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The ionic nature of methylsulfur trichloride species

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ABSTRACT

The Raman spectrum of the methyldichloro-sulfonium(IV) chloride, $CH_3SCl_2^+Cl^-$, is reported. The unambiguous vibrational assignment for the $CH_3SCl_2^+$ cation is made on the basis of the solid state Raman spectra aided by high-level quantum chemical calculations and a normal mode analysis. Actually, the former reported methylsulfur trichloride, CH_3SCl_3, can be now described as $CH_3SCl_2^+Cl^-$.

Introduction. Halodimethylsulfonium halide chemistry started with the discovery of bromodimethylsulfonium bromide [1,2], a compound that offers considerable promise as a potent reagent in current organic chemistry [3,4]. Chlorodimethylsulfonium chloride was early synthesized [5] and its implications in the atmospheric chemistry were discussed recently [6]. However, less is known on the analogous monomethylated species, possible due to their inherent instability. "Methylsulfur trichloride", CH_3SCl_3, was first synthesized by Brower and Douglas in 1951 [7] by chlorination of methyl disulfide in nearly quantitative yield. The crystalline compound is unstable and decomposes on standing at room temperature mainly into chloromethane sulfenyl chloride and methanesulfenyl chloride [8]. As early stated, CH_3SCl_3 is insoluble in non-polar solvents and it is hydrolyzed by water into methanesulfinic acid [7]. Moreover, chlorination of different types of organic sulfur compounds, such as thioesters and xanthates, also leads to the formation of alkylsufur trichlorides, which were chemically characterized [9,10]. Further studies concerning the mechanism of chlorination of sulfenyl chorides have been reported [11,12]. Although unstable, these compounds are useful reagents for the synthesis of sulfur compounds. Thus, when organosulfur trichlorides, $RSCl_3$, are treated with water, alcohols, or carboxylic acids, solvolysis occurs and the corresponding sulfinyl chlorides, RS(O)Cl, are smoothly produced in excellent yields [13]. Moreover, the reaction with optically active alcohols produced alkyl chlorides with a high degree of inverted configuration [14].

The structure of CH_3SCl_3, whether ionic or covalent, has remained unresolved. As early stated by Douglass and coworkers in the series of very informative articles on CH_3SCl_3, "no evidence other than its solubility characteristics has been found for an ionic structure for the compound" [7]. More recently, related methyldihalo-sulfonium species were synthesized and the vibrational assignments for $CH_3SCl_2^+SbCl_6^-$ [15–17] and $CH_3SCl_2^+AsF_6^-$ [18] were discussed. In this letter, we report the Raman spectrum of the solid product formed by chlorination of methyl methylxanthate [10]. The analysis of this spectrum together with the results from the quantum chemical calculations strongly suggests a $CH_3SCl_2^+Cl^-$ ionic structure instead of covalence for this compound. Moreover, a definite assignment for the $CH_3SCl_2^+$ cation is given.

Experimental. Methyl methylxanthate was dissolved in freshly distilled hexane and chlorinated according to the method of Douglass and Osborne [10]. A gentle stream of chlorine was passed into the cooled solution until, after alternately shaking and settling, no more solid appeared to form. This orange liquor was filtered and the solid washed several times with chilly hexane. A 6 mm o.d. tube was filled with the solid and dried in a vacuum. The tube was flamed-sealed and maintained in liquid nitrogen until the measurement.

The FT-Raman spectra were recorded in the region 4000–100 cm^{-1} using a Bruker IFS 66v spectrometer equipped with Nd:YAG laser source operating at 1064 μm line with 7.5 mW power of spectral width 2 cm^{-1}. Higher laser power leads to decomposition of the sample, evidenced by the appearance of a red-yellow liquid.

Quantum chemical calculations were performed with the GAUSSIAN03 program package [19]. MP2 and B3LYP methods and gradient techniques were used for the geometry optimizations and calculation of the vibrational properties, together with standard basis sets up to the Pople-type 6-311++G**, which includes diffuse and polarization functions. The more extended aug-cc-pVTZ basis set was also applied with the B3LYP functional. Recommended frequency scale factor was applied [20] and the calculated Raman activities were converted to relative Raman intensities following the usual methodology [21]. For the

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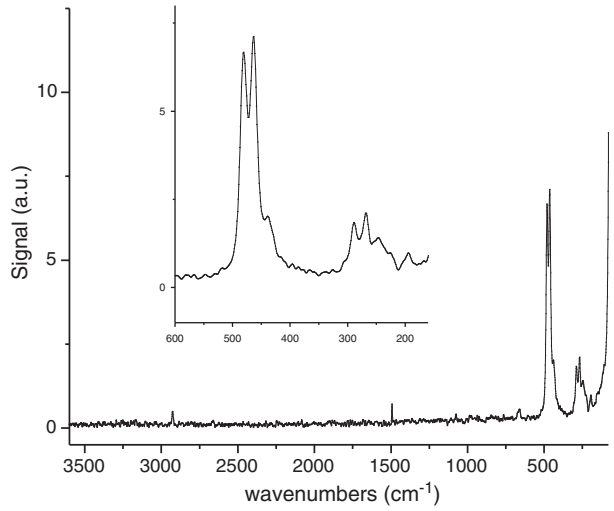

Fig. 1. Raman spectrum of solid $CH_3SCl_2^+Cl^-$.

normal coordinate analysis, transformations of the ab initio Cartesian harmonic force constants to the molecule-fixed internal coordinates system were performed, as implemented in the ASYM40 program [22]. This procedure evaluates the potential energy distribution (P.E.D.) associated with each normal vibrational mode under the harmonic assumption. The internal and symmetry coordinates used to perform the normal coordinate analysis are defined in Figs. S1 and Table S1, respectively (given in the Supplementary Material).

Results and discussion. The Raman spectrum obtained for the solid is shown in Fig. 1. Table 1 lists the observed bands together with the computed value obtained for the $CH_3SCl_2^+$ cation and our proposed bands assignments. The $CH_3SCl_2^+$ cation, with C_S symmetry, presents 9 "in-plane" (A′) and 6 "out-of-plane" (A″) normal mode of vibrations, all of them are both IR and Raman active. The Raman data for methyldichloro-sulfonium salts previously reported, $CH_3SCl_2^+SbCl_6^-$ [15–17] and $CH_3SCl_2^+AsF_6^-$ [18] are also included in Table 1. As recognized by Askew et al. [16] the assignment for the low-energy modes of $CH_3SCl_2^+$ is complicated by the presence of strong bands due to the anion ($SbCl_6^-$ or AsF_6^-). In our case, however, the Raman spectrum is very simple, allowing for a straightforward assignment, especially when assisted by the quantum chemical calculations and the determination of the PED contribution for each normal mode. The scaled MP2 and B3LYP (6-311++G**) computed frequency values are similar and the inclusion of large basis set (B3LYP/aug-cc-pVTZ) has a little influence in the computed spectrum (see Table 1), given the confidence to the theoretical description on the vibrational properties of $CH_3SCl_2^+$.

The weak band at 2927 cm^{-1} was assigned to the totally symmetric stretching mode of the methyl group on $CH_3SCl_2^+$. All the other normal modes observed in the Raman spectrum are related with the heavy atom skeleton. Thus, the ν(C–S) stretching is observed as a weak band at 662 cm^{-1}, in very good agreement with the reported values for related species [15–18].

The two strong signals at 482 and 463 cm^{-1} can be confidently assigned to the antisymmetric and symmetric motions on the SCl_2 group, respectively. The observed splitting of 19 cm^{-1} is in fine agreement with the computed values (20 cm^{-1}). There exist discrepancies between the available assignments for the $CSCl_2$ deformation modes on $CH_3SCl_2^+$ [15–18]. Our data suggest to assign the band at 289 cm^{-1} to the symmetric deformation [$\delta_s(CSCl_2)$] and the broad band at 268 cm^{-1} for the antisymmetric counterpart, in line with the analysis by Minkwitz and coworkers for the $CH_3SCl_2^+AsF_6^-$ complex [18].

With the help of quantum chemical calculation, the following broad and weak band is tentatively assigned to the torsion mode of the CH_3 group around the C–S bond, with contribution of the $\delta_{as}(CSCl_2)$ deformation with proper symmetry (A″). The detailed analysis of the Raman spectrum of $CH_3SCl_2^+SbCl_6^-$ leads Askew et al. [16] to recognize that the strong band at 173 cm^{-1} due to $SbCl_6^-$ presents a shoulder at 180 cm^{-1}, which was tentatively assigned to the cation. In our case, a signal at 194 cm^{-1} can be unambiguously determined in the Raman spectrum without the interference of the $SbCl_6^-$ anion. This band is assigned to the $\delta(SCl_2)$ fundamental.

Conclusion. By using Raman spectroscopy and quantum chemical calculations the ionic nature of the methyldichloro-sulfonium chloride, $CH_3SCl_2^+Cl^-$, has been determined. The first unambiguous vibrational assignment for the $CH_3SCl_2^+$ cation (with C_S symmetry) is presented.

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Table 1
Raman bands (cm^{-1}) for the $CH_3SCl_2^+$ cation observed in salts $CH_3SCl_2^+X^-$ with (X = Cl, AsF_6 and $SbCl_6$). Computed (B3LYP and MP2 methods with the 6-311++G** basis sets) vibrational data for $CH_3SCl_2^+$ with the proposed assignment and Potential Energy Distribution (PED) values.

Raman (solid)				B3LYP[a]		MP2[a]	Symmetry/assignment (% PED)
X = Cl[This work]	X = $SbCl_6$ [16]	X = $SbCl_6$ [17]	X = AsF_6 [18]	Aug-cc-pVTZ	6-311++G**	6-311++G**	
				3072	3065 (6)	3058 (7)	A′/ν_{as} (CH_3) (100)
				3044	3041 (10)	3044 (11)	A″/ν_{as} (CH_3) (100)
2927 (6)				2947	2941 (27)	2931 (29)	A′/ν_s (CH_3) (100)
				1391	1379 (7)	1367 (8)	A″/δ_{as} (CH_3) (56) + A′/δ_{as} (CH_3) (43)
				1387	1377 (6)	1365 (9)	A′/δ_{as} (CH_3) (87) + A′/δ_s (CH_3) (12)
				1307	1319 (2)	1337 (2)	A′/δ_s (CH_3) (100)
				961	974 (2)	983 (3)	A′/ρ_s (CH_3) (90) + A′/δ_s (CH_3) (10)
				953	963 (1)	965 (2)	A″/ρ_{as} (CH_3) (71) + A″/δ_{as} (CH_3) (25)
662 (6)	670	666	670 m	619	608 (17)	689 (19)	A′/ν (C–S) (100)
482 (93)	536	535	545 w	506	474 (34)	514 (36)	A″/ν_{as} (SCl_2) (100)
463 (100) 441 sh	512	513	523 w	494	464 (98)	489 (77)	A′/ν_s (SCl_2) (100)
289 (27)	290 ($SbCl_6^-$)	290 ($SbCl_6^-$)	305 w	272	268 (54)	278 (49)	A′/δ_s($CSCl_2$) (77) + A′/δ_s(CH_3) (10)
268 (35)	260	263 ($SbCl_6^-$)	270 w	228	223 (17)	244 (1)	A″/δ_{as}($CSCl_2$) (65) + A″/τ(—CH_3) (35)
249 br (17) 226 sh	212	213	221 m	211	217 (28)	228 (41)	A″/τ(—CH_3) (65) + A″/δ_{as}($CSCl_2$) (35)
194 (10)	180	176 ($SbCl_6^-$)	–	193	190 (100)	199 (100)	A′/$\delta(SCl_2)$ (75) + A′/δ_s($CSCl_2$) (23)

[a] Scaled computed frequencies, in parenthesis computed Raman intensities (see details in the Experimental section).

Appendix A. Supplementary material

Symmetry and internal coordinates for $CH_3SCl_2^+$ (C_S) used in the PED analysis are given in Table S1 and Figs. S1, respectively. Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2012.09.027.

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