

SPECTROSCOPIC STUDIES OF SALTS OF 4-METHYL-BENZENESULFONIC ACID

II. THE SPECTRUM OF THE AMMONIUM IONS IN AMMONIUM 4-METHYL-BENZENESULFONATE

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Two bands of unequal intensity and half-width are found in the O-D stretching region of the room-temperature spectra of slightly deuterated ammonium 4-methyl-benzenesulfonate. The band at *higher* frequencies is broader and more intense than that having a lower frequency value. Such a spectral picture suggests an effective symmetry of the NH_3D^+ ions not much different from the ideal C_3v one, despite the fact that the site symmetry of the ammonium ions in the structure is only C_1 . Within each NH_3D^+ ion, the proton participating in the formation of the strongest hydrogen bond seems to be unique, whereas the remaining three are essentially equivalent, perhaps because of the rapid reorientation of the ions in the structure. The spectroscopic picture is not consistent with the published crystallographic data.

An ammonium ion librational band is found in the low-temperature spectra (around 430 cm^{-1}).

INTRODUCTION

Continuing our spectroscopic studies of salts of 4-methylbenzenesulfonic acid [1,2], we decided to study the spectra of ammonium 4-methyl-benzenesulfonate (abbreviated, hereafter, ApTS) and of its partially deuterated analogues.

Two recent papers [3,4] deal with the *crystal structure* of the title compound. In these papers, different settings ($\text{Pna}2_1$ and $\text{Pn}2_1\text{a}$ respectively) of the space group C_2v^9 (no. 33) were chosen. One type of ammonium ions, situated on sites with C_1 symmetry, exist in the structure of the title compound. According to the data contained in the more recent reference [4], the ammonium ions form four non-equivalent hydrogen bonds with $\text{N}\cdots\text{O}$ distances ranging from 273 to 302 pm (the values calcula-

ted by us* are 272.9, 277.3, 284.9 and 302.5 pm). The authors of ref. 3, however, state that only *three* hydrogen bonds are formed**. Such a statement apparently reflects the feeling of these authors that the N...O distance of ≈ 303 pm (the equivalent of the longest of the distances reported in [4]) does *not* represent a true hydrogen bond.

It should be noted that the distances determined by the two groups of authors, do not coincide within the limits of the reported experimental error.

As far as the ammonium ions are concerned, no mention is made, in either of the two papers, for a possibility of any kind of disorder.

The infrared spectra of ammonium 4-methyl-benzenesulfonate do not seem to be analyzed in detail and only the frequencies and the estimated intensities of the bands are given by Volodina *et al.* [5].

The complete analysis of the infrared spectrum of the 4-methyl-benzenesulfonate anion will be reported in due time [6]. In the present paper we shall focus our attention to the spectrum of the ammonium ions - protiated and partially deuterated.

EXPERIMENTAL

Ammonium 4-methyl-benzenesulfonate was prepared from ammonium carbonate and the monohydrate of 4-methyl-benzenesulfonic acid*** and recrystallized from water. ApTS was also obtained as a result of the action of ammonia vapours on a solution of 4-methyl-benzenesulfonic acid.

The deuterated analogues of ApTS were prepared similarly, but using H₂O/D₂O mixtures of appropriate composition.

The infrared spectra were recorded on a Perkin-Elmer 580 infrared spectrophotometer using Nujol and Fluorolube mulls and pressed disks in KBr. No significant difference were found between the two sets of spectra. The spectra in the region below 500 cm⁻¹ which are presented in this paper were recorded from Nujol mulls placed between polyethylene windows.

* These values were calculated from the atomic coordinates given in [4].

** The N...O distances are, reportedly, close to 274, 280 and 282 pm.

*** The latter compound is, in fact, oxonium 4-methyl-benzenesulfonate [7].

RESULTS AND DISCUSSION

The infrared spectra, recorded at room-temperature (RT) and the boiling temperature of liquid nitrogen (LNT) of ammonium 4-methylbenzenesulfonate are given in Fig. 1.

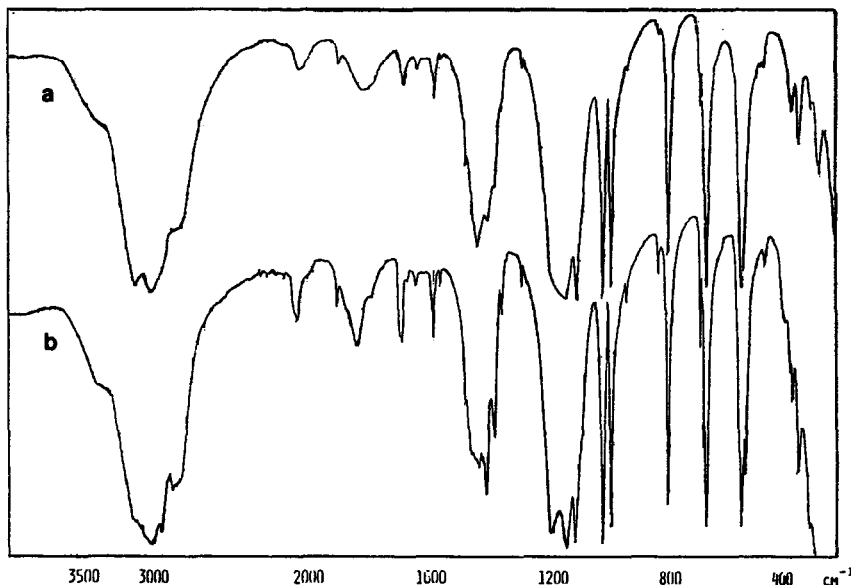


Fig. 1. RT (a) and LNT (b) spectra of ammonium 4-methylbenzenesulfonate

Stretching vibrations

As in practically all ammonium compounds, numerous and not well-resolved bands are observed in the N-H stretching region of the protonated ApTS (Fig. 1). The information which can be extracted from this spectral region is, thus, of limited value. Previous investigations [8-12] have, in fact, shown that in order to correlate the spectroscopic data with the structural features, best results can be obtained if the spectrum of isotopically isolated NH_3D^+ ions is studied. These ions are, of course, the predominant deuterium-containing species in the case of samples with very low deuterium content. The appearance of the spectra in the N-D stretching region of the slightly deuterated compound is shown in Fig. 2. The spectra were recorded at different temperatures, from RT (bottom curve) to LNT (uppermost curve).

As seen, in the RT spectrum two bands are found in the N-D stretching region of the sample with low (less than 10 %) deuterium content. The band at around 2235 cm^{-1} is considerably

less intense and its half-width is much less than that of the band centered around 2305 cm^{-1} . Such a spectral picture is quite unexpected if the crystallographic results [3,4] are taken into account. Namely, for ammonium ions situated on C_1 sites and forming four unequal hydrogen bonds [4] one would, rather, expect four bands with nearly equal intensity [9]. Because each of the four protons has an approximately equal chance of being replaced by a deuteron, four non-equivalent NH_3D^+ ions could be formed and, consequently, four N-D stretching bands should appear.

The observed spectral picture is, in fact, consistent with an effective symmetry of the NH_3D^+ ions close to C_{3v} and closely resembles that found by Oxtun *et al.* [10] in the case of ammonium tetrafluoroborate. As in this latter case, our RT spectra suggest that the proton forming the strongest hydrogen bond has a relatively fixed position, the three remaining protons being probably involved in rather rapid change of their position in the crystal. On the infrared time-scale this would, obviously, lead to an apparent equalization of these protons and, hence, to a symmetry of the NH_3D^+ ions approximating C_{3v} . Under such symmetry, the four expected N-D stretches of the isotopically isolated NH_3D^+ ions would group into one triply degenerate and one non-degenerate mode. The observed intensity of the two RT bands and their general appearance are consistent with such an explanation.

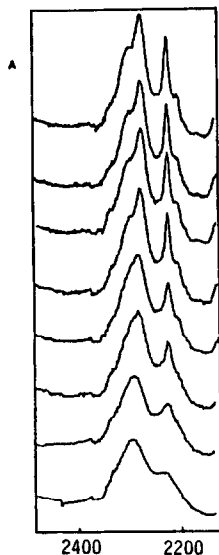


Fig. 2. The N-D stretching region in the spectra of slightly deuterated ApTS

When the temperature is lowered, an additional maximum becomes clearly visible next to the 2235 cm^{-1} band and a shoulder develops on the high-frequency side of the 2305 cm^{-1} band (cf. Fig. 2). Whether this represents a sign of a phase change is not clear at this point. It should be noted that phase transitions in ammonium 4-methyl-benzenesulfonate have been indicated [5].

Bending vibrations

An idealized NH_4^+ ion has one doubly degenerate and one triply degenerate bending vibrations. If the symmetry is lowered to C_{3v} , the degeneracy of the latter mode is partly removed and as a result two doubly degenerate modes of E symmetry and one non-degenerate of A_1 symmetry appear. For an NH_3D^+ ion of such symmetry, the expected frequencies are close to 1615 cm^{-1} (E), 1420 cm^{-1} (A_1) and 1260 cm^{-1} (E) [13]. The easiest to observe and thus

the most useful of these is the last of the three, since it falls in a region removed from the vibrations of the NH_4^+ ions.

As seen in Fig. 3*, the spectra of the slightly deuterated ammonium 4-methyl-benzenesulfonate in the $1290 - 1280 \text{ cm}^{-1}$ region differ from those of the protiated compound. It is unfortunate that in these latter spectra a band (assignable to a benzene ring vibration) is already present at 1309 cm^{-1} . It seems, nevertheless, that two new bands appear, the intensity and width of the band at lower wavenumber values exceeding those of the higher-frequency one. The situation is, thus, qualitatively similar to that found in the N-D stretching region, but with an inverted order of frequencies. This, of course, is something to be expected since as a rule *higher* bending frequencies of hydrogen-bonded species correspond to *lower* stretching frequencies. Thus, the analysis of this region seems to support the conclusions made earlier.



Fig. 3. The N-D bending region in the spectra of slightly deuterated ApTS

It is worthwhile mentioning that only one ND_4 bending band is observed (around 1080 cm^{-1}) in the spectrum of the sample with highest deuterium content. It must be kept in mind that strong bands exist at higher frequencies and an overlap with some of them could not be ruled out.

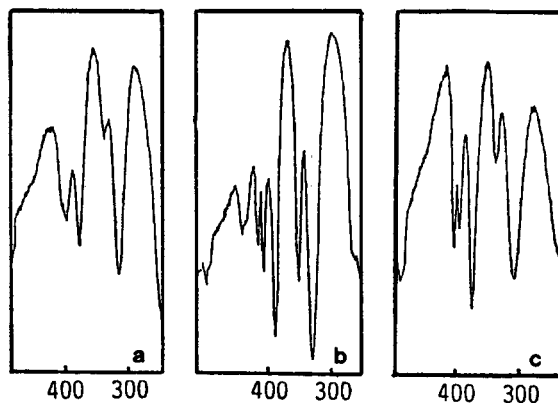


Fig. 4. RT (a) and LNT (b) spectra of protiated ApTS and LNT spectrum of deuterated ApTS (c) in the region of NH_4^+ librations

* The uppermost curve, as in Fig. 2, shows the LNT spectrum and the bottom curve - the spectrum recorded at RT.

Ammonium ion librations

In the spectra of ammonium compounds bands of non-negligible intensity are quite often seen in the 2200 - 1800 cm^{-1} region. Such bands are interpreted as due to second-order transitions involving the librations of the ammonium ions. The librational band itself is often of weak intensity or masked by other bands and is, thus, difficult to locate. As in other cases, in our spectra (Fig. 1) bands are seen around 2120 and 1855 cm^{-1} which can be interpreted as due to combinations of the ammonium ion libration with the symmetric and antisymmetric NH_4^+ bending respectively. The frequency of the libration, estimated from those of the above-mentioned bands, would be close to 430 cm^{-1} . A careful examination of the respective region (Fig. 4) shows that on lowering the temperature a band gains in intensity and shifts slightly towards higher wavenumber values - a behaviour typical for bands of librational origin. It is thus safe to assign to the librational mode the feature whose LNT frequency is close to 430 cm^{-1} . The sensitivity to deuteration and the temperature behaviour of this and the alleged combination bands is consistent with such an assignment.

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