Next one has to consider structures that are chemically like I and III, with symmetrical O—H—O bonds and chemically identical formate moieties, but with conformations other than planar *trans*. For a planar *cis* (C$_{2v}$) or non-planar (C$_2$) conformation, two C—H stretching, etc., vibrations are allowed in the infrared and in the Raman spectrum, with splitting of the frequencies as a result of coupling between the two moieties. Actually the magnitudes of some of the frequency separations (e. g. ca. 100 cm^{-1} between the C—H stretches) look far too great to be reasonably attributed to such coupling. Also, the absence of a substantial downward shift from ν_{OH} to ν_{OD} virtually

rules out a symmetrical O—H—O bond. But in view of the indistinctness of that band and the importance of this question further evidence is called for.

This is provided by the spectrum in Figure 1e, of the isotopic mixture obtained from 1 : 1 $HCO_2H — DCO_2Na$. If the complex ions are chemically of the type of I and III, there are *three* isotopic species in this solution: $(HCO_2)_2H^-$ (ca. 25%), $(DCO_2)_2H^-$ (ca. 25%), and $(HCO_2)(DCO_2)H^-$ (ca. 50%). With ions of the type of II and IV there must be four: $HCO_2^-·HCO_2H$, $DCO_2^-·DCO_2H$, $HCO_2^-·DCO_2H$ and $DCO_2^-·HCO_2H$ (ca. 25% of each).

The isotopically mixed species $(HCO_2)(DCO_2)H^-$ with two chemically equivalent formate moieties would show *new* bands, e. g. one CH stretching band (and *only* one) in place of the two CH stretching frequencies of $(HCO_2)_2H^-$, and about mid-way between them. Similarly for C—D stretching; i. e. the isotopic mixture would show three bands where the isotopically pure species show only two, exactly as was found for solid HCl—DCl mixtures by Hornig and Hiebert.[18] Things are more complicated, for some of the other vibrations that are still coupled in such an isotopically mixed complex, but the band that appears at 1353 cm^{-1} for $(HCO_2)_2H^-$ and 1326 cm^{-1} for $(DCO_2)_2H^-$ would appear at ca. 1340 cm^{-1} for this $(HCO_2)_2 DCO_2)H^-$ ion.

Actually, spectrum 1e shows all the bands present in spectra 1b [$(HCO_2)_2H^-$] and 1d [$(DCO_2)_2H^-$], and *no* extra bands. There is no mixed species $(HCO)_2 · (DCO_2)H^-$ in which the formate moieties are chemically identical. The chemical nature of the complex is as in structures II and IV, and not as in structures I and III.

Furthermore, the absence of significant frequency shifts in spectrum 1e as compared with spectra 1b and 1d shows that the spectrum of the HCO^-_2 (or DCO_2^-) portion of the complex is the same, irrespective of whether it is partnered by HCO_2H or DCO_2H. Likewise, the spectrum of the formic acid moiety is unaffected by the isotopic composition of its partner. Thus there is no significant vibrational coupling between the two components of the complex across the hydrogen bond.

The frequency assignments in Table I, based on a bisformate structure of the type of II and IV, are mostly straightforward, the assignments for formic acid[19] and formate ion[20] being well established. The exhaustive studies of formic acid were carried out on the gaseous and low-temperature matrix--isolation states;[19] comparison of such spectra with those for liquid and aqueous formic acid shows that strong hydrogen-bonding raises strongly not merely the OH bending[9] but also the OCO scissoring and C—O stretching frequencies. If this is borne in mind the assignments of the observable bisformate frequencies pose no problems. (OH in- and out-of-plane bending are too broadened to be observable, probably because of Coriolis interaction with the OH stretching continuum.

The frequencies of aqueous formate ion are practically the same as those of their counterpart in bisformate; the formate moiety is essentially unchanged chemically after complexing. The formic acid portion of the complex, by contrast, is appreciably modified. This is scarcely surprising. The molecular geometries of acids RCO_2H differ appreciably[21] as between gaseous $(RCO_2H)_1$ and gaseous $(RCO_2H)_2$. The changes on going to solid $(RCO_2H)_∞$ are greater still.[22] I. e. hydrogen bonding, even if less strong than in a complex $RCO_2^- ·$ $· RCO_2H$, has a modifying effect on the acid.

General Comparison between Aqueous Bisformate Ion, and its Solid Sodium and Potassium Salts

By means of the infrared spectra of solid $KH(HCO_2)_2$ and $KD(HCO_2)_2$ obtained here, both for discs in potassium bromide and for mulls in Nujol and Fluorolube (and by the use of more concentrated mulls, especially for the OD complex, than used earlier[12]), it has now been possible to place the centres of gravity of the very broad very intense hydroxyl stretching bands of this salt: ν_{OH} at ca. 1400 cm^{-1} for discs and mulls, ν_{OD} at ca. 1400 cm^{-1} in discs and ca. 1300 cm^{-1} in mulls. In other respects the present spectra are like those of Hadži and Orel.[12]

These spectra are practically Hadži type ii spectra, though ν_{OH} is a little higher than usual for these, and the extent to which the OH band obliterates many features one might reasonably expect to see, too, is unusual. Thus, in regard to ν_{OH} and ν_{OD}, the $(HCO_2)H^-$ spectrum in the solid K^+ salt and in water are similar, but otherwise they deviate from the norm for type ii spectra in opposite senses. The infrared spectrum of solid sodium hydrogen bisformate[15] is a normal Hadži type ii spectrum (see Figure 2d); its ν_{OH} and ν_{OD} are around 1100 cm^{-1}, i. e. within the usual type ii range. In all three media, ν_{OD}/ν_{OH} for the bisformate ion is close to 1, and in all three it must have the very remarkable type of potential energy hypersurface[8,23] for which this very remarkable ratio is possible.

The spectra of aqueous bisformate ion and solid sodium bisformate are very similar to one another (1) in regard to the number of bands shown and the number of infrared-Raman frequency coincidences, (2) in that the spectrum of the isotopic mixture »$(RCO_2)(DCO_2)H^-$« is simply the sum of the $(HCO_2)_2H^-$ and the $(DCO_2)_2H^-$ spectrum. Practically all the differences between the spectrum in water and that of the Na^+ salt are direct or indirect consequences of the difference in the strength of the hydrogen bonding: the OCO scissoring and C—O stretching frequencies of the formic acid moiety are lower for $_{aq}(HCO_2)H^-$, and $\nu(C—O)$ shows the anomalous upward shift on deuteration only in $_{aq}(HCO_2)_2H^-$. This latter is due to interaction with OH in-plane bending; in the solid sodium salt that bending frequency is so high that it interacts noticeably with C=O rather than C—O stretching. There is a drastic difference in the Raman intensity of C=O stretching in the two phases, to be discussed elsewhere[15]; see Figure 2b and 2c.

Solid sodium bisformate shows a broad Raman band around 450 cm^{-1}; $(HCO_2)_2H^-$ and $(HCO_2)_2D^-$ show it with greater prominence than the salts based on $(DCO_2)_2$, but the band there in Figure 2c is real. It is tentatively assigned to $H \cdot \cdot O$ (colloquially »$O \cdot \cdot O$«) stretching. For $_{aq}(HCO_2)_2H^-$ no such Raman band can be identified; presumably its frequency is lower, but it is the authors view that this band is too broad to be seen (not only here, but also for many other compounds that show Hadži type ii or comparable infrared spectra), cf. p. 265.

Inverted bands are a common feature in type ii spectra. Solid $(HCO_2)_2HNa$ shows a partly inverted CH in-plane bending band near 1400 cm^{-1}; its counterpart for solid $(DCO_2)_2HNa$ is quite prominent (near 1000 cm^{-1} in Figure 2d, i. e. near the centre of the continuum). Solid $(HCO_2)_2HK$ and $(HCO_2)_2DK$ show this as a fully inverted band at 1392 cm^{-1}, but the startling deep inverted

band (almost reaching base line) is at 735 cm^{-1} for the HK and at 730 cm^{-1} for the DK salt.

With the knowledge now accumulated this can be assigned to OCO scissoring in the HCO$_2$H (or HCO$_2$D) moiety, and it is inverted because[15] this moiety, in the K$^+$ salt, has[13] the O=C and OH bonds *trans* to one another, as in formula II (and I). For the Na$^+$ solid salt this band near 730 cm^{-1} points upward in the normal manner (for all isotopic species); it is reasonable to infer that in the Na$^+$ salt the O=C and OH bonds are *cis* to one another as in formula IV. This latter conformation is the only one that is known for[21] free (HCO$_2$H)$_1$ and (HCO$_2$H)$_2$, and there are some indications that it is also the principal conformation in aqueous (HCO$_2$)$_2$H$^-$, but there is no clear evidence on this point, and the above type of reasoning unfortunately cannot be used here.

The bisformate OH absorption continuum in water does not extend as far as 700 cm^{-1}, so the band there obviously points upward. Moreover, $_{aq}$(HCO$_2$)H$^-$ fails to show any clear inverted band comparable to those reported for liquids by Evans[24] (contrary to the present author's hopes). According to the theory of antiresonances[25,24] the prospects of obtaining prominent inverted bands increase as the intensity of the continuum absorption increases; thus $_{aq}$(HCO$_2$)$_2$H$^-$ does not present favourable conditions. (Interaction between continuum and discrete level merely causes band broadening e. g. at 1008 cm^{-1} for $_{aq}$(DCO$_2$)$_2$H$^-$, an op be band of $_{aq}$(HCO$_2$)$_2$H$^-$ may be inverted.)

The remainder of this paper will be concerned with the problem of why the OH bands are continua in Hadži type ii and related infrared spectra; and they must be genuine, and not apparent, continua, for »antiresonances«, partly inverted, and wholly inverted bands as observed to occur.[25,24,4] The present finding that the OH stretching band of (HCO$_2$)$_2$H$^-$ varies greatly in frequency and intensity as among aqueous solution, solid Na$^+$ and solid K$^+$ salt demonstrates the great variability of the O—H stretching potential energy curve, within the potential energy surface, depending on the exact disposition of charges and dipoles in the vicinity. Such strong variability is at the root of continuum character.

Attention needs to be drawn, however, to yet one more aspect of importance to hypersurfaces. Extremely low O—H stretching frequencies imply extremely short hydrogen bonds, but experience shows that they do not imply extremely strong ones (contrary to Emsley's extrapolation[7]). Aqueous (HCO$_2$)$_2$H$^-$ is appreciably dissociated[17] in all but very concentrated solutions. The most troublesome experimental difficulty in spectroscopic work with solid sodium bis formate in discs, and even more so in mulls, is posed by the ease with which it dissociates under (manual) pressure. The K$^+$ salt is only marginally less troublesome in this regard. All this implies that somewhere in the potential energy hypersurface there is a not very high-lying, and readily accessible, valley heading to disscociation. This implies a high H··O and (O··O) stretching vibration amplitude.

THE PROBLEM OF OH ABSORPTION CONTINUA

Earlier Theories

The basic reasons[26] why *liquids* (e. g. water and alcohols) show broad continuous O—H stretching bands are: (i) at any moment there is a wide range

of intermolecular (O$\cdots$O) separations, and a wide range of relative orientations among pairs of adjoining neighbour molecules; this gives rise to wide range of OH frequencies; (ii) as the molecules move (translate, and librate or rotate) relative to one another the frequencies change with time. There have been numerous extensions, generalizations, and elaborations of this theory, associated with expressions such as »dephasing«[27] and »fluctuation hypothesis«[28]; and the broadening due to the high polarizability of the hydrogen band has been stressed.[29]

Evans[24] explained the breadth and continuum character of OH and NH bands in liquids and solids alike by the above theory. However, in solids, also within an aqueous $(HCO_2)_2H^-$ ion, the atoms engaged in OHO bonding all vibrate about equilibrium positions that are fixed relative to one another; in liquids this is true for only a fraction of the hydrogen bonds. For solids, etc., the above explanation does not suffice, and most workers have recognized that the additional factor that has to be invoked is anharmonicity (mechanical and electrical), in particular sizeable anharmonic cross-terms.

According to the Stepanov-Batuev-Sheppard[30] and Bratoz-Hadži[31] theories, the observed »XH stretching« band of an X—H$\cdot\cdot$Y system is an envelope containing contributions from a number of satellite bands, with frequencies given by formula (1), and infrared-allowed (even intense) because of anharmonicity.

$$\nu = \nu_{XH} + n'\nu'_{H..Y} - n\nu_{H..Y} \cdots \tag{1}$$

where n and n' are the initial and the final quantum numbers, $\nu_{H..Y}$ is the hydrogen-bond stretching frequency in the ground state, $\nu'_{H..Y}$ that for the state in which XH stretching is excited.

Other low-frequency vibrations such as XH$\cdot\cdot$Y bending could also give rise to a progression. The $-n\nu_{H..Y}$ term corresponds to transitions from states which are vibrationally excited initially; such »hot« bands should weaken on cooling.

In practice, in Hadži type ii spectra, the low-frequency wings in which most of the »hot« bands would be, do not weaken on cooling. More especially, these spectra do not show progressions of »hot« inverted bands, attributable to transitions from initially excited levels to the vibrational level in »antiresonance« with the continuum, and removable by cooling. It would appear that the satellite bands represented by formula (1) are in general not nearly intense enough to account for the intense broad bands characteristic of type ii spectra.

The frequencies in (1) as formulated originally are those for collective vibrations in the solid for wich the wave-vector quantum number is $k = 0$. A recent extension of the theory[32] attributes major broadening to multiphonon combinations corresponding to formula (1), but with the individual k values not restricted to 0, though $\Sigma k = 0$. Such combinations, highly forbidden with harmonic vibrations but weakly allowed as a result of anharmonicity, appear (broad) in the spectra of larger crystallites. How to account on this basis for the unique breadth of Hadži type ii spectra, even for well dispersed small crystallites in dicsc, still seems problematical. For present purposes it is important to note that the *individual* energy levels in all these theories[30-32] are sharp. There are no genuine continua, merely enough nearby states (often of different symmetry species) to produce the appearance of a continuum.

Relevant Work on the Classical Mechanics and Quantum Mechanics of Three-Particle and Larger Systems

For a bound quantum-mechanical two-particle system all energy levels are discrete and sharp. When quantum-mechanical theory was well advanced two workers[33] undertook the formidable task of proving that the energy levels of the helium atom (a three-particle system with a relatively simple potential) also are discrete (spins were neglected). The simple but treacherous short-cut of saying: »The potential energy of the system depends only on the spatial coordinates of the particles, and not explicitly on time, hence the system, if isolated, is in a stationary state, and the energy levels must be sharp« was not taken.

For a system of many particles (three or more) the motions in the various degrees of freedom may be separable and their eigenfunctions all orthogonal, as in simple harmonic and soliton-like[34] motions (completely non-ergodic situations), and the sharpness of the vibrational energy levels may then be taken for granted. For the majority of anharmonic systems the motions are nonseparable, however, and matters are more complicated. The problem of three bodies moving in one another's field is not universally solved in classical mechanics.

That a vibrationally excited anharmonically vibrating collection of atoms is not in a stationary state seems to have been said first by Bauer[35] in connection with lattice vibrations in solids, viz. one phonon »decaying« into two or three. Band breadth was attributed[36] to the finite »decay times« involved. By contrast, it is very hard to see in the literature any expression such as »non-stationary state« or »inexact eigenstate«[37] in regard to vibrationally excited, anharmonically vibrating, single molecules; though non-stationary states are implicit in theories of quantum-mechanical ergodicity.[38] For cases in which excited states have been regarded as better represented by local modes[39] than by normal modes of vibration, the excited states have been explicity recognised to be non-stationary[40], but at least in the simpler instances such as H_2O the energy levels remain sharp.[40b]

The work published during the last ten years on the classical, semi-classical and quantum mechanical aspects of vibrational[41] excitation and energy redistribution in model systems of two or three coupled anharmonic oscillators is very extensive. The systems have usually been sufficiently simple to permit numerical treatment, i. e. the number of anharmonic cross terms (though not their magnitude) has been kept small. The principal method has been to trace the trajectory of the system in »phase space« (momenta being plotted against phase). The main result is that below a certain energy called the »critical energy« the motions are ordered and more or less quasiperiodic, and separations among energy levels are fairly regular. Above the »critical energy«, which may be far below the lowest dissociation energy of the system, the motions often mecome disordered or chaotic (onset of ergodic behaviour) and the energy spectrum irregular (though, for certain potentials ordered motion reappears above a certain energy[42]).

It needs to be stressed, however, that almost invariably the energy levels obtained were sharp, with ordered and chaotic motion alike.[42,43] As a corollary, all the nodes of the wave functions depicted by Stratt et al[43b] are sharp (and these show some narrowly avoided[44] crossings!). Percival[45] con-

cluded that under conditions of poor resolution irregular energy »spectra« may look like continua, but individual levels are sharp (though very sensitive to perturbation). Broadened calculated energy »spectra«, and »spectra« containing banded regions appear, so far, to have been reported for only two kinds of model systems of three coupled anharmonic oscillators.[46] Uncertainty has been expressed[47] as to the extent to which semi-classical results obtained for stochastic oscillating systems may be carried over into quantum mechanics; the question as to whether the Schroedinger equation always has stable solutions for molecular systems in chaotic motion is scarcely ever raised.

The Present Approach to Sharpness versus Breadth in Energy Levels, via Goodeve-Type Potential Energy Surfaces, with Allowance Made for the Short Duration of the Excitation Process

The Born Correspondence Principle. Duration of Excitation Process. — The Born correspondence between energy and frequency will be introduced by two quotations:[48] »The mathematical similarity between the classical theory of normal modes and the quantum mechanical theory of steady states is, however, much more complete . . .« »Energy quantization therefore arises for the same reason that the normal frequencies in vibrating systems are discrete«.

The present work, of course, is concerned with vibrating systems in which the frequencies change with time, and not with genuinely steady states, but three examples of the above will be given, viz. the energy of excitation ΔE from the $v = 0$ ground state to the $v = 1$ state, by absorption of a photon, for (a) the harmonic diatomic vibrator — equation (2), the simple Born correspondence; (b) the anharmonic diatomic vibrator[49a] — equation (3); and (c) the polyatomic vibrator[50a] in the theory of *small* anharmonicities — equation 4. h = Planck's constant; ν_p = frequency of oscillation of electromagnetic field of photon being absorbed; ν_v = frequency of vibrator being excited.

$$\Delta E = h\nu_v = h\nu_p \ldots \ldots \tag{2}$$

$$\Delta E = h\nu_v' = h\nu_p = h(\omega + 2x + ..) \ldots \ldots \tag{3}$$

$$\Delta E_{1|} = h \cdot {}_1\nu_v'' = h\nu_p = h\left[\omega_1 + 2x_{11} + \tfrac{1}{2}\Sigma\,(x_{12} + x_{13} + ..) + ..\right] \ldots \ldots \tag{4}$$

ν_v' in equation (3) is the frequency for a state midway between[49a] initial and final state, ${}_1\nu_v''$ in equation (4) is the corresponding mean frequency of vibration »1«, which is now affected by anharmonic coupling to vibrations »2«, »3«, etc. The customary manner of expressing them as sums[49a,50a] of a zero-order frequency ω and anharmonicity constants x, x_{11} and anharmonic cross-terms x_{12}, etc., its also shown. (For anharmonic vibrators the actual vibration frequencies usually decrease as v increases, i. e. at least for stretching vibrations x and x_{11} are negative). In polyatomic vibrators with *small* anharmonicities x_{12}, similarly y_{112}, etc., are constants, and the total motion, in a given level, is the resultant of motions of constant frequency, and sums and differences of these constant frequencies. For all the above situations the vibrational energy levels and absorption bands are sharp; details of the absorption process are not necessarily of consequence.

However, when the vibration frequencies are not constant, the *duration* of the excitation process, t_{ex}, needs to be taken into account explicitly. This

appears not to have been done before. According to the Heisenberg uncertainty principle, the time interval t_{ex} during which the energy of a system is uncertain within a range ΔE is given by equation (5). For excitation by a photon $\Delta E = h\,_{abs}\nu_p$, which gives equation (6). (Here absolute frequencies

$$\Delta E \cdot t_{ex} \gg h/4\pi \tag{5}$$

$$\sigma/b\,_{abs}\nu_p \cdot t_{ex} \gg 1/4\pi$$

$$\sigma/b, \sigma/b\,_{abs}\nu_p \cdot t_{ex} = \,_{abs}\nu_v{}' \cdot t_{ex} \simeq 1 \tag{6'}$$

$_{abs}\nu$, in s^{-1}, are used; if ν is in cm^{-1} and the velocity of light, c, in $cm\ s^{-1}$, $_{abs}\nu = c\nu$). Taking into account the physical nature of the photon, one may obtain a closer estimate of t_{ex}, viz. equation (6'), by two routes.

Firstly, absorption of a photon by a Hertzian oscillator (or rotator) of frequency $_{abs}\nu$ obviously occurs over approximately one dipole oscillation period, i. e. $1/_{abs}\nu\ (\equiv 1/_{abs}\nu_p)$. Secondly, the electromagnetic field of the photon has extensions and amplitude of the order of its wavelength λ; with photon — molecule separations up to ca. $1\,\lambda$ there is a reasonable probability of interaction between the two (though the probability is higher with smaller separations). A photon travels with high speed to (and from) a molecule, covering a distance $2\,\lambda$ in time $2/_{abs}\nu_p$. During this period (or, for a large supermolecule, such as a solid particle of size $< \lambda$, during a period $3/_{abs}\nu_p$) the photon is *either* »transmitted« (with unchanged energy), *or* reflected or scattered (with unchanged or changed energy), *or* absorbed. These are upper limits for t_{ex}; the most probable values of t_{ex} are a little lower, i. e. as given by equation (6'), where $_{abs}\nu_v{}'$, in the case of a vibrator of constantly changing frequency, is the average frequency *during the time interval* t_{ex}.

Model of the Ball in a Goodeve-Type Potential Energy Surface for Vibrations of High Anharmonicity with Large Amplitude. — The most instructive way of considering the nature of the vibrations of a polyatomic molecule with a complicated potential energy surface is by means of the model of a point--sized ball (»molecular image point«), with mass, moving on the surface without friction, under the action of gravity. For an understanding of what follows familiarity is esential with Herzberg's discussion[50b] of the moving ball in the original Goodeve model[51] with orthogonal axes, and also his later discussion[52] of the realistic model for CO_2 with the 55⁰ angle between the coordinates for C—O_I and C—O_{II} stretching (the inconvenient angle is necessary if the kinetic energies of the modes of vibration, as well as the potential energy of the molecule, are to be represented correctly by the moving ball). In order to have a problem in only three dimensions, i. e. three variables, here potential energy V and two bond lengths r, the molecule needs to be triatomic and with the bond angle fixed (here at 180⁰). The vibrations will still be referred to as ν_1 and ν_3, as in CO_2.

At any point in such a potential energy surface, the forces on the ball act along two (vertical) planes of principal curvature (»principal planes«), one along the line of steepest descent into the potential energy valley, the other along the slope of the valley itself. The total motion of the ball is the resultant of the component motions in these two principal planes, (i. e. of two modes of vibration). The wave function for a quantum mechanical energy

level has to be constructed in a horizontal plane above this surface at that energy (cf. the diatomic case[49b]).

For reference, the following properties of the *simple harmonic*, permanently linear, triatomic vibrator (e. g. an idealised CO_2 molecule), in a Goodeve-type model are stressed: (A) The potential energy surface is paraboloid; all principal planes corresponding to ν_1 are parallel to one another, likewise all principal planes corresponding to ν_3, and the angle between ν_1 and ν_3 planes is 90^0. (B) If q_1 and q_3 are the normal coordinates, $\partial^2V/\partial q_1^2$ has the same value everywhere, i. e. the force constant k_1 and hence the frequency ν_1, are genuinely constant; likewise for $\partial^2V/\partial q_3^2$, k_3 and ν_3. (C) In a given traversal by the ball, the point at which one of the component motions of the ball has maximum velocity classically has the same $r(C—O_I)$ and $r(C—O_{II})$ as the nodal point for the mode in the $v = 1$ state in quantum-mechanical motion (cf. the harmonic diatomic case[49b]). For a given $v = 1$ level, all nodal points obtained in successive traversals lie along one straight line (the angle between the $v_1 = 1$ and $v_3 = 1$ nodal lines is 90^0; at a nodal point, the atoms, quantum mechanically, move with »infinite velocity«).

As an example of a highly *anharmonic* vibrator, a highly energised carbon dioxide molecule will be used; see Figure 66 in ref. 50 and Figure 163 in ref. 52, and visualise the motion of the ball starting from rest near the point where $r(C—O_I) = 2.2$ r_e and $r(C—O_{II}) = 0.9$ r_e. Instead of (A) to (C) above, one then finds that: (D) The principal planes going through one point on the surface are not normally parallel to those at another point; e. g. the angles between the principal planes and the coordinate axes are quite different near the equilibrium configuration and in the energy valleys leading to dissociation into CO + O. (E) The shape of the potential energy curve across a valley, or along a valley, varies from point to point, i. e. the principal curvatures $\partial V/\partial q_1$ and $\partial V/\partial q_3$, and hence $\partial^2V/\partial q_1^2$ and $\partial^2V/\partial q_3^2$, the effective instantaneous force »constants« (also anharmonicity »constants«) vary, in both magnitude and direction, from point to point.* (F) The vibration coordinate q_1, which at the equilibrium configuration is symmetric OCO stretching, changes, gradually but smoothly, into stretching of the shorter CO bond (the vibration »across the valley«), while q_3, which at the equilibrium configuration is antisymmetric OCO stretching, changes gradually but smoothly into stretching of the longer CO bond (the vibration »along the valley«). (G) In Wilson's $F\,G$ notation[53] (E) means that the effective F changes with configuration, and ipso facto with time, while (F) means that G, too, changes. (H) Thus, within a given high energy level, *the frequencies ν_1 and ν_3 change with time as the character of each vibration changes from largely local mode type over the valley to normal-mode type at equilibrium.*

(I) For a given change in total energy, vibration 3 changes in character and frequency much more than does vibration 1, because »3« leads to dissociation OCO → O + CO, which occurs at a much lower energy than the dissociation OCO → O + C + O accessible by »1«. Quantum-mechanically the energy levels for ν_3 converge much more rapidly than those for ν_1 (this contradicts a statement by Herzberg;[52] for evidence, see below).

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* $\partial^2v/\partial q_1\,\partial q_3$, and hence the interaction force »constant« k_{13}, also vary from point to point.

(J) For relevant information about the nodal lines one has to consider a high-lying level with $v_1 = 1$ and $v_3 = n$ where n is high. There are n nodal lines in directions roughly across the valley, for vibration 3, and these are irrelevant at the moment. The relevant nodal line is that vaguely »parallel« to the valley, for vibration 1. Classically, the important quantity for the ball, traversing the valley by a highly curved path, is *that* component of the velocity which is in the principal plane roughly across the valley and which corresponds to dq_1/dt. Inspection of the model (see also Figure 163 in ref. 52) shows that, in a traversal over a given point in the valley, the magnitude of that component (and hence dq_1/dt) depends on the exact direction from which the ball has travelled. The point at which this velocity component reaches its maximum value classically during a traversal, and therefore the (now somewhat displaced) nodal point in the $v_3 = 1$ level in quantum-mechanical motion, are thus determined by the *previous history* of the molecule (stochastic behaviour). The same applies to the short-term values of the atomic distribution functions ψ^2 (ψ is the amplitude of the wave function). The position of the (highly curved) nodal line obtained on successive traversals of the valley changes from one series of traversals to the next.* In experimental situations, it may be the *short-term* averages of ψ, and of the nodal line positions, rather than the long term averages as time $t \to \infty$, that are relevant. Conversely, in a high-lying state $v_1 = n$, $v_3 = 1$, with high n, the long-term average position of the nodal line for v_3 is in the plane of symmetry through the Goodeve model. Again the experimentally important quantity may be a short-term average wave function, rather than the above.

This applies in particular if such a level is the initial state in a process of short duration such as vibrational excitation by a photon. The dependence of the average v_v'' (and of ψ) on the particular range of configurations attained during the brief t_{ex} involved gives rise *to intrinsically broad absorption bands.* Transitions lead to very »inexact eigenstates«.

The above discussion of highly energised CO_2 is for illustrative purposes only; for several reasons it is not of practical relevance to the observable vibration spectrum of carbon dioxide, which involves states inside the deep potential energy trough, for which the anharmonicities are small. Only point (I) above is already in evidence[54] there, in small measure: x_{33} (-12.5 cm^{-1}; cf. $\omega_3 = 2396.3$) is considerably greater than x_{11} (-3.0 cm^{-1}; cf. $\omega_1 = 1354.0$). (The above theory of band broadening is expected to be relevant to the electronic spectroscopy of compounds with large-amplitude anharmonic low-frequency vibrations).

Application to Systems Containing OHO Bonds. — For a permanently linear OHO triatomic system, with the properties deduced from experiment as prevailing in the complex ion $HCO_2^- \cdot HCO_2H$, the qualitative appearance of the energy contour lines expected in a realistic Goodeve-type model is as shown in Figure 3. (This could apply to an OHO^{3-} ion in vacuo.) With nuclear masses 16, 1, 16 the realistic angle[52] between the $r(HO)$ coordinates in 19.89°. The empirically incorporated features are: (i) a double-minimum potential; (ii) the inclination of the valleys (leading to dissociation) relative to the

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* For comparison, nodal lines are fixed for a harmonic vibrator in a non-degenerate state not involved in Fermi resonance.
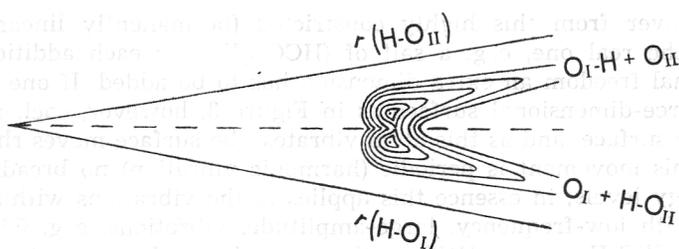
Figure 3. Goodeve-type model for linear OHO triatomic system, as applicable to (HCO$_2$H)H$^-$. Qualitative diagram of potential energy contour lines in lower regions of surface. Equilibrium configurations (minima) indicated by dots. For on O—H—O system, O . . . O stretching occurs along the bisector between the coordinate axes (dashed line), and OHO antisymmetric stretching along a line perpendicular to this. For harmonic oscillators the contour lines are ellipses, centred on the equilibrium configuration(s) and elongated in a direction close to O . . . O (for the O—H—O system, exactly along 0 . . . O). At the coordinate axes the potential energy is infinite. (Outside the diagram finite energies again occur, but correspond to H . . . O . . . O systems.)

coordinate axes, and the increasing narrowness and steepness of the valleys, respectively reflect the decrease in r(O—H) and the increase in ν_{O-H} as r(H··O) increases; (iii) »horns« in the lower contour lines pointing into the valleys reflect the accessibility of dissociation. (The corresponding diagram for a single-minimum potential is readily constructed by reference to Fig. 163 of ref. 52). In spite of considerable differences among the potential energy hypersurfaces for different compounds, the gist of what follows is expected to apply to all compounds with Hadži type ii spectra.

The vibration amplitude of the (very light) H atom is quite high during OH stretching if ν_{OH} is in the range 1400 cm^{-1} to 600 cm^{-1}, and so (for a different reason) is that of O··H (»O···O«) stretching. For the ground state energy level ($v_1 = v_3 = O$) the energy contour line shape is expected to be more or less like the lowest contour line in Figure 3, while the second-lowest contour line shown is expected to be a good approximation to that for the $v = 1$ level of ν_{O-H}. The movement of the frictionless ball in a potential energy surface such as that in Figure 3 corresponds to chaotic vibratory motion (even in the ground state). Eventually the ball will go over every point in the surface, and the whole of »phase space« should be filled, especially as in quantum mechanics there is a finite probability of the ball (molecule) penetrating[55] a little through the potential energy surface.

The points (D), (E), (G), (H) and (J) made in the previous section apply here in all essentials, and already at low energies of excitation. [Points (F) and (I) do not apply, or only to a very minor extent, but this is unimportant.] Photonic excitation is expected to give rise to broadened bands, for both O—H and H··O stretching. In the Schroedinger equation for this system, (7), where m are the nuclear masses, and the z direction is along the internuclear axis

$$\frac{h^2}{8\pi^2} \sum_{i=1}^{3} \frac{1}{m_i} \frac{d^2\psi}{dz_i^2} - (V - E)\,\psi = 0 \qquad (7)$$

the wave function amplitude ψ and energy E both have ranges of values in $v = 1$ states (and, by inference also in higher ones). (Some Fermi resonance between $v_{OH} = 1$ and states with $v_{O..H} > 1$ no doubt occurs, but this is immaterial here).

Going over from this highly constricted (permanently linear triatomic) system to the real one, e. g. a salt of $(HCO_2)_2H^-$, for each additional degree of vibrational freedom an extra dimension has to be added. If one still wishes to use a three-dimensional surface as in Figure 3, however, each added atom changes the surface, and as this atom vibrates, the surface moves rhythmically. Provided this movement is periodic (harmonic vibration) no breadth is added to the energy levels; in essence this applies to the vibrations within the HCO_2 moieties. With low-frequency, large-amplitude, vibrations, e. g. OHO bending and other HCO_2H versus HCO_2^- vibrations, it no longer quite applies. If these vibrations are themselves highly anharmonic, the motions of the potential energy surface of Figure 3 are liable to be chaotic, and further breadth is added to the excited OH stretching level.

This must be expected to apply to anion versus cation and anion versus anion vibrations in the solid salts, and to a lesser degree to anion versus H_2O motions in aqueous solution, because of the experimentally established drastic effect of nearby charges on the OH band. (Alternatively, one could construct a Goodeve-type model with, e. g. $r(O—H)$ and $r(H \cdot \cdot cation)$ as the coordinates, all other interatomic coordinates being kept fixed; the same conclusion would be reached.)

The O—H *Stretching Bands in Inelastic Neutron Scattering.* — In the inelastic neutron scattering spectra, at 80 K, of the acid oxalates of lithium (infrared spectrum of Hadži type ii, ν_{OH} ca. 600 cm^{-1}), potassium (i. r. ν_{OH} ca. 1500 cm^{-1}) and sodium (i. r. ν_{OH} ca. 1900 cm^{-1}) De Villepin et al.[56] were unable to pick out ν_{OH}. From first principles this band is expected to be intense, especially for the Li salt, in which the hydrogen vibration amplitude must be very high. These workers suggested that the band is too broad to be seen.

These results should be compared with those for solid[57,58] KHF_2, where ν_3 of HF_2^- was not resolved at all, and solid $NaHF_2$, where ν_3 is[57] of low intensity, at 1467 cm^{-1}, whereas in the infrared[59] spectrum it is of very high intensity and at 1560 cm^{-1}. Some comments on the difference between vibrational excitation by photonic absorption and by bombardment with (medium energy) neutrons are called for.

In a solid, only an all-in-phase collective vibration ($k = 0$) can be excited by a photon. In inelastic neutron scattering there is no such restriction, even if all motion is simple harmonic. This results in a difference in ν_{max}, and obviously makes bands broad. However, if even the infrared absorption band is several hundred cm^{-1} wide, it is doubtful whether this would add significant extra width in inelastic neutron scattering.

If one applies the type of reasoning used above, it is not obvious that t_{ex} for a collision between a neutron and a nucleus must be as brief as it is in photon — (super)molecule collisions; hence it is not obvious that the band broadening due to high anharmonicity would be as great. But other band-broadening factors are now present. Firstly, in these, highly localised, transitions, momentum in *one* direction (translational, angular, or both) is imparted, in the first instance to one nucleus (the proton much more frequently than oxygen), but a little later to the molecule as a whole. The translational symmetry normally present in a crystal is thus destroyed around the excitation site, and a situation somewhat like that in a liquid obtains locally. Secondly, it is now quite *likely* that on collision between the neutron and

the proton a second vibration is excited in addition to OH stretching, e. g. a lattice translation or libration, $H \cdots O$ stretching, or OHO bending. Thus all the combination frequencies envisaged by Stepanov[30], Batuev[30], Sheppard[30], and Angeloni et al.[32] are now genuinely allowed; even the restriction $\Sigma k = 0$ for multiphonon transitions does not operate. Though at 80 K difference bands will have very low intensities, »OH stretching« bands so spread out as to be invisible can be envisaged now.

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IZVLEČEK

Vibracijska spektroskopija spojin z zelo kratkimi vodikovimi vezmi. Vodni bisformatni ion. Primerjava z dvemi solmi v kristaliničnem stanju in nekaj opomb na široke, zvezne vibracijske trakove OH

Ernest Spinner

Predstavljeni so infrardeči spektri bisformatnih ionov, in sicer $(HCO_2)_2H^-$, $(HCO_2)_2D^-$, $(DCO_2)H^-$ in $(DCO_2)_2D^-$ v vodni raztopini in njihove izotopske mešanice $(HCO_2)(DCO_2)H^-$. Absorpcijski maksimum vOH in vOD je pri teh spojinah pri 1400 cm^{-1} in 1100 cm^{-1}, 1400 cm^{-1} pa pri odgovarjajočih Na$^+$ in K$^+$ soleh. Infrardeči in ramanski spektri vsebujejo vse trakove formatnega iona in večino trakov, ki jih pričakujemo od mravljinčne kisline. V bistvu gre za nespremenjen formatni ion, ki je kompleksiran z znatno spremenjeno mravljično kislino. Kompleks nima centrosimetrične strukture s točkovno grupo C$_{2h}$, ki jo sicer napoveduje -ab-initio račun z molekulskimi orbitalami, niti nima centrične vodikove vezi.

Velika odzivnost infrardečega spektra bisformatnega iona na molekulsko okolico kaže na to, da so krivulje potencialne energije, ki tvorijo energijsko hiper ploskev zelo spremenljive, kar tudi povzroča zvezni karakter traku vOH. Tega pripišemo naključno neurejenim fluktuacijam, ki so visoko anharmonične, valenčni nihanji vO—H in vH...O pa se spreminjata od dokaj normalnega do bolj »neobičajnega«, zaradi frekvenčnih fluktuacij. Pri tem je upoštevati kratkoživost fotonskega vzbujevalnega procesa, glede na te fluktuacije.