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IR-Spectra of Substituted Sodium Benzoates in Aqueous and Deuterium Oxide Solution

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The IR-spectra of the sodium salts of a series of substituted benzoic acids have been studied in aqueous and deuterium oxide solution in the region of the CO-stretching vibrations. Compared with the corresponding vibrations for the sulfinate group studied earlier these vibrations correlate poorly with the Hammett equation, and possible implications of these results are discussed.

The SO-stretching vibrations of a series of substituted aromatic sodium sulfinates, have been investigated in aqueous solution and correlated with the Hammett equation.[1] In discussing the character of the SO-bonds it was considered to be of interest to compare the results with a similar series of sodium benzoates. Although a considerable amount of IR work has been done on carboxylic acids [2-4] and their salts,[5-7] no systematic investigations on substituted alkali benzoates suitable for the present purpose could be found. The CO-stretching vibrations for a series of substituted sodium benzoates were therefore investigated under conditions comparable to those used in the investigation of the sulfinates, *i.e.* the spectra were recorded in ~10 % aqueous solution. The results are described in detail and discussed in this paper.

Since the asymmetric vibration occurred near a total absorption band in water, the spectra were also recorded in deuterium oxide, which is transparent in this region.[8] Thus it was ascertained that no serious distortions were caused in the peaks most close to the water absorption. In both solvents fairly sharp, well resolved strong peaks were obtained for both the asymmetric and symmetric vibrations.

RESULTS

Some typical spectra recorded in aqueous solution are shown in Fig. 1 and spectra recorded in deuterium oxide are shown in Fig. 2. The asymmetric and symmetric stretching vibrations in water and deuterium oxide are listed in Table 1. The asymmetric vibration occurs in the region 1530—1580 cm^{-1} and the symmetric vibration, which is much less sensitive to substituent

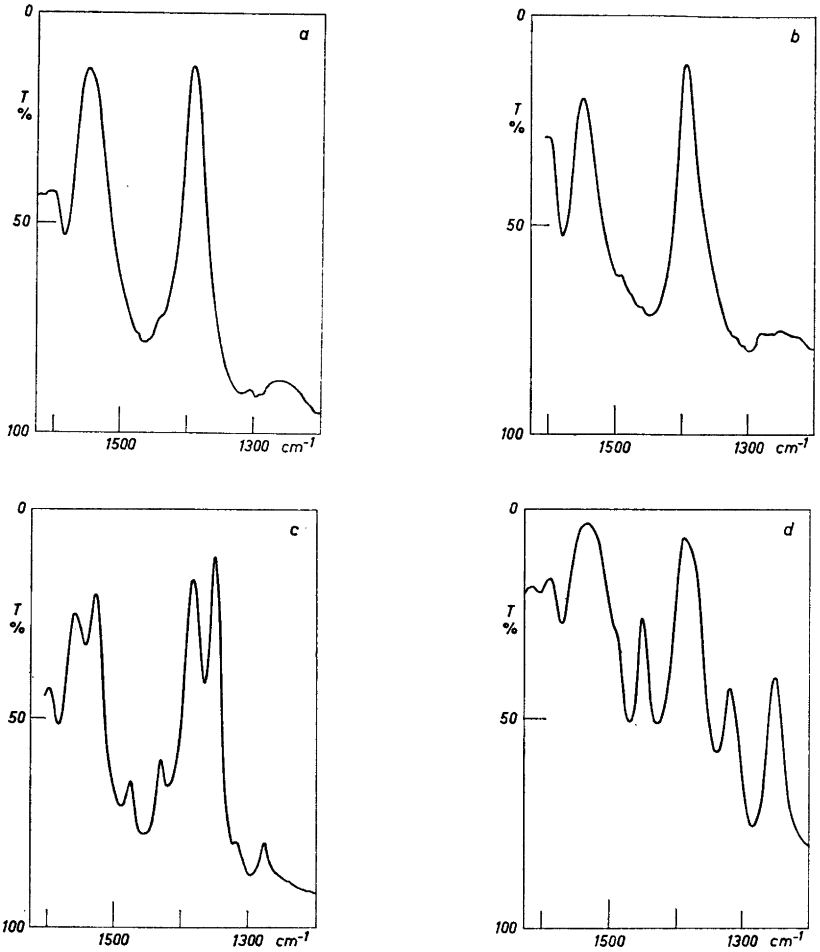


Fig. 1. IR-Spectra of substituted sodium benzoates in 10 % aqueous solution. a) no substituent, b) *p*-chloro, c) *m*-nitro, d) *o*-amino.

effects, near 1390 cm^{-1}. The frequencies are essentially the same in water and deuterium oxide, and the mean values for both solvents have been used for the plots.

In Fig. 3 the results for the *meta-* and *para*-substituted members have been plotted against the Hammett σ-constants. Appreciable scattering and deviations from a linear correlation are evident in both solvents. The use of other substituent constants, as for instance σ^+, which are only available for a smaller number of substituents, or averaging the asymmetric and symmetric frequencies do not result in better correlations. It can therefore be concluded that in contrast to the sulfinates, which correlate fairly well with the Hammett equa-

Table 1. IR-Spectra of substituted sodium benzoates in aqueous and deuterium oxide solution.

Substituent	10 % H_2O			0.55 M (8−12 %) D_2O				Average		
	σ [a]	ν_{CO} s.	ν_{CO} as.	ν_{CO} s.	ν_{CO} as.	Arom.	Misc.	ν_{CO} s.	ν_{CO} as.	ν_{CO} av.
H	0	1391	1548	1390	1549	1596 s	—	1391	1549	1469
p-NH_2	−0.66	1388	1532	1386	1532	1608	1589	1387	1532	1460
p-OH	−0.36	1386	1540	1384	1538	1602 s	1595 s	1385	1539	1462
p-OCH_3	−0.27	1389	1540	1388	1541	~1603 s	1595 s	1389	1541	1464
p-CH_3	−0.17	1391	1539	1390	1540	1640 sh	1589 s	1391	1540	1465
p-COO^-	0.13	1380	1562 br	1379	1562	—	1398 m	1380	1562	1471
p-Cl	0.23	1391	1544	1389	1543	—	1589 s	1390	1544	1467
p-SO_2O^-	0.37 [b]	1392	1552	1394	1553	—	1596 s	1393	1553	1473
p-NO_2	0.78	1392	1570	1390	1570	1610 m	—	1391	1570	1482
m-$N(CH_3)_2$	−0.21	1386	1550	1386	1550	1585 m	1410 sh	1386	1550	1486
m-CH_3	−0.07	1385	1548	1387	1548	1590 m	1410 sh	1386	1548	1467
m-OH	0.02	1390	1553	1385	1551	1592 m	1431 m	1388	1552	1470
m-SO_2O^-	0.31 [b]	1388	1555	1382	1554	1590 s	1416 w	1385	1555	1469
m-Cl	0.37	1382	1552	1381	1551	1589 s	1414 m	1382	1552	1467
m-NO_2	0.71	1382	1557	1381	1559	1594 s	1429 m	1382	1558	1470
o-NH_2		1385	1531	1387	1536	1580 s	1611 s	1386	1534	1460
o-OH		1391	~1585	1385	1555	1595 s	1624 s	1388	1555	1472
o-OCH_3		1399	1558	1395	1554	1582 s	1597 s	1397	1556	1477
o-CH_3		1405	~1560	1400	1552	1572 sh	1599 m	1403	1552	1478
o-COO^-		~1400	~1570	1400	1570	1690 m	1348 m	1400	1570	1485
o-Cl		1390	~1580	1393	1569 br	—	1328 m	1392	1569	1480
o-NO_2		~1398 as	≈1580	1392	1581 br	—	—	1392	(1581)	—

[a] σ-values taken from the compilation of Jaffé.[21]
[b] σ-values taken from Zollinger *et al.*[22]

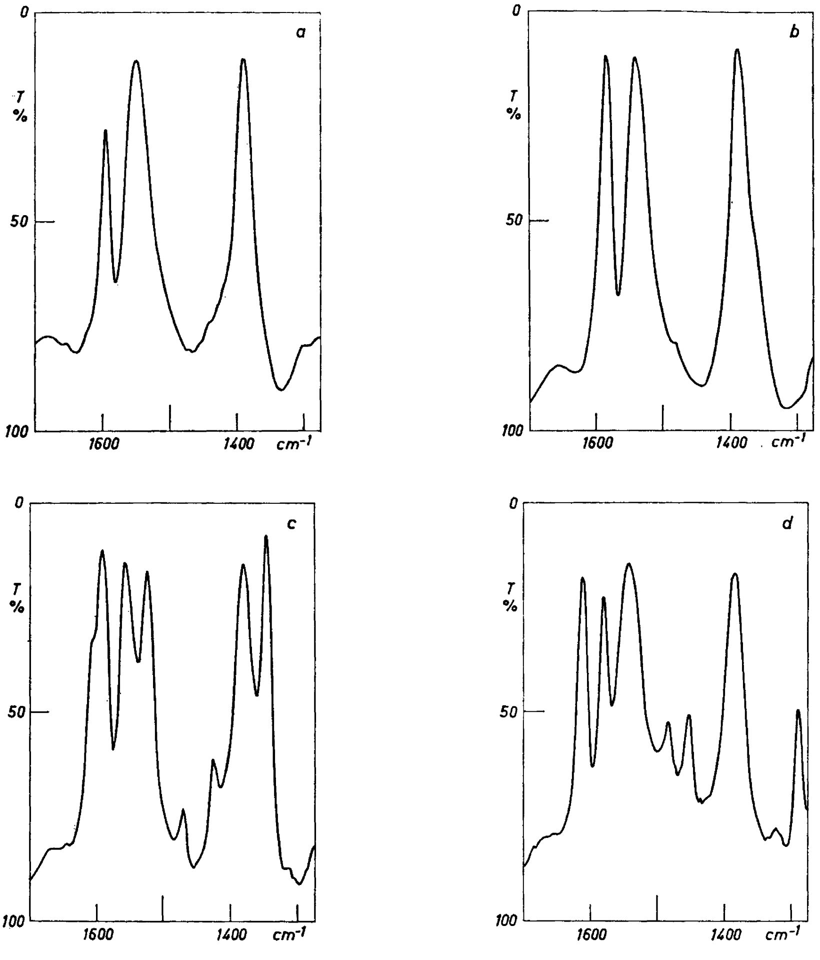


Fig. 2. IR-Spectra of substituted sodium benzoates in 8—12 % deuterium oxide solution. a) no substituent, b) *p*-chloro, c) *m*-nitro, d) *o*-amino.

tion, the benzoates fit the Hammett equation rather poorly. For the purpose of comparison with other groups approximate ϱ-constants have been estimated from the average slope, obtained by the method of least squares omitting the most deviating points (unfilled points in Fig. 3). The general trend is that the asymmetric vibration increases its frequency appreciably with the electron attracting power of the substituents ($\varrho = 21$, $r = 0.93$), whereas the symmetric vibration seems almost insensitive to substituent effects ($\varrho = -1$).

The value for the asymmetric vibration of the *para*-carboxy substituted benzoate seems to lie outside the general pattern. The asymmetric CO-frequency is too high and the symmetric CO-frequency seems too low. The average

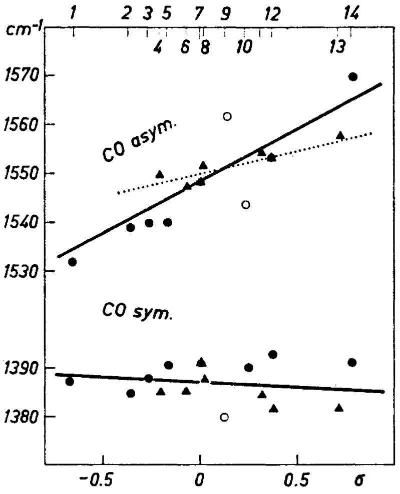


Fig. 3. Asymmetric and symmetric CO-stretching vibrations for substituted sodium benzoates. Substituents: 1, *p*-NH_2; 2, *p*-OH; 3, *p*-OCH_3; 4, *m*-$N(CH_3)_2$; 5, *p*-CH_3; 6, *m*-CH_3; 7, none; 8, *m*-OH; 9, *p*-COO^-; 10, *p*-Cl; 11, *m*-SO_3^-; 12, *m*-Cl; *p*-SO_3^-; 13, *m*-NO_2; 14, *p*-NO_2. ▲ *meta*-substituents. ●,○ *para*-substituents.

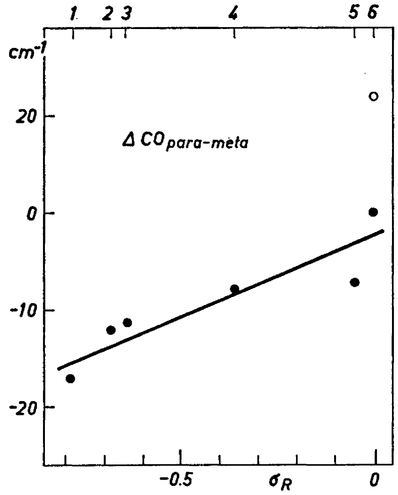


Fig. 4. Difference between the asymmetric CO-stretching vibration of *para*- and *meta*-substituted sodium benzoates. Substituents: 1, NH_2; 2, OH; 3, OCH_3; 4, Cl; 5, CH_3; 6, NO_2.

of the asymmetric and symmetric frequencies, however, falls into the general pattern for the *para*-substituted benzoates (Table 1).

The asymmetric CO-vibration of the *meta*-substituted benzoates (triangles in Fig. 3) is less susceptible to the substituent effects than that of the *para*-substituted benzoates and falls on a line with a smaller slope than the average slope (dotted in Fig. 3). A similar phenomenon has recently been reported[9] for substituted benzaldehydes, for which the *meta*-substituents fall on a different line from that of the *para*-substituents.

One possible explanation for poor correlation of IR-data with the Hammett equation could be that IR-frequencies and reactivities differ in their susceptibility to the resonance and inductive effects. The difference between the frequencies of the *para*- and the corresponding *meta*-substituted members, or between *para*-substituted members and the line obtained plotting the *meta*-substituted members against σ_I (in cases when no *meta*-substituted members are available for comparison) should then be roughly proportional to σ_R, and in several cases Krueger and Thompson[10] have observed such a proportionality. In Fig. 4, the difference between the asymmetric CO-frequencies in the *para*- and *meta*-substituted benzoates has been plotted against σ_R, and except in the case of the nitro group a rough proportionality is observed.

Recently Exner and Boček[11] have obtained very interesting results from an IR-study of the valence vibration of the C≡N bond in a large series of substituted aromatic nitriles. When correlating this vibration with the σ-constants for the substituents they observed three different classes of behaviour. *para*-Substituents with no free electron pair in the α-position raised the frequency proportionally to their σ_p-constant. *para*-Substituents with a free electron pair in the α-position strongly conjugated as donors with the benzene nucleus as well as with the cyano group, *i.e.* + M substituents, caused a larger lowering of the frequency than expected from their σ_p-constants, and this behaviour could not be accounted for by the σ^+-constants. The *meta*-substituents gave in all cases frequencies higher than expected from the σ_m-constant. If the asymmetric CO-frequencies are analyzed with these facts in mind, three different classes of substituents could possibly be distinguished also here; *cf*. Fig. 5. The *meta*-substituents (triangles), as already indicated in Fig. 3, fall on a separate line. The *para*-substituents with free electron pairs (+M substituents, plotted as squares) fall on a lower line of similar slope. The rest of the *para*-substituents (open circles, *para*-carboxy substituent omitted) fall on another line of greater slope. Using the average values of the asymmetric and symmetric CO-frequencies, the *para*-carboxy group becomes "normal". In Fig. 6, the averages for the *para*-substituents have been plotted. They also fall on two different lines with a relation between the slopes similar to that in Fig. 5.

As indicated in Fig. 5, the symmetric CO-frequency for the *meta*-substituted benzoates also seems to fall on a different line from that of the *para*-substituted

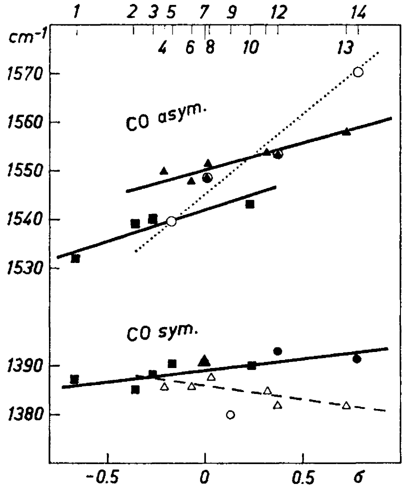


Fig. 5. Asymmetric and symmetric CO-stretching vibrations for substituted sodium benzoates. Substituents: Numbered as in Fig. 3. ▲,△ *meta*-substituents. ■ *para*-substituents with free electron pairs. ●,○ *para*-substituents with no free electron pairs.

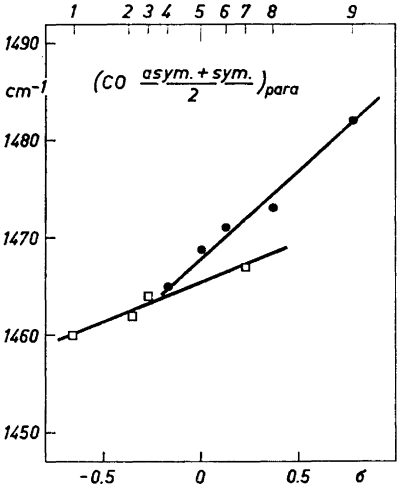


Fig. 6. Average of asymmetric and symmetric CO-stretching vibrations for *para*-substituted sodium benzoates. Substituents: 1, NH_2; 2, OH; 3, OCH_3; 4, CH_3; 5, none; 6, COO^-; 7, Cl; 8, SO_3^-; 9, NO_2. □ *para*-substituents with free electron pairs. ○ *para*-substituents with no free electron pairs.

Table 2. NO-stretching vibrations in sodium nitrobenzoates.

Substituent	NO sym./asym.		
	H_2O	D_2O	Average
p-NO_2	1346 s 1522 s	1343 s 1520 s	1345 1521
m-NO_2	1350 s 1526 s	1349 s 1526 s	1350 1526
o-NO_2	(1354)s [a] (1530)s [a]	1346 s 1522 s	1346 1522

[a] Peaks overlapping the CO-peaks.

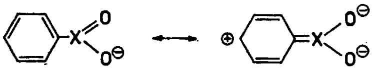
benzoates. In Table 2, the NO-stretching frequencies for the *nitro*-substituted benzoates have been given separately.

In considering these results, it must be realized that because of the small number of substituents and the experimental errors, it would probably not have been possible to distinguish two classes of *para*-compounds independently of the inferences arising from comparison with other sources, especially Ref. 11. In order to attach statistical significance to the existence of two different classes of *para*-substituents a much larger number of substituents is needed. However, when such distinctions are once ascertained in a few large series, they may be helpful for the understanding of apparent deviations in smaller series, provided they are used with due caution.

DISCUSSION

A priori there is no general reason why IR-frequencies should be expected to correlate well with the Hammett equation. However, in several cases, they do correlate fairly well, and groups, which are similar to the carboxylate group, *e.g.* the isoelectronic nitro group [12–14] or the sulfur analogue, the sulfinate group,[1] give fairly good correlations.

Difference between carboxylate and sulfinate group. The different behaviour of the aromatic carboxylate group may therefore be of general interest. It is of course very difficult at present to ascertain any definite reason for these different behaviours. However, it may be of value to discuss some possible reasons:



Ia Ib

1. IR-spectra of XO_2-groups may be expected to depend on the conjugation of the XO_2-group with the benzene ring, (I a, b) since such conjugation may change the bond orders of the bonds in the XO_2-group appreciably. A change in the bond orders of the XO- and XC-bonds will affect the XO- and XC-vibrations. It has been demonstrated that a change in the XC-bond order also affects the symmetric XO-vibration.[12,13] The effects of conjugation are therefore best studied on the asymmetric vibration.

In the nitro group, the symmetric NO-vibration for *para*-substituents is insensitive to the substituent effects for substituents with $\sigma > 0$ because of an abrupt change in the C—N bond order, which affects the NO-frequency.[13] Since the symmetric vibration of the carboxylate group is also found to be almost insensitive to substitution a similar effect seems to operate over the whole range of substituents in this case.

It has been suggested that the carboxyl and carboxylate groups conjugate to some degree with the benzene ring, which means that σ-constants determined by measurements on benzoic acids may include contributions from resonance effects,[15] and because of this the ordinary σ-constants for +M substituents are considered abnormal by Bekkum *et al.*[16] The carboxylate group may thus possess a weak —M effect. However, the CO-frequencies do not correlate well with either σ^+- or σ-constants. By contrast, because of the strong —M character of the nitro group, the asymmetric NO-vibration correlates well with the σ^+-constants,[14] which are usually employed in cases of enhanced conjugation.

As regards the sulfinate group, there is ample evidence that oxygen carrying sulfur (in sulfoxides and sulfones) can accept electrons from a benzene ring by utilization of 3*d* orbitals.[17,18] Hence it seems reasonable that the sulfinate group could also possess a weak —M effect. However, in contrast to the asymmetric CO-vibration of the carboxylate group the SO-vibrations of the sulfinate group correlate well with the σ-constants. This may seem contradictory, but there is a fundamental difference between the conjugation of the benzene ring with oxygen carrying sulfur groups and the conjugation with nitro, carbonyl, or cyano groups. This conjugation can occur in the oxygen carrying sulfur groups without necessarily affecting or involving the sulfur-oxygen bonds; *i.e.* the conjugation effect need not be transmitted to the sulfur-oxygen bonds, whereas it is transmitted to the carbon-oxygen bonds in the carboxylate group. This could possibly be a reason for the more regular behaviour of SO-stretching vibrations as compared with CO-stretching vibrations.

If one considers the conjugative properties of the XO-bonds, the carboxylate group could perhaps be regarded as being intermediate between the strongly conjugating nitro and weakly conjugating sulfinate groups causing the IR-frequencies to be more sensitive to differences in the conjugative properties of the substituents.

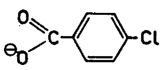
2. Another important difference between the carboxylate and sulfinate group is that sulfur is heavier (and larger) than carbon. The sulfinate group is therefore better "isolated"[19] than the carboxylate group and hence the SO-vibrations are less susceptible to mass or coupling effects from the rest of the molecule.[20]

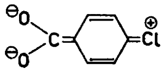
3. In aqueous solution, possible effects of hydrogen-bonding on the vibrations must be considered. It seems, however, rather unlikely that irregularities

in hydrogen-bonding properties, which could disturb the XO_2-frequencies, should be present in the carboxylate group, if they are not present in the sulfinate group.

The behaviour of the carboxylate group. Since IR-vibrations depend on bond orders, it seems reasonable that in certain cases the resonance components of the σ-constants affect vibrations more than reactivities. Since these are larger in σ_p- than in σ_m-constants, the *para*-substituted members of a series would in such a case be expected to differ in general behaviour from the *meta*-substituted members, and *para*-substituents with strong M effects would be expected to deviate appreciably from the correlation obtained with the *meta*- or ordinary *para*-substituents. The following two examples may be considered as illustrations:

1. The +M effect of the *chloro*-substituent diminishes the CO-bond order (II b), and consequently the *para*-chlorobenzoate (as well as other +M *para*-substituents) could be expected to fall on a lower line than the *meta*-substituted benzoate.


II a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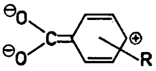
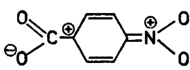

III a


III b

2. The weak —M effect of the carboxylate group alone, operating on the benzene ring will also diminish the CO-bond order to some extent (III a). When the carboxylate group is conjugated with a strong —M *para*-substituent like the nitro group, the competition from the stronger —M group could be expected to weaken its conjugation with the benzene ring (III b). The CO-bond order would thus become greater, and the *para*-nitrobenzoate would be expected to show a higher frequency than expected from comparison with the *meta*-nitrobenzoate. This suggests the use of the σ^--constants for —M substituents, and in fact if both σ^+- and σ^--constants are used, the general correlation improves somewhat.

It seems reasonable that differences in susceptibilities of frequencies and reactivities to such effects as described above could give rise to different classes of *para*-substituents. However, until more experimental evidence has accumulated, this explanation must be regarded as tentative.

EXPERIMENTAL

The sodium benzoates were prepared from commercial analytical grade or recrystallized reagent grade benzoic acids and recrystallized. Solvent of crystallization was carefully removed.

The IR-spectra were recorded with a Unicam SP 100 spectrophotometer. 0.55 M solutions (8 – 12 %) and a liquid cell with Irtran-2 windows and 25 μ path length were used. Polystyrene was used for calibration. The uncertainty in the evaluation of wave numbers from the peaks is estimated to ± 2 cm^{-1} in deuterium oxide. In aqueous solution it may in some cases be somewhat larger for the asymmetric vibration. The accuracy of the measurements is estimated to ± 2 cm^{-1}.

Note added in proof. Recently a paper dealing with vibrational spectral studies on a large series of substituted sodium benzoates in the solid state was published by Spinner.[24] Some benzoates were also measured in aqueous solution. The results are interpreted by a different approach than the present one, and it was concluded that instead of being a symmetrical resonance hybrid, the carboxylate grouping undergoes rapid conversion between classical structures. This offers an explanation for the nonsensitivity to polar effects of the absorption peak usually supposed to be due to a symmetric CO-stretching.

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