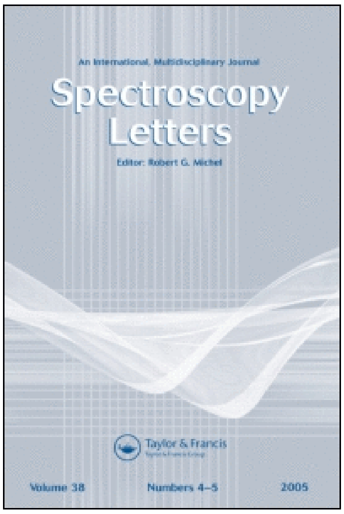

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Infrared and Raman Spectra of Tribromoacetic Acid and Its Potassic Salt

F. Márquez[a]; M. I. Suero[b]; J. C. Otero[c]; J. I. Marcos[c]
[a] Department of Physical Chemistry, University of Granada, Spain [b] Department of Physics, University of Extremadura, Spain [c] Department of Physical Chemistry, University of Malaga, Spain

To cite this Article Márquez, F. , Suero, M. I. , Otero, J. C. and Marcos, J. I.(1992) 'Infrared and Raman Spectra of Tribromoacetic Acid and Its Potassic Salt', Spectroscopy Letters, 25: 6, 821 — 830
To link to this Article: DOI: 10.1080/00387019208020714
URL: http://dx.doi.org/10.1080/00387019208020714

SPECTROSCOPY LETTERS, 25(6), 821-830 (1992)

INFRARED AND RAMAN SPECTRA OF TRIBROMOACETIC ACID AND ITS POTASSIC SALT

Key Words: Infrared, Raman, Structure, Tribromoacetic.

F. Márquez[#], M.I. Suero*, J.C. Otero** and J.I. Marcos**.

Department of Physical Chemistry. University of Granada. Spain.
*Department of Physics. University of Extremadura. Spain.
**Department of Physical Chemistry. University of Malaga. Spain.

ABSTRACT

Infrared and Raman spectra of tribromoacetic acid and its potassic salt have been recorded as solid and aqueous solutions. A general assignment of the vibrational spectrum of the acid has been proposed on the basis of a symmetry of centrosymmetric dimers. The results agree with those for other halogen derivatives of acetic acid.

[#] Author to whom correspondence should be addressed. Departamento de Química Física, Facultad de Ciencias Experimentales, Paraje las Lagunillas, 23071 Jaén, España.

INTRODUCTION

Previously we have carried out several studies on the vibrational spectra, infrared and Raman, of molecules containing the CBr_3 group, such as tribromoacetamide[1], tribromoacetonitrile[2-4] and tribromoacetaldehyde[5]. In this paper the vibrational spectra of tribromoacetic acid as well as its potassic salt are presented and discussed.

No vibrational study of that acid has been published, though a partial study of the ion has been reported[6]. Neither the solid structure has been reported too, for this reason a tentative for a complete assignment on the basis of the experimental data is done. Anyway, we have obtained an optimization of geometry through MNDO, AM1 and PM3 semiempiric methods.

The crystal structures of some halogen-substituted derivatives of acetic acid have been reported. Both trifluoroacetic acid[7] and trichloroacetic acid[8] are composed of hydrogen-bonded centrosymmetric dimers packing with normal van der Waals separations whereas the acetic acid has been found[9] to form infinite chains in the crystalline state.

Since the spectroscopic researches of the trifluoroacetic acid[10], bromoacetic acid[11] and β-chloroacetic acid[12] are consistent with hydrogen-bonded dimer structure we have considered the centrosymmetric dimers with C_{2h} symmetry in order to discuss the proposed assignments of solid tribromoacetic acid.

EXPERIMENTAL

Tribromoacetic acid was obtained from Aldrich with a 99°/₀ of purity. Purification was carried out by dissolving the acid in an aqueous solution of KOH and treating it several times with active charcoal. Solutions were filtered, evaporated and dried under vacuum over P_2O_5. Potassium salt as well as its saturated aqueous solutions were prepared starting with the previously purified acid by neutralization with KOH and following the same procedure for purification. Other samples of potassium salt were prepared from the acid and an amount of KOH exceeding the stoichiometric one by a 10°/∘. These samples were used to obtain saturated aqueous solutions in order to avoid hydrolysis of the salt. Raman spectra of these solutions were recorded.

Deuterated samples were obtained using D_2O (99.9°/∘) solutions and subsequently crystallizing twice from the same solvent. Infrared analysis showed that -COOH group was deuterated by more than a 97°/∘.

Infrared spectra were recorded in the range 4000-200 cm^{-1} on a Beekman 4260 and a Perkin Elmer 399 spectrophotometers in different matrices (KBr, Nujol and polyethylene). No significant interaction with the matrices was detected. The experimental error was ±0.5 cm^{-1}.

The Raman spectra were recorded on a Jobin Ivon U-1000 spectrometer using 514.5 nm radiation from a Spectra-Physics 164 Ar^+ laser for excitation. Calibrations were made by using either plasma lines from the laser itself or from an Ne lamp. The uncertainty of measurement is of the order of ±2 cm^{-1}.

Both Table 1 and 2 summarize the infrared and Raman frequencies as well as the intensities, the depolarization ratios and the proposed assignments.

RESULTS AND DISCUSSION.

For to have an approximate molecular structure, the molecular geometry of the monomer and the dimer of tribromoacetic acid was optimized by using the MNDO, AM1 and PM3 semiempirical methods. The respective $r(O\cdots H)$ distances are 3.117, 2.119 and 2.423 Å, and the stabilization energy for dimer is 1.7, 6.0 and 1.6 Kcal/mol, respectively. Although the distances exhibit some high values (see Table 3) and the energies exhibit low ones when compared with typical values for hydrogen bonding, the AM1 method provides the more

TABLE 1.- Summary of the Frequencies (in cm^{-1}) and Proposed Assignments for the Fundamentals Bands of the Vibrational Spectrum of Tribromoacetic Acid and its Deuterated Derivative.

IR	IR(D)	Raman	Assignment
3100 mb	2350 mb		$\nu(OH)(OD);B_u$
1721 vs	1720 vs		$\nu(C{=}O);B_u$
		1687 s	$\nu(C{=}O);A_g$
		1425 s	$\delta(OH);A_g$
1410 s	1043 m		$\delta(OH)(OD);B_u$
		1252 s	$\nu(C-O);A_g$
1244 vs	1328 m		$\nu(C-O);B_u$
		944 w	$\nu(C-C);Ag$
930 w	929 vw		$\nu(C-C);B_u$
867 mb	643 vw		$\gamma(OH)(OD);A_u$
		797 s	$\nu'_s(CBr_3);A_g$
782 vs	779 vs		$\nu'_s(CBr_3);B_u$
		680 vs	$\delta(OCO);A_g$
679 s	681 m		$\delta(OCO);B_u$
		614 vs	$\nu_{as}(CBr_3);B_g$
600 s	600 m		$\nu_{as}(CBr_3);A_u$
479 vw	500 vw		$\gamma(CCO);A_u$
431 s	433		$\delta(CCO);B_u$
		396	$\delta(CCO);A_g$
352 vw			$\nu_s(CBr_3);B_u$
		343 s	$\nu_s(CBr_3);A_g$
		233 vs	$\delta_{as}(CBr_3);B_g$
228 vw			$\delta_{as}(CBr_3);A_u$
		221 s	$\delta'_s(CBr_3);A_g$
209 vw			$\delta'_s(CBr_3);B_u$
		203 m	$\delta_s(CBr_3);A_g$
202			$\delta_s(CBr_3);B_u$
		157 sh	$r_{as}(CBr_3);B_g$
		153 s	$r_s(CBr_3);A_g$
		83 m	
		68 sh	
		56 w	

vs=very strong; s=strong; m=medium; w=weak; b=broad and sh=shoulder.

TABLE 2.- Summary of the Frequencies (cm^{-1}), Depolarization Ratios and Proposed Assignments for the Fundamentals Bands of Tribromoacetate ion.

IR	Raman	ρ	Assignment
1654 vs	1654 vs		ν_{as}(OCO);A'or A''
1356 vs	1367 vs	p	ν_s(OCO);A'
917 m	928 m		ν(CC);A'
758 vs	764 vs	p	$\nu'_s(CBr_3)$;A'
724 714 s	722 vs	p	δ(OCO);A'
605 s	610 vs	dp	$\nu_{as}(CBr_3)$;A''
495 w			γ(OCO);A'
434 b	412 m		r(OCO);A'or A''
	323 s	p	$\nu_s(CBr_3)$;A'
	260 vw	dp	$\delta_{as}(CBr_3)$;A''
	214 vs	p	$\delta'_s(CBr_3)$;A'
	185 m	p	$\delta_s(CBr_3)$;A'
	163 s		$r_{as}(CBr_3)$;A''
	145 m		$r_s(CBr_3)$;A'
	81 w		$t(CBr_3)$;A''

acceptable results. In Fig. 1 it can be seen the optimized AM1 geometry for the dimer of tribromoacetic acid.

In agreement with this C_{2h} symmetry, the representation of the internal vibrations is $\Gamma_{int} = 12A_g+6B_g+6A_u+12B_u$. For the anion with a C_s symmetry their 3N-6=15 vibrations distribute 10A'+5A'' or 9A'+6A'' depending on the orientation of COO^- group with respect the molecular plane.

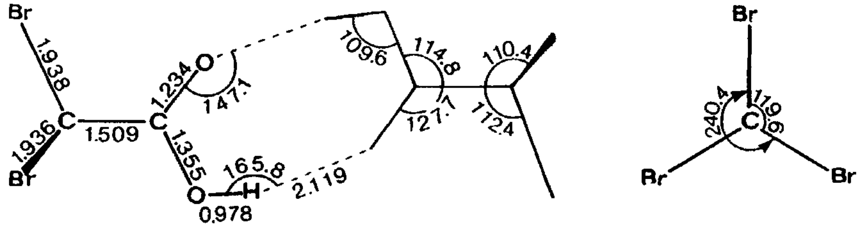

FIG. 1.- Molecular parameters for the dimer of tribromoacetic acid.

Vibrational assignment:

4000 cm^{-1} to 1000 cm^{-1} region.- The fundamental modes expected in this region are OH and C=O stretching modes as well as the coupling between both C-O stretching and the OH in-plane bending modes. Concerning the salt, only two modes are expected in this region, i.e. symmetric and asymmetric OCO stretching. The broad band centred at about 3100 cm^{-1} in the infrared spectra correspond to the OH stretching vibrations (2350 cm^{-1} in the deuterated compound). The Raman active one is too weak to be observed. It is also interesting to note that beside of this broad band there appear a series of less intense bands, which some authors call submaxima[13]. Concerning the C=O stretching modes, they are readily assigned being well known characteristic bands. The very strong absorption band observed at 1721 cm^{-1} in the IR spectrum is assigned to the C=O linkage. It remains also in the deuterated acid. The corresponding Raman band of A_g symmetry appears to 1687 cm^{-1}. The splitting of these vibrations is quite typical of dimer acid spectra. With regard to ν(C-O) and δ(OH) modes, as it is well-known, the δ(OH) couples strongly with ν(C-O)[14]. Although there is a marked disagreement in the literature concerning their precise assignments. The absorption band at 1410 cm^{-1} has been assigned to the δ(OH);Bu mode, this frequency apparently shifts to 1043 cm^{-1} in the deuterated molecule, the ratio of the frequencies in the two isotopic species is 1.35 which is a reasonable value for a δ(OH) vibration[11].

On the other hand, the ν(C-O);Bu mode has been assigned to the band at 1244 cm^{-1} in the IR spectrum that shifts to 1328 cm^{-1} in the deuterated molecule. Both vibrations appears at 1425 cm^{-1} and 1252 cm^{-1} in the Raman respectively. Concerning the ion, there are two modes in this region of the spectrum, ν_{as}(OCO) and ν_s(OCO), the first one can be assigned to the intense band at 1654 cm^{-1} in both spectra. Therefore, the second one has to be assigned to the strong IR band at 1356 cm^{-1}, which corresponds with the Raman band at 1367 cm^{-1}. No depolarization ratios could be determined for these bands.

1000 cm^{-1} to 500 cm^{-1} region.- The assignment of the bands in the region below 1000 cm^{-1} is very difficult due to the nature of the vibrations here expected. These include the out-of-plane OH deformation mode, the C-C stretching mode, the OCO skeletal angle-bending mode and the $-CBr_3$ group stretching.

The γ(OH);Au bending mode is recorded as a broad band at about 867 cm^{-1} in the IR spectra and at 643 cm^{-1} in the corresponding deuterated derivative, the frequencies ratio being 1.35.

Both ν(CC);Ag and Bu modes appear at 944 cm^{-1} and 930 cm^{-1} in the Raman and infrared spectra respectively. In the anion this mode has been measured at 928 and 917 cm^{-1} respectively.

The $-CBr_3$ stretchs occur at a frequency consistent with other compounds containing three C-Br bonds and are readily assigned. We have assigned the very strong band at 782 cm^{-1} in the IR to $\nu_s'(CBr_3)$;Bu mode and the strong band at 797 cm^{-1} in the Raman to the Ag symmetry species. In the anion, they have been registred at lower frequency both infrared and Raman spectra. Finally, the $\nu_{as}(CBr_3)$ modes have been assigned to the bands at 600 cm^{-1} and 614 cm^{-1} in the IR and Raman spectra respectively. These modes appear in the salt at practically the same frequency with very strong intensity.

The remaining two Ag and Bu vibrations, corresponding to the δ(OCO), are essentially associated with the two bands at 680 cm^{-1}

and 679 cm^{-1} in the Raman and IR spectra respectively. In the salt spectra, they have been recorded at higher frequency but also with very strong intensity.

Region below 500 cm-1.- In this region of the spectrum, the skeletal deformation vibrations and the deformational modes of $-CBr_3$ group as well as the $\nu(CBr_3)$ mode of lower frequency should be expected.

The $\gamma(CCO);A_u$ mode is assigned to the very weak band at 497 cm^{-1} in the IR. It has been assigned in the salt spectra practically at same frequency; this mode is missing in the Raman spectra.

Both $\delta(CCO)$ of B_u and A_g symmetry have been assigned to the strong bands at 431 cm^{-1} (433 cm^{-1} in the deuterated compound) and 396 cm^{-1} in the infrared and Raman spectra respectively. In the salt spectra it is not possible to decide between A′and A″ symmetry because of the absence of depolarization ratios, as in the case of $\nu_{as}(OCO)$.

Concerning the $-CBr_3$ modes, they have been assigned by correlation with the bromal spectra. In this way, we have assigned the strong band at 343 cm^{-1} to $\nu_s(CBr_3);A_g$ in the Raman spectrum. The B_u mode is assigned to the weak band at 352 cm^{-1} in the IR spectrum. At 323 cm^{-1} in the salt spectra, it appears a polarized Raman band that we assigned to this mode. On the other hand, the bands at 233 cm^{-1} (very strong), 221 cm^{-1} and 203 cm^{-1} in the Raman spectrum are assigned to $\delta_{as}CBr_3);B_g$, $\delta'_s(CBr_3);A_g$ and $\delta_s(CBr_3);A_g$ respectively. The modes active in the IR are assigned to bands at 228 cm^{-1}, 209 cm^{-1} and 202 cm^{-1} respectively. In this region of the Raman spectrum of the salt we have three bands, two polarized ones and another depolarized, since the depolarized band appear at higher frequency, it is evident that it must be assigned to the $\delta_{as}(CBr_3)$ mode of A″ symmetry, whereas the other bands have been assigned to the A′ modes, the order of appearing is in agreement with other molecules containing the CBr_3 group.

The rocking vibrations were assigned to shoulder at 157 cm^{-1} and the strong band at 153 cm^{-1} for the asymmetric and symmetric

TABLE 3.- O···O distances and γ(OH) and δ(OCO) frequencies for various halogen-substituted derivatives of acetic acid.

	d(O···O)(Å)	γ(OH)(cm^{-1})	δ(OCO)(cm^{-1})
CH_3-COOH[a]	2.631(8)	941	645
CF_3-COOH[b]	2.648(3)	904	717
CCl_3-COOH[c]	2.666(6)	873	667
CBr_3-COOH	3.077(0)	867	679

a) Refs.(9),(15).
b) Refs.(7),(10).
c) Ref.(8).

vibrations respectively, both in the Raman spectrum. In the corresponding salt spectrum they appear more or less at the same frequency.

The spectral region below 150 cm^{-1}, is rather complex, containing some very low torsional internal modes, besides lattice and hydrogen-bond vibrations for the acid. In the anion, the band al 81 cm^{-1} can be assigned to the torsional mode.

Finally, Table 3 shows the O···O distances in the hydrogen bonded dimers as well as the observed frequencies for γ(OH) and δ(OCO) modes along the series of halogen-derivatives of acetic acid. This complete the results by Collins and Haywood[15].

As can be deduced therefrom, correlation between O···O distances and frequencies of γ(OH) modes is due to weakening of the hydrogen bond when going from the lighter to the heavier derivatives. Data for tribromoacetic acid are in complete agreement with the previous ones, although the O···O distance is the calculated one, and seems to be overestimated. Nevertheless, the observed frequencies for δ(OCO) modes do not show any systematic behaviour with the hydrogen bond strength.

REFERENCES

1. Suero M.I., Robles J., Márquez F. Spectrosc. Lett. 1986; 19: 851.
2. Arenas J.F., Marcos J.I., Suero M.I. J. Raman Spectrosc. 1984; 15: 132.
3. Cardenete A., Arenas J.F., Márquez F. Can. J. Spectrosc. 1985; 30: 41.
4. Suero M.I., McNeil L.E., Márquez F. J. Raman Spectrosc. 1987; 18: 273.
5. Suero M.I., Márquez F., Martín Delgado M.J. Spectrosc. Lett. 1990; 23: 771.
6. Spinner E. J. Chem. Soc. 1964; 4417.
7. Nahringbauer I., Lundgren J.O., Andersen E.K. Acta Cryst. 1979 B35: 508.
8. Jönsson P.G., Hamilton W.C. J. Chem. Phys. 1972; 56: 4433.
9. Jönsson P.G. Acta Cryst. 1971; 27: 893.
10. Berney C.V. J. Am. Chem. Soc. 1973; 95: 708.
11. Katon J.E., Kleinlein R.L. Spectrochim. Acta 1973; 29A: 791.
12. Sinha D., Katon J.E., Jakobsen R.J. J. Mol. Struct. 1975; 24: 279.
13. Bratož S., Hadži D., Sheppard N. Spectrochim. Acta 1956; 8: 249.
14. Hadži D., Sheppard N. Proc. Roy. Soc. (London) 1953; A216: 274.
15. Collins M.F., Haywood B.C. J. Chem. Phys. 1970; 52: 5740.

Date Received: 02/10/92
Date Accepted: 03/12/92