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Raman and IR spectra of the unstable ionic species potassium trimethylsilanolate: The role of the counterion in its theoretical interpretation

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We have accomplished a reliable assignment of the vibrational spectra of the ionic species potassium trimethylsilanolate, which is unstable towards hydrolysis and self-condensation, by means of the combined use of experimental data and theoretical density functional theory (DFT) calculations. We report the first record of the Raman spectrum of the pure solid. Additionally, we have newly recorded its IR spectrum in Nujol mull and for the first time in Fluorolube mull, completing the experimental data available in the literature about this chemical species. Further, in order to discuss the convenience of including the counterion in the model used for the quantum-mechanical calculations of its vibrational spectra, we have compared the performance of three different theoretical models, namely, the isolated trimethylsilanolate anion, a theoretical monomer of potassium trimethylsilanolate and a simplified ionic cluster model based on its crystalline structure. Copyright © 2007 John Wiley & Sons, Ltd.

INTRODUCTION

Metallic alkylsilanolates have attracted the attention of several disciplines, as material science and catalysis, owing to their potential applicability to the preparation of inorganic materials.[1–8] Moreover, alkylsilanolates are intermediates of sol–gel processes of organometallic compounds of industrial relevance, for the obtaining of materials with improved properties.[9] IR and Raman spectroscopies jointly with NMR spectroscopy are the main tools for the monitoring of these processes,[10–17] and thus a deep knowledge of the vibrational spectra of reagents, intermediates, and products participating in them would be desirable.

However, due to the strong tendency of alkylsilanolates to react with atmospheric water (hydrolysis) and to self-condensation, the obtaining of experimental spectral information for these compounds is difficult, and the number of works dealing with their vibrational spectra are scarce in the literature. An overview reveals the existence of only two studies dealing with the vibrational spectra of

potassium trimethylsilanolate. Thus, in 1952, Tatlock and Rochow[18] described the preparation of several silanols and their alkaline salts. The mixture of metallic potassium and trimethylsilanol in anhydrous ether led to the obtaining of small cubic crystals of the salt. In this work, the first IR spectrum of the title species in the range 1200–600 cm^{-1} was also reported.

In 1964, Schmidbaur *et al.*[19] newly recorded the IR spectrum of the potassium trimethylsilanolate salt in Nujol mull in the same spectral range, and attempted a first assignment of the vibrational spectrum of this chemical species. In a latter work, also in 1964, Schmidbaur[20] reported the IR spectra in Nujol mulls of several related chemical species, with molecular formula $M^1[M^2(OSiR_3)_4]$ (with M^1 = Li, Na, K, M^2 = Al, Ga and R = CH_3), obtaining some additional, but likewise incomplete, spectral information of the trimethylsilanolate moiety.

Thus, the first goal of this work is to revise and to complete extensively the experimental spectroscopic information of potassium trimethylsilanolate (Fig. 1). For this task, we have recorded for the first time, the Raman spectrum of the pure solid and the IR spectrum of samples of this species in Fluorolube mull,

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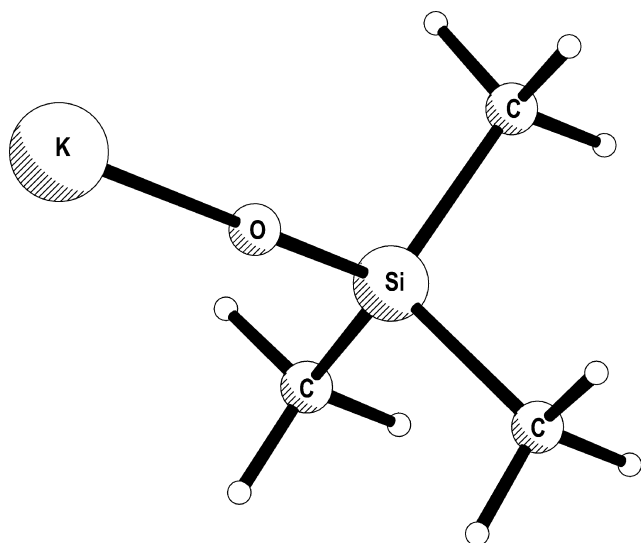E-mail: jjlopez@ujaen.es

Figure 1. Molecular representation of a theoretical monomer of potassium trimethylsilanolate.

and obtained new records of its IR spectrum in Nujol mull.

Moreover, theoretical calculations at the density functional theory (DFT) level were carried out in order to accomplish a complete analysis of the vibrational spectrum of potassium trimethylsilanolate. Therefore, bearing in mind recent works that have pointed out the convenience of including the counterion in the theoretical models used for a correct calculation of the vibrational spectra of charged species,[21,22] our second task is to compare the results from three different models: the isolated trimethylsilanolate anion, a theoretical monomer of potassium trimethylsilanolate, and a simplified ionic cluster model based on the potassium trimethylsilanolate tetramers previously described as the structural unit of the solid by means of X-ray diffraction.[23,24] The validity of the latter model and its ability to reproduce the experimental structure of the trimethylsilanolate group is thoroughly discussed in a previous work.[25]

Finally, the scaled quantum mechanics force field (SQMFF) methodology[26−28] was also implemented (only for the isolated anion and the monomer) to propose a reliable assignment of the vibrational spectra to the normal modes of potassium trimethylsilanolate in the range 3000–150 cm^{-1}.

EXPERIMENTAL

Samples of potassium trimethylsilanolate (98%, purchased from ABCR GmHb) were further purified by recrystallization using anhydrous ether as solvent and handled under Ar atmosphere to avoid hydrolysis and self-condensation processes. Additionally, as a previous step to the spectral acquisition, these purified samples were frozen in liquid nitrogen.

The Raman spectrum of the pure solid in the 3100–150 cm^{-1} region (Fig. 2), was recorded with an FT-Raman Bruker RF100/S spectrometer equipped with an Nd : YAG laser (λ = 1064 nm) and a Ge detector cooled to liquid nitrogen temperature.

The IR spectra from 3100 to 600 cm^{-1} were recorded in a FT-IR Bruker Vector 22 spectrophotometer equipped with CsI optics, a global source and a deuterated triglycine sulphate (DTGS) detector, at room pressure and temperature. The spectral records of the samples were made in Fluorolube and Nujol mulls. This first allowed the observation of the spectral region from 3000 to ~2800 cm^{-1}, (Fig. 3(A)). The vibrational spectrum of the species in Nujol mull, which has been used for the study of the 1300–600 cm^{-1} region, is shown in Fig. 3(B) along with the vibrational spectrum of pure Nujol recorded by us in the same conditions (exception made of the thinner spacer used) for comparison.

All the spectra were recorded with a resolution of 1 cm^{-1} and 100 scans.

COMPUTATIONAL DETAILS

The vibrational spectra of the isolated anion, the potassium trimethylsilanolate monomer, and the simplified ionic cluster model were calculated with the DFT/B3LYP method and the 6-31G* and 6-31+G* basis sets using the GAUSSIAN 03 program package.[29] The optimized structures of all the three models (the theoretical monomer is shown in Fig. 1 while the isolated anion and the cluster model are represented in Fig. 4) were reported elsewhere.[25]

The DFT-calculated force fields for the anion and the monomer were transformed into an appropriate system of the so-called natural coordinates (Table 1), as required for the use of the SQMFF methodology.[26−28] The scale factors associated with the force constants in terms of the natural coordinates defined in the case of the monomer, and the isolated anions were refined from their starting
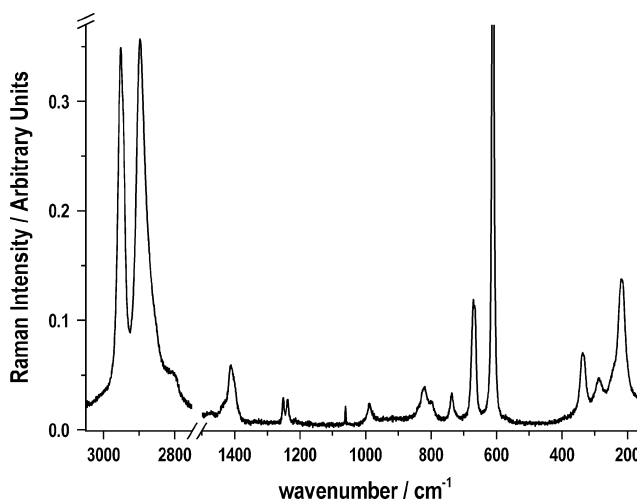

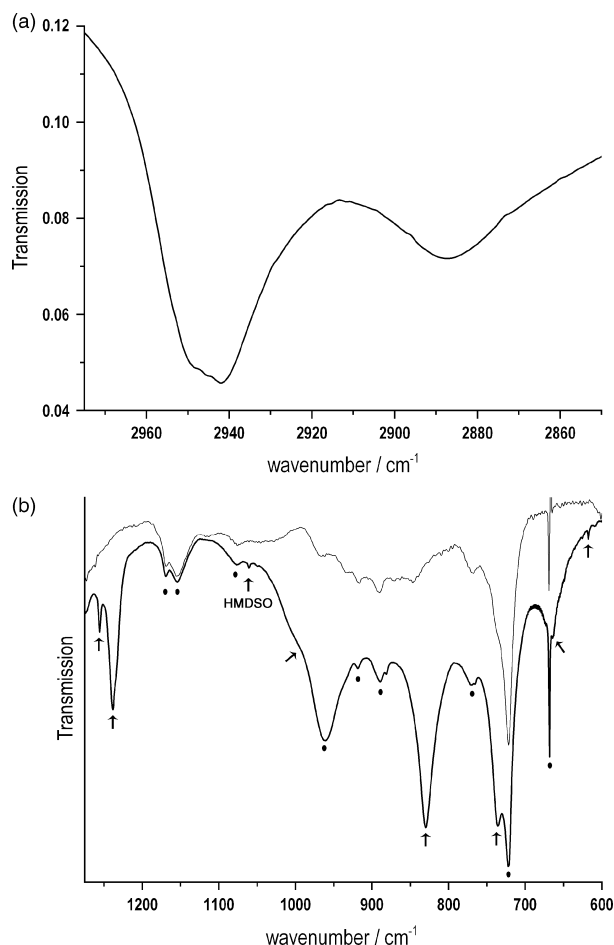**Figure 2.** Raman spectrum of potassium trimethylsilanolate.

Figure 3. A, upper: 2970–2850 cm^{-1} region of the IR spectrum of potassium trimethylsilanolate in Fluorolube mull; and B, lower: 1260–600 cm^{-1} region of the IR spectrum of potassium trimethylsilanolate in Nujol mull (in black) compared with the same region of the IR spectrum of pure Nujol (in gray). Solvent bands are marked with dots.

Table 1. Natural coordinates as defined for trimethylsilanolate anion[a]

Number	Description[b]	Definition[c]
1–3	ν SiC	R_{1-3}
4–12	ν CH	r_{4-12}
13	ν SiO	R_{13}
14–16	δ^sCH$_3$	$6^{-1/2}(\alpha_{1,4,7} + \alpha_{2,5,8} + \alpha_{3,6,9}$ $- \beta_{1,4,7} - \beta_{2,5,8} - \beta_{3,6,9})$
17–19	δ^{as}CH$_3$	$6^{-1/2}(2\alpha_{1,4,7} - \alpha_{2,5,8} - \alpha_{3,6,9})$
20–22	δ^{as}CH$_3$	$2^{-1/2}(\alpha_{2,5,8} - \alpha_{3,6,9})$
23–25	ρCH$_3$	$6^{-1/2}(2\beta_{1,4,7} - \beta_{2,5,8} - \beta_{3,6,9})$
26–28	ρCH$_3$	$2^{-1/2}(\beta_{2,5,8} - \beta_{3,6,9})$
29	δ^sSiC$_3$	$6^{-1/2}(\theta_1 + \theta_2 + \theta_3 - \phi_1 - \phi_2 - \phi_{3,})$
30	δ^{as}SiC$_3$	$6^{-1/2}(2\theta_1 - \theta_2 - \theta_{3,})$
31	δ^{as}SiC$_3$	$2^{-1/2}(\theta_2 - \theta_3)$
32	ρSiC$_3$	$6^{-1/2}(2\phi_1 - \phi_2 - \phi_3)$
33	ρSiC$_3$	$2^{-1/2}(\phi_2 - \phi_3)$
34–36	τ SiC	$9^{-1}(\tau_{1,10,19} + \tau_{2,11,20} + \tau_{3,12,21} +$ $\tau_{4,13,22} + \tau_{5,14,23} + +\tau_{6,15,24} +$ $\tau_{7,16,25} + \tau_{8,17,26} + \tau_{9,18,27})$

[a] For the potassium trimethylsilanolate monomer model three extra coordinates were defined, namely, the stretching of the OK bond and the deformations of the SiOK group in the two directions perpendicular to the SiOK lineal angle.
[b] Symbols used: ν, stretching; δ, deformation (superscripts 's' and 'as' denote symmetric and asymmetric); ρ, rocking; τ, torsion.
[c] Symbols used: r, bond stretching; α, bending HCH; β, bending HCSi; θ, bending CSiC; ϕ, bending CSiO; τ, bending HCSiO dihedral angle.

cluster, all the normal modes belong to the unique irreducible representation (A) of their symmetry point group C$_1$.

We have considered the observed vibrational bands from the Raman spectrum of the potassium trimethylsilanolate in solid phase as reference for the scaling and later refinement of the scale factors of the force constants. This is because the Raman spectrum is free of Nujol and Fluorolube bands[37] (that can occur in the IR spectra) and moreover, it is possible to work with a wider spectral range (3100–150 cm^{-1}). Henceforth, we will refer to them throughout this discussion.

The results of the whole vibrational assignment are collected in Table 2, where the scaled wavenumbers for the isolated anion and the monomer of potassium trimethylsilanolate, and the unscaled wavenumbers for the trimethylsilanolate moiety of the ionic cluster model are reported, along with the observed bands in the Raman and IR spectra recorded in the present work and the main terms of the potential energy distribution matrix (PEDM) for each normal mode.

Vibrational assignment

For clarity, the vibrational assignment is discussed dividing the mid-IR spectral region into several zones.

values, i.e. 1.000, using a least squares procedure, in order to reproduce the experimental frequencies from their B3LYP/6-31+G* initial theoretical values. Further, for the potassium trimethylsilanolate monomer, the B3LYP/6-31G* force field was also scaled with the set of scale factors previously obtained by our group from the study of a family of related compounds.[30–34] In both cases, the scale factors associated with the normal coordinates in which the counterion participates have remained unscaled. These tasks were accomplished using the program MOLVIB.[35,36]

RESULTS AND DISCUSSION

Theoretical and experimental data

According to its C$_{3v}$ molecular geometry, the 36 vibrational normal modes of the trimethylsilanolate anion are arranged by symmetry species as follows: 8A$_1$ + 4A$_2$ + 12E. For the potassium trimethylsilanolate monomer and the ionic
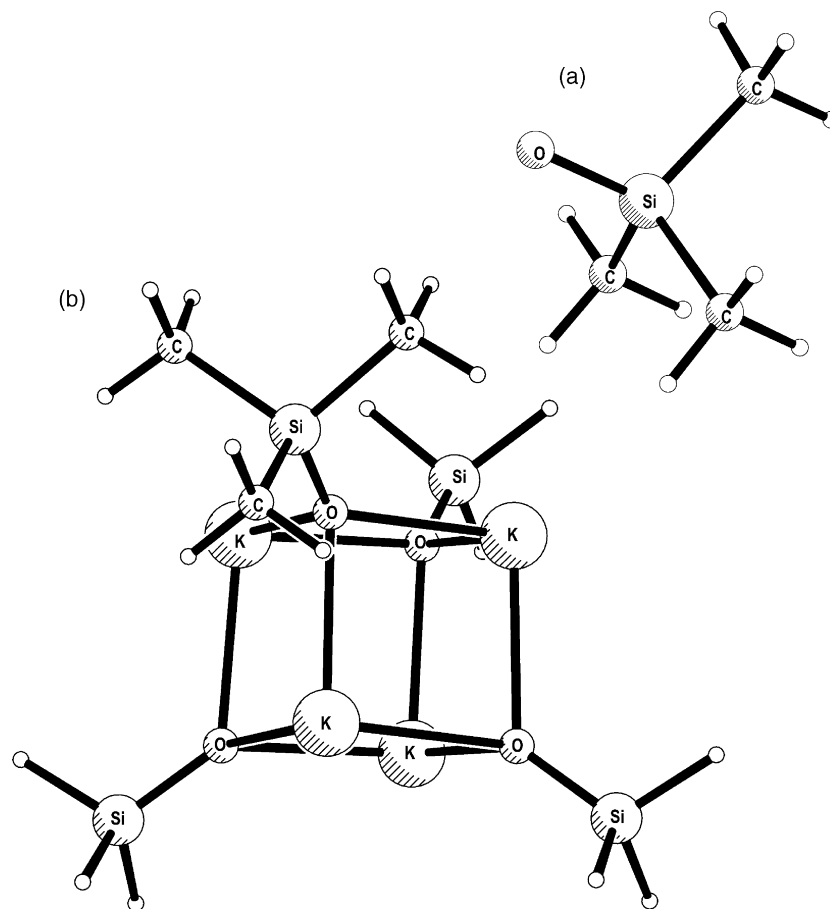
Figure 4. Molecular representation of the trimethylsilanolate anion (A, upper) and a theoretical simplified ionic cluster model constructed from the experimental structure of potassium trimethylsilanolate (B, lower).

C−H stretchings region

The use of Fluorolube has allowed us to make the first proposal of assignment for the spectral bands in this region.

We observed two vibrational bands in the Raman spectrum of the solid, i.e. at 2951 cm^{-1} and 2897 cm^{-1} (2942 cm^{-1} and 2887 cm^{-1} in the IR spectrum in Fluorolube mull). We have assigned them to the asymmetric and symmetric CH stretching normal modes respectively, as indicated in Table 2, obtaining a good correlation among the values calculated using both the isolated anion and the monomer approximation. Additionally, we have obtained reasonable values for the refined scale factors associated with these normal modes, which are reported in Table 3.

Methyl group deformations region

The record of the Raman spectrum has allowed us to firstly observe and assign the bands for the asymmetric methyl deformation normal modes. These modes are masked in the IR spectrum, as in previous works,[18−20] due to the intense Nujol absorptions around 1400 cm^{-1}.

In agreement with their calculated values, we have assigned the two vibrational bands appearing in the Raman spectrum of the solid, namely at 1430 cm^{-1} (sh) and 1410 cm^{-1}, to the asymmetric methyl deformations motions, as reported in Table 2.

Once again, a good correlation is found between the scaled frequencies obtained for both the isolated anion and the monomer, and reasonable values for the scale factors are calculated after its refining at B3LYP/6-31+G* level.

Only one band from the symmetric methyl deformations spectral region is reported in the literature,[19,20] at 1250 cm^{-1}. Nevertheless, in the present work, two vibrational bands have been observed in the Raman of the solid, at 1251 and 1237 cm^{-1}, and in the IR (Nujol mull), at 1256 and 1238 cm^{-1}. Those observed bands have been assigned to the two normal modes predicted by the theory to appear in this region as reported in Table 2.

Si−O bond stretching region

In the Raman spectrum of the solid, we have observed only two bands at 1061 and 988 cm^{-1} in this region. Nonetheless, this zone presents a complex shape in the IR spectrum where several peaks are observed around 1000 cm^{-1}; i.e. in addition to small absorptions of Nujol (at 919, 890, and 881 cm^{-1}), we have observed a peak at 1061 cm^{-1} and a broad band centered at 961 cm^{-1} with a shoulder at 986 cm^{-1}. As seen in

Table 2. Scaled B3LYP/6-31G* wavenumbers (in cm^{-1}) for the monomer of potassium trimethylsilanolate, scaled B3LYP/6-31+G* frequencies for the same monomer, and the isolated anion [OSiMe$_3^-$] and unscaled B3LYP/6-31+G* frequencies for the simplified ionic cluster used in the present work along with the bands observed experimentally and its assignment

B3LYP/6-31+G* (unscaled)	B3LYP/6-31+G* (scaled)		B3LYP/6-31G* (scaled)[c]	Experiment[d]		
Ionic cluster[a,b]	KOSiMe$_3$	[OSiMe$_3$]$^-$	KOSiMe$_3$	Solid Raman	Solid IR[e]	Assignment[f,g]
3090	2957	2963 (E)	2942	2951 vs	2942*	ν^{as}CH$_3$
3086	2955		2939			
3085	2955	2961 (A$_1$)	2939			
3079	2952	2954 (A$_2$)	2937			
3075	2951	2947 (E)	2936			
3074	2951		2936			
3016	2895	2895 (A$_1$)	2875	2897 vs	2887*	ν^sCH$_3$
3012	2891	2888 (E)	2871			
3011	2890		2871			
1503	1426	1428 (A$_1$)	1429	1430 sh		δ^{as}CH$_3$
1498	1415	1413 (E)	1420	1410 m		
1498	1415		1420			
1487	1407	1408 (E)	1412			
1486	1407		1412			
1485	1402	1400 (A$_2$)	1410			
1315	1247	1247 (A$_1$)	1242	1251 w	1256 w	δ^sCH$_3$
1305	1239	1239 (E)	1234	1237 w	1238 m	
1304	1239		1234			
					1169 vw	Nujol
					1154 vw	
				1061 w	1061 vw	HMDSO[h]
985	988	990 (A$_1$)	1058	988 w	986 sh	ν SiO
					961 m	Nujol
				918 vw		
				890 vw		
				881 vw		
857	827		817			
		822(E)		818 m		
					830 s	ρCH$_3$ (ν SiC$_3$)
856	827		817			
835	817	803 (A$_1$)	812	801 sh		
					770 vw	Nujol
759	735		726			
		738 (E)		736 w	736 s	ρCH$_3$ + νSiC$_3$
756	735		726			
					720 s	Nujol
656	659		650	670 m	668 m	
		654 (E)				ν SiC$_3$ + ρCH$_3$
653	657		649	666 m	664 vw	
615	622	627 (A$_2$)	624			ρCH$_3$
584	617	618 (A$_1$)	608	611 vs	618 vw	ν SiC$_3$
326	308					
			323	337 m		ν OK
324						
	293		300			
		288 (E)		287 w		ρSiC$_3$
	292		300			

(*continued overleaf*)

Table 2. (*Continued*)

B3LYP/6-31+G* (unscaled)	B3LYP/6-31+G* (scaled)		B3LYP/6-31G* (scaled)^c	Experiment^d		
Ionic cluster^{a,b}	KOSiMe$_3$	[OSiMe$_3$]$^-$	KOSiMe$_3$	Solid Raman	Solid IR^e	Assignment^{f,g}
	191	227(A$_1$)	200	220 m		δ^sSiC$_3$
	188		188			
		184 (E)				δ^{as}SiC$_3$
	184		187			
	164		164			
		154 (E)				τ SiC
	158		163			
	135	124 (A$_2$)	144			
	31		39			δ SiOK
	31		38			

^{a} Stoichiometry K$_4$[(OSiMe$_3$)(OSiH$_3$)$_3$].

^{b} Only shown modes belonging to the trimethylsilanolate moiety.

^{c} The scale factors used are shown in Table 3.

^{d} Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad.

^{e} All bands from the IR spectrum were recorded in Nujol mull, except those marked with * that were recorded in Fluorolube mull.

^{f} Only shown contributions higher than 10%.

^{g} Symbols used: ν, stretching; δ, deformation; ρ, rocking; τ, torsion. Superscripts 's' and 'as' denote symmetric and asymmetric motions.

^{h} HMDSO = hexamethyldisiloxane.

Fig. 3(B), pure Nujol presents some weak absorption peaks around 960 cm^{-1}, whose intensity is somehow enhanced in the spectrum of potassium trimethylsilanolate in Nujol mull. This may be due to the use of different spacers for the recording of each spectrum and to the mixed contribution of the proper band of Nujol and the 986 cm^{-1} band, which as will be explained below, is considered to be a fundamental vibrational band of the sample.

In this way, two bands appear simultaneously in both spectra (IR and Raman), i.e. those at 1061 and 988 cm^{-1}. The first has been described[38] as the asymmetric Si–O–Si stretching of hexamethyldisiloxane (HMDSO), which is a very common impurity in these types of samples, formed from the condensation of two trimethylsilyl fragments in presence of atmospheric water. This reaction can occur even during the recording of the spectra and, hence, is not easy to avoid.

Therefore, we have assigned the band at 988 cm^{-1} to the SiO stretching normal mode, in agreement with previous authors,[19,20] who assigned the SiO bond stretching to a band around 970 cm^{-1} in the IR of the solid in Nujol mull. As theoretical calculations concern, we have obtained a surprisingly low and possibly erroneous value of the scale factor associated with the SiO stretching natural coordinate from the isolated anion model, i.e. 0.837 (Table 3). Nevertheless, the value of this parameter is more reasonable (0.930) when the counterion is taken into account in the potassium trimethylsilanolate monomer model. At B3LYP/6-31G* level, the scale factor transferred from trimethylmethoxysilane,[33] i.e. 1.030, did not succeed in reproducing the experimental value.

Table 3. Refined values of scale factors obtained in the present work for the trimethylsilanolate group (B3LYP/6-31+G*) along with those transferred from related molecules to the potassium trimethylsilanolate monomer (B3LYP/6-31G*)^a

	B3LYP/6-31+G*^{b}		B3LYP 6-31G*
	KOSiMe$_3$	[OSiMe$_3$]$^-$	Ref. (30–34)^c
ν SiO	0.930	0.837	1.030
ν SiC	1.132	1.275	1.069
ν CH	0.920	0.934	0.905
δ^{as}CH$_3$	0.899	0.901	0.893
δ^sCH$_3$	0.912	0.953	0.886
ρCH$_3$	0.885	0.938	0.859
δ^{as}SiC$_3$	1.000	1.000	1.000
δ^sSiC$_3$	1.000	1.000	1.000
ρSiC$_3$	1.000	1.000	1.000
τ SiC	1.000	1.000	1.000

^{a} Symbols used: ν, stretching; δ, deformation; ρ, rocking; τ, torsion. Superscripts 's' and 'as' denote symmetric and asymmetric motions.

^{b} Obtained in the present work.

^{c} The scale factors associated with δ^{as}SiC$_3$, δ^sSiC$_3$, ρSiC$_3$ and τ SiC motions were fixed to 1.000.

Remarkably, the B3LYP/6-31+G* calculation over the ionic cluster (without scaling) yields a value of 985 cm^{-1} for the SiO stretching normal mode of the trimethylsilanolate group, that is very close to the experimental value.

From these results, it seems to be clear that taking into account the counterion in the model lead to a sensible improvement of the calculated value of the SiO stretching normal mode wavenumber compared to the observed experimental value.

CH₃ rockings and SiC bond stretchings region

For clarity, this spectral zone is divided into two subregions, i.e. between 840 and 700 cm⁻¹ and between 700 and 600 cm⁻¹.

In the Raman spectrum, we have observed three vibrational bands in the first subregion, namely at 818, 801, and 736 cm⁻¹. The first of them may be located under the contour of the intense band at 830 cm⁻¹ appearing in the IR spectrum mixed with an absorption band of Nujol at 840 cm⁻¹. The third band observed in the Raman spectrum appears at 736 cm⁻¹ in the IR, in a region where two more bands are observed due to the use of Nujol, i.e. at 770 and 720 cm⁻¹.

In accordance with the results of the scaling of the calculated force field, we have assigned these bands to the rocking normal modes of the methyl groups (with certain contributions of the SiC and SiO stretching normal modes), as reported in Table 2.

Three vibrational bands are observed in the Raman spectrum between 700 and 600 cm⁻¹, i.e. at 670, 666, and 611 cm⁻¹ that have their corresponding vibrational bands in the IR spectrum at 668, 664, and 618 cm⁻¹. As shown in Table 2, we assigned those bands to the SiC stretching fundamental normal modes, reaching an acceptable agreement between theory and experiment.

Remarkably, from the isolated anion model, the refined scale factor associated with the SiC stretching force constant reaches an excessively high and possibly erroneous value of 1.275, contrasting with potassium trimethylsilanolate monomer model, from which this parameter reaches a more reasonable value of 1.132. Additionally, the unscaled B3LYP/6-31+G* values calculated for the SiC stretching normal modes within the simplified ionic cluster model are reasonably close to the experimental frequencies (Table 2).

We conclude that in this case, as occurred with the SiO stretching mode, the introduction in the theoretical model of the counterion improves the calculated values of the SiC stretching normal modes.

Skeletal motions region

The scale factors related with the force constants associated with the natural coordinates involved in the description of the normal modes appearing in this region remained fixed to 1.000, within the SQMFF methodology.

The first band observed in this region appears at 336 cm⁻¹. In the case of the potassium trimethylsilanolate monomer, B3LYP/6-31+G* calculation predicts the presence of a band at 308 cm⁻¹, described as the OK stretching band. A couple of bands are also calculated at 326 and 324 cm⁻¹ describing the same motion from the ionic cluster model (Table 2). In contrast, no vibrational bands are

predicted in this region above 300 cm⁻¹ from the isolated trimethylsilanolate anion model, evidencing the convenience of including the potassium cation in the model to achieve a good description of the spectral features.

At lower wavenumbers, we have observed and assigned two bands, at 287 and 220 cm⁻¹ respectively, to the rocking and the symmetric deformation of the SiC₃ group, as reported in Table 2.

CONCLUSIONS

1. The new records of the IR spectrum of potassium trimethylsilanolate in Nujol mull and the first records of its Raman spectrum and IR spectrum in Fluorolube mull, have allowed us to complete the experimental data available in the literature for this chemical species.[18–20]

2. We have extensively completed and revised the vibrational assignment for the species, including the first proposal of assignment of the regions around 3000 cm⁻¹ (CH bond stretchings), 1400 cm⁻¹ (asymmetric methyl deformations), and below 350 cm⁻¹ (skeletal motions).

3. Theoretical calculations at B3LYP/6-31+G* and B3LYP/6-31G* levels and the latter use of the SQMFF methodology have demonstrated that the inclusion of the counterion in the theoretical models meanly improve the results of the vibrational assignment:

   a. More reasonable values of the scale factors associated with the SiO and SiC stretching normal modes are obtained when the theoretical monomer of potassium trimethylsilanolate is implemented, compared to the results obtained using the isolated trimethylsilanolate anion.

   b. Accurate theoretical values of the SiO and SiC stretching normal modes are calculated at the B3LYP/6-31+G* (without scaling) using a simplified ionic cluster model[25] based on the experimental structure of potassium trimethylsilanolate.[23,24]

   c. The vibrational band appearing at 335 cm⁻¹ in the Raman spectrum (assigned to νOK) is reproduced by both the monomer and the ionic cluster models, while no vibrational bands are predicted in this region when the trimethylsilanolate anion model is implemented.

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