

SPECTROSCOPIC STUDIES OF SALTS OF 4-METHYLBENZENESULFONIC ACID. IV. INTERNAL VIBRATIONS OF THE CATION IN THE INFRARED SPECTRA OF OXONIUM 4-METHYLBENZENESULFONATE

Mirjana Ristova and Bojan Šoptrajanov

*Institut of Chemistry, Faculty of Sciences, The "St. Kiril i Metodij" University Skopje
P.O. Box 162, Republic of Macedonia*

Abstract: The infrared spectra of the title compound, oxonium 4-methylbenzenesulfonate were studied, in the high-frequency region, at room temperature and at the boiling temperature of liquid nitrogen. Also studied were the spectra of the analogues in which the protium atoms were partly substituted with deuterium. The spectral picture in the region of H_3O^+ stretching vibrations is in agreement with the crystallographically determined short O...O contacts. A complex and structured feature reminiscent of the classical *A,B,C* trio and apparently due to Fermi resonances of the Evans type is observed in this region. The most likely candidates for such an interaction producing a transmission window (Evans hole) near 3260 cm^{-1} are the symmetric stretching H_3O^+ vibration and the overtone or a suitable combination of factor-group components of the symmetric bending mode (by implication, the frequency of the symmetric bending vibration must be close to 1150 cm^{-1}). In a situation like this, it is futile to seek a precise determination of the two stretching frequencies and, as a consequence, of the order in which these two modes appear in the spectrum. The asymmetric bending mode gives rise to a band whose frequency is close to 1640 cm^{-1} .

Introduction

Among the salts of 4-methylbenzenesulfonic acid¹, the title compound occupies a special position. This compound, widely known as *p*-toluenesulfonic acid monohydrate, has been proven [1, 2] to be, in fact, oxonium 4-methylbenzenesulfonate – one of the not very numerous compounds containing the oxonium cation, H_3O^+ . All three hydrogens of each oxonium ion are involved in the formation of quite strong, practically linear and almost equivalent hydrogen bonds with three different 4-methylbenzenesulfonate anions, the O...O distances ranging from 252.0 to 253.8 pm. The H–O–H and O...O...O angles

¹ An alternative (and even more common) name for this compound is *p*-toluenesulfonic acid from which the shorthand representation *p*TS for its anion is derived.

are also very similar. The values for the analogous parameters in the deuterated compound [3] are not significantly different. Although the H_3O^+ ions are situated in general positions, their effective symmetry is very close to the ideal C_{3v} one. Each of the three oxygen atoms of the SO_3 group serves as a proton-acceptor in a hydrogen bond formed with a different oxonium ion. A network of strong hydrogen bonds is thus formed suggesting that oxonium 4-methylbenzenesulfonate might act as a proton conductor.

In view of the rather exceptional structural characteristics, the infrared spectra of the title compound have received surprisingly little attention. To the best of our knowledge, the only published work is that of Basile *et al.* [4] who studied the infrared spectra (at room temperature only) of both protiated and highly deuterated oxonium 4-methylbenzenesulfonate. Under the impression that some of the conclusions of these authors are questionable, we decided to subject the title compound to a more rigorous infrared study, the spectra being recorded at room-temperature (RT) and at the boiling temperature of liquid nitrogen (LNT). Only the results concerning the spectral regions of the internal H_3O^+ vibrations are presented in the current paper and it is planned to publish the rest of the results in due time. It should be pointed out that the present study is a continuation of our previous work [5–7] on the infrared spectra of salts of 4-methylbenzenesulfonic acid.

Experimental

The protiated form of oxonium 4-methylbenzenesulfonate was a commercial product (Merck, p.a.) recrystallized from a 30 % aqueous solution of ethanol in an inert atmosphere. The crystals were hygroscopic. The deuterated analogue was obtained by repeated recrystallization from $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures of appropriate composition or from pure D_2O . The infrared spectra were recorded on a Perkin-Elmer 580 infrared spectrophotometer. For the low-temperature measurements a variable-temperature cell (RIIC, London) was used. Liquid nitrogen was used as a coolant. Spectra from both KBr pressed discs and Nujol mulls were recorded.

Results and discussion

An idealized pyramidal H_3O^+ ion with C_{3v} symmetry is expected to have two stretching vibrations – one symmetric, ν_1 (with A_1 symmetry) and one asymmetric, ν_3 (it is doubly degenerate, with E symmetry). The corresponding bands are expected in the high-frequency part of the mid-infrared region, their exact frequencies (and, perhaps, even the order of appearance) depending mainly on the hydrogen-bond strength. In addition to these, there is a non-degenerate bending vibration ν_2 of A_1 symmetry (usually found around 1150 cm^{-1}) and a doubly degenerate bending mode ν_4 of E symmetry (it appears between 1700 and 1600 cm^{-1}) [4]. Since the site group of the H_3O^+ ions in the

presently studied compound is only C_1 , all degeneracies should be removed and all vibrations should become both infrared and Raman active. Because of the presence of four formula units in the crystal unit cell, each of the non-degenerate modes and of the components of the doubly degenerate ones could be additionally split (as a result of interactions between identical oscillators in the unit cell) into two infrared active and two Raman active components. As mentioned above, however, the geometry of the H_3O^+ ions in oxonium 4-methylbenzenesulfonate is such that one does not expect a pronounced site-group splitting of the degenerate modes, the extent of the correlation-field splitting being difficult to anticipate *a priori*.

As already pointed out, practically all internal vibrations of the H_3O^+ ions give rise to bands appearing above 1600 cm^{-1} and if one is interested in these vibrations only², then it is sufficient to study the spectra in the $4000\text{-}1600\text{ cm}^{-1}$ region. The only mode falling outside the aforementioned region is the totally symmetric bending vibration ν_2 which is difficult to locate in the spectrum of the protonated compound since it is expected to appear in the region of strong absorption which is predominantly due to the stretching vibrations of the SO_3 groups (the attempts to locate the ν_2 oxonium band will be discussed near the end of the present paper). For a compound containing a benzene ring and a CH_3 group, bands due to C-H stretches and stronger sharp bands arising from ring stretching modes are also expected in the above-mentioned region.

The RT and LNT infrared spectra of oxonium 4-methylbenzenesulfonate recorded from KBr pellets are shown in Fig. 1. Immediately apparent is the broad complex feature covering practically the whole region down to 1550 cm^{-1} , but several sharp bands are also easy to notice. The latter bands (as well as the sharp bands appearing around 3000 cm^{-1} which are better visible in the LNT spectrum) are due to tolyl vibrations and, therefore, are not relevant to the present study.

The appearance of the rather strong band above 3200 cm^{-1} (such a band has not been mentioned before [4]) made us to suspect that it is an artefact due to some impurity or to some sort of interaction of the sample with the matrix. So, as mentioned in the experimental part, the spectra were recorded from samples dispersed both in KBr discs and in Nujol and the two sets of spectra were compared (Fig. 2). It is easily noticeable that the band under discussion is practically absent in the Nujol spectrum but, fortunately, the remaining bands in the two types of spectra are essentially identical, at least in the investigated region. It should be noted that our spectrum in Nujol corresponds very well to that reported by Basile *et al.* [4], except that these authors do not show the whole region and their spectra (of the protonated and deuterated oxonium 4-methylbenzenesulfonate) begin at around 2800 cm^{-1} .

² The oxonium ions in a crystal are expected to have external vibrations (hindered rotations and translations) as well. These latter modes are outside the scope of the present paper.

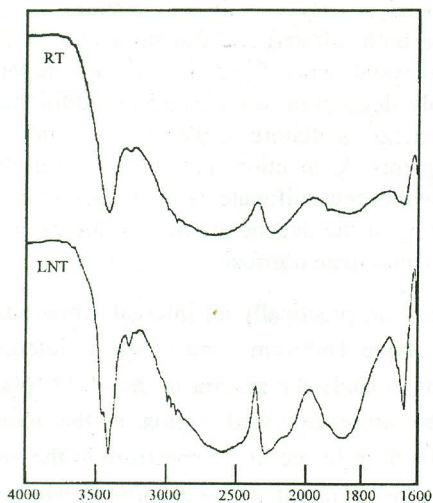


Fig. 1. – The high-frequency region of the infrared spectra of oxonium 4-methylbenzenesulfonate recorded at room temperature (RT) and at the boiling temperature of liquid nitrogen (LNT) from KBr pellets

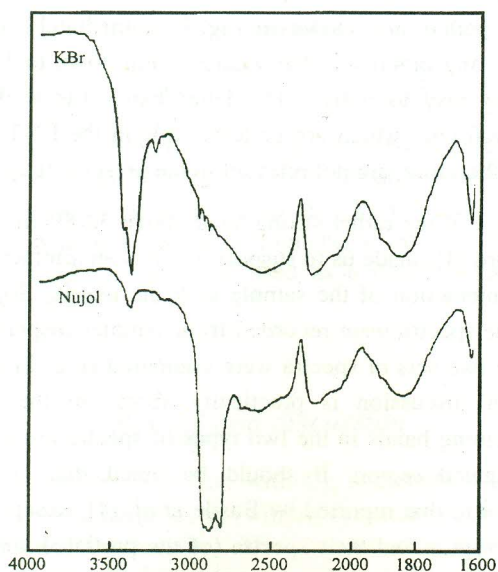


Fig. 2. – The high-frequency region of the spectra of oxonium 4-methylbenzenesulfonate recorded in a KBr pellet and in Nujol

Ignoring the bands above 3200 cm^{-1} , it is necessary to interpret the origin of the remaining ones. Basile *et al.* [4], mainly on the basis of their normal-coordinate treatment of the vibrations of the oxonium ion, concluded that the ν_1 mode has a *higher* frequency than the asymmetric stretching mode ν_3 and assigned the former mode to a 2700 cm^{-1} maximum and the latter to a much less pronounced peak appearing at around 2600 cm^{-1} . A rather guarded assignment along similar lines was given, for the case of $\text{H}_3\text{O}^+\text{SbF}_6^-$ and $\text{H}_3\text{O}^+\text{AsF}_6^-$ by Christie *et al.* [8] while other authors [9,10] prefer the opposite order of the stretching frequencies.

The fact of the matter is that in the case of such broad and structured features in the O–H stretching region as is the case here, it is difficult to say whether the observed peaks indeed arise from *true* bands or they just *seem* to represent bands. Namely, for a strongly hydrogen bonded system such as the present one, both ν_3 and ν_1 should give broad bands which may have similar frequencies, the spectral picture being further complicated by vibrational interactions of the fundamental stretching vibrations (one or both of them) with second-order transitions. The existence of a sharp (especially at LNT) transmission window around 2260 cm^{-1} strongly supports the notion of Fermi resonance (vibrational interaction of the Evans type [11–13]) of the stretching fundamentals with second order transitions (most probably, involving factor-group components of the ν_2 mode which should, then, have a frequency of 1150 cm^{-1} or slightly lower, i.e. exactly in the region where it is expected). If this is true, then the peaks flanking the window *do not* represent bands and no significance should be attached to their frequencies. Since the symmetry of the oxonium ion could not be significantly different from C_{3v} , a better candidate for interaction with the overtone of the ν_2 (under the C_{3v} symmetry, it is of the A_1 type) would be the totally symmetric mode ν_1 (its symmetry is A_1 , the same as that of $2\nu_2$) rather than ν_3 .

A strong (true or apparent) band centered around 1850 cm^{-1} is found in the spectrum of the protiated compound and is absent in that of the deuterated one (Fig. 3). It exists also in the spectra reported by Basile *et al.* [4] but is left there without any explanation. Its behaviour on deuteration proves that it originates from some H_3O^+ mode and it is highly probable that the transmission window somewhat below 2000 cm^{-1} is another example of Fermi resonance which would then qualify the 1850 cm^{-1} band as an equivalent of the third component (usually called 'band C') of what is known as *A,B,C* trio³ [14]. Such a trio is, it should be noted, characteristic for systems where there are hydrogen bonds of strength comparable to that of the H-bonds found in oxonium 4-methylbenzenesulfonate [15]. It is not clear whether only one of the stretching modes or both of them give rise to features of the '*A,B,C* trio' type. The difficulties of finding an equivalent of the 'band C' in the spectrum of the deuterated analogue is consistent with the known behaviour of this band on deuteration [16, 17].

The assignment of the band at around 1640 cm^{-1} to the asymmetric bending mode ν_4 is not only in agreement with the work of Basile *et al.* [4] (their frequency is somewhat higher) but is supported by its temperature and deuteration behaviour – on

³ The 'bands' *A* and *B* of the trio are expected at higher frequencies.

going from RT to LNT it is shifted towards higher frequencies while on deuteration it disappears. Its equivalent in the partly deuterated compound is found above 1180 cm^{-1} (cf. the middle curve in Fig. 3).

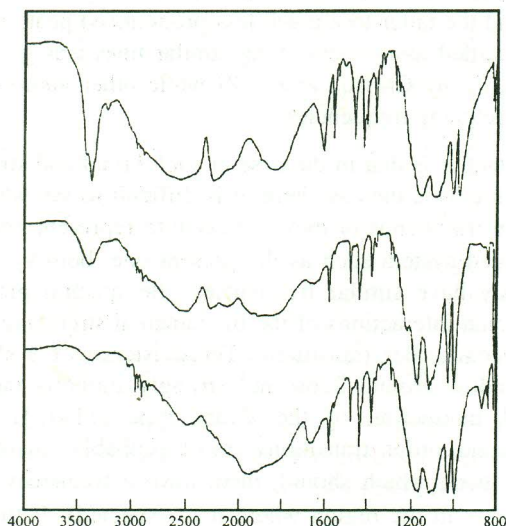


Fig. 3. – The spectra of the protonated oxonium 4-methylbenzenesulfonate and of two partially deuterated analogues (the deuterium content increases from top to bottom)

As already discussed, the Evans hole at around 2260 cm^{-1} can be interpreted as due to Fermi resonance between one of the oxonium stretching vibrations and the overtone of the symmetric bending vibration ν_2 . It is difficult to see whether or not a *band* sensitive to deuteration exists around 1150 cm^{-1} although it is clear that the bands around that frequency become narrower in the spectrum of the partly deuterated sample (the middle curve in Fig. 3). However, a new band of considerable intensity is clearly visible around 870 cm^{-1} in the spectrum of the most deuterated sample (the bottom curve in Fig. 3) and it is highly likely that it is due to $\nu_2(\text{D}_3\text{O}^+)$. Assuming a value of 1.32 for the isotopic ratio, the counterpart of this band in the spectrum of the protonated sample should indeed have a frequency close to 1150 cm^{-1} .

Conclusions

What has been said above can be summarized as follows:

- the two stretching vibrations apparently have similar frequencies and at least one of them (probably the symmetric one) is involved in Fermi resonance of the Evans type with the overtone of the symmetric bending vibration;

- because of such interactions, it is practically impossible to determine the *exact* frequencies of the two stretching modes, although it is likely that the symmetric stretching vibrations has a frequency close to that of the transmission window found around 2340 cm^{-1} ;
- the symmetric bending mode has a frequency of $\approx 1150\text{ cm}^{-1}$;
- the asymmetric bending mode gives rise to a band whose frequency is close to 1640 cm^{-1} .

Acknowledgment

The studies of the spectra of oxonium 4-methylbenzenesulfonate and its deuterated analogues were carried out as a part of a research project financed by the Fund for scientific research of the Macedonian Academy of Sciences and Arts. The authors are grateful for the financial assistance.

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Резиме

СПЕКТРОСКОПСКИ ИЗУЧУВАЊА НА СОЛИ НА 4-МЕТИЛБЕНЗЕНСУЛФОНСКАТА КИСЕЛИНА. IV. ВНАТРЕШНИ ВИБРАЦИИ НА КАТЈОНОТ ВО ИНФРАЦРВЕНИТЕ СПЕКТРИ НА ОКСОНИУМ 4-МЕТИЛБЕНЗЕНСУЛФОНАТ

Мирјана Ристова и Бојан Шоптрајанов

*Институт за хемија, ПМФ, Универзитет „Св. Кирил и Методиј“,
П. фах 162, 91001 Скопје, Македонија*

Изучувани, во високофреквентната област, се инфрацрвените спектри на оксоениум 4-метилбензенсулфонатот и тоа на собна температура и на температурата на вриење на течниот азот. Покрај тоа, изучувани се и спектрите на аналозите на ова соединение во кои дел од атомите на протииум се заменети со атоми на деутериум. Спектралната слика во подрачјето на валентните X_3O^+ вибрации е во согласност со постоењето на куси $O \cdots O$ растојанија, онакви какви што се најдени кристалографски. Во ова подрачје е најдена комплексна и структурирана лента што потсекава на класичното А,Б,Ц трио и, најверојатно, е резултат на фермиевски резонанци од евансовски тип. Најверојатните кандидати за вакви интеракции коишто доведуваат до појава на трансмисионо окно (евансовска дупка) на околу 3260 cm^{-1} се симетричната валентна X_3O^+ вибрација и овертонот, односно некоја погодна комбинација на фактор-груповите компонентни на симетричната деформациона вибрација која, во ваков случај, мора да лежи близу до 1150 cm^{-1} . При ваква ситуација, напразно е барањето фреквенциите на двете валентни вибрации да бидат точно определени и, како последица на ова, невозможно е да се утврди редоследот по кој тие две вибрации се појавуваат во спектарот. Асиметричната деформациона вибрација дава лента чија фреквенција е блиска до 1640 cm^{-1} .