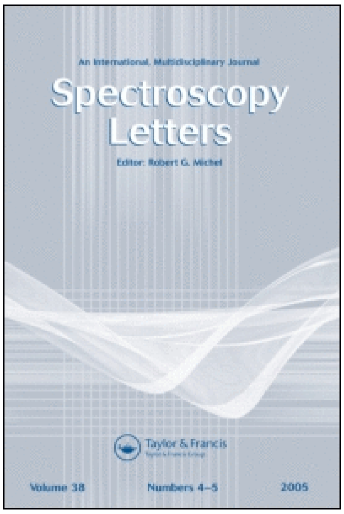

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# Vibrational Spectrum of Tribromoethanol

M. I. Suero[a]; M. J. Martín-Delgado[a]
[a] Department of Physics, Badajoz, Spain

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# VIBRATIONAL SPECTRUM OF TRIBROMOETHANOL

Key Words: Infrared, Raman, Structure, Tribromoethanol.

M.I. Suero* and M.J. Martín–Delgado.
Department of Physics. (06071) Badajoz. Spain.

## ABSTRACT:

The molecular structure of tribromoethanol has been studied by Ab Initio theoretical calculations. The IR spectrum has been recorded in the range 4000–200 cm$^{-1}$. Whereas, the Raman spectrum has been determined by means of a SPEX 1403 spectrometer using the 5145Å exciting line of a Spectra–Physics 164 Ar ion laser. Depolarization ratios were also measured. The fundamental vibrations of $CBr_3CH_2OH$ as well as some overtones, combinations and difference bands were assigned.

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* Author to whom correspondence should be addressed. Departamento de Física, Ftad. de Ciencias, Avda. de Elvas, s/n. 06071 Badajoz, Spain.

## INTRODUCTION

Many investigations have been carried out in regard to assignment of infrared and Raman spectra of similar molecules. The interpretation of the vibrational spectra of 2,2,2 –trichloroethanol[1-7] and 2,2,2 –trifluoroethanol[3-12] have been extensively studied however, a detailed study has not been published for 2,2,2 –tribromoethanol so far. The few data published on 2,2,2 –Tribromoethanol is the I.R. spectra related only to the solid state and in dilute solution, from 1500 to 450 cm$^{-1}$, by Travert and Lavalley[6].

We have recently studied the vibrational spectra of tribromo compounds with two carbon atoms such as tribromoacetamide[13-14], tribromoacetonitrile[15-17], tribromoacetic acid[18-19] and tribromo acetaldehide[20]. We now complete the series with a study of the vibrational spectrum of 2,2,2 –Tribromoethanol.

A complete structural analysis for 2,2,2 –tribromoethanol is not available. In this paper we assume that the equilibrium structure has $C_s$ symmetric by correlation to similar molecules[6-7, 21-23].

Ab Initio theoretical calculations were used to optimize the geometry. On this basis, the IR and Raman spectra of tribromoethanol has been assigned for all the recorded bands in the range 4000 – 50 cm$^{-1}$.

## EXPERIMENTAL

The sample of 2,2,2 –tribromoethanol from Aldrich was purified by recrystallization.

TABLE 1.– Summary of the frequencies ($\nu$) and propossed assignments in infrared and Raman spectra of 2,2,2 –tribromoethanol.

| IR $\nu(cm^{-1})I^a$ | IR (D) $\nu(cm^{-1})I^a$ | RAMAN $\nu(cm^{-1})I^a\ \rho^b$ | ASSIGNMENT |
|---|---|---|---|
| 3294 vs | | | $\nu(OH)$; A' |
| 2945 s | 2939 m | | $\nu_{as}(CH_2)$; A'' |
| 2915 vs | 2910 s | | $\nu_s(CH_2)$; A' |
| 2853 m | 2852 s | | $2.\delta_{as}(CH_2)$ |
| | 2456 m | | $\nu(OD)$; A' |
| 2340 m | 2338 m | | $\delta'_s(CH_2) + \nu(CO)$; A' |
| 1504 w | 1500 w | | $\nu_s(CH_2)-\delta_{as}(CH_2)$;A'' |
| 1440 m | 1437 m | | $\delta_{as}(CH_2)$; A'' |
| 1395 s | | | $\delta(OH)$; A' |
| 1355 s | 1355 s | | $\delta'_s(CH_2)$; A' |
| 1234 s | 1231 m | | $\delta_s(CH_2)$; A' |
| 1086 vs | 1086 vs | | $\nu(CO)$; A' |
| 1075 sh | | | $\nu(CC)$; A' |
| 1009 s | 1009 m | | $r(CH_2)$; A'' |
| | 902 m | | $\delta(OD)$; A' |
| 749 vs | 745 s | 748 m(p) | $\nu'_s(CBr_3)$; A' |
| 632 s | 630 s | 630 m(dp) | $\nu_{as}(CBr_3)$; A'' |
| 604 sh | | 610 m (d) | $\gamma(OH)$; A'' |
| 484 s | 482 vs | 450 m(p) | $\nu_s(CBr_3)$; A' |
| 445 m | | 440 w(p) | $\delta(CCO)$; A' |
| 360 w | | 362 w | $2\delta_s(CBr_3)$; A'' |
| 344 w | 344 vs | 343 s (dp) | $\delta_{as}(CBr_3)$; A'' |
| 290 m | | 290 m | $\tau(OH)$; A'' |
| 219 w | | 218 vs (p) | $\delta'_s(CBr_3)$; A' |
| | | 184 m (p) | $\delta_s(CBr_3)$; A' |
| | | 155 vs (dp) | $r_{as}(CBr_3)$; A'' |
| | | 142 s (p) | $r_s(CBr_3)$; A' |

a) For comparison of relative intensities, the symbols v = very; s = strong; m = medium and w = weak are used.

b) p = polarized band; dp = depolarized band.

Raman Spectra were obtained with a Cary 82 and a Jobin Ivon U–1000 spectrometer using the 5145Å exciting line of a Spectra–Physics 164 Ar ion laser.

Infrared spectra was recorded in the region 4000–200 $cm^{-1}$ with a Perkin–Elmer 399 spectrophotometer. KBr pellets and mull techniques were used and no significant interaction with the halide was detected. The instrument was calibrated with poliestyrene films as well as with indene/camphor/cyclohexanone mixtures[24]. We estimated an error of ± 2 $cm^{-1}$ in the Raman frequencies and ± 0.5 $cm^{-1}$ in the IR data.

The experimental results are summarized in Table 1 where frequencies and the propossed assignments are given for the fundamentals, overtones, combinations and difference bands, respectively.

The numerical calculations were performed on a VAX–3100 STATION Computer.

## RESULTS AND DISCUSSIONS

The vibrational assignments of 2,2,2 –tribromoethanol are based on correlations to the related molecules, 2,2,2 –trichloroethanol[1-7], 2,2,2 –trifluoroethanol[3-12], tribromoacetamide[13-14], tribromoacetonitrile[15-17], tribromoacetic acid[18-19] and bromal[20]. According to the $C_s$ point group, the fundamental vibrations of 2,2,2 –tribromoethanol can be decomposed into 13 vibrations of A' species and 8 vibrations of A'' species. In the Table 2 the symmetry coordinates, the fundamental vibrations an the correspondence symmetry species for 2,2,2 –tribromoethanol can be observed.

TABLE 2.– The symmetry coordinates, the fundamental vibrations and the correspondence symmetry species for 2,2,2 –tribroethanol.

| Symmetry coordenates | Fundamental vibrations | Symmetry species |
|---|---|---|
| $S_1 = d$ | $\nu$(OH) | A' |
| $S_2 = r$ | $\nu$(CO) | A' |
| $S_3 = l$ | $\nu$(CC) | A' |
| $S_4=1/\sqrt{2}(t_1+t_2)$ | $\nu_s(CH_2)$ | A' |
| $S_5=1/\sqrt{2}(t_1-t_2)$ | $\nu_{as}(CH_2)$ | A'' |
| $S_6=1/\sqrt{6}(2\omega-\psi_1-\psi_2)$ | $\delta_s(CH_2)$ | A' |
| $S_7=1/2(\varphi_1+\varphi_2-\psi_1-\psi_2)$ | $\delta'_s(CH_2)$ | A' |
| $S_8=1/\sqrt{2}(\varphi_1-\varphi_2)$ | $\delta_{as}(CH_2)$ | A'' |
| $S_9=1/\sqrt{2}(\psi_1-\psi_2)$ | $r(CH_2)$ | A'' |
| $S_{10}=1/\sqrt{6}(2\beta-\psi_1-\psi_2)$ | $\delta$(CCO) | A' |
| $S_{11}=1/\sqrt{3}(s_1+s_2+s_3)$ | $\nu_s(CBr_3)$ | A' |
| $S_{12}=1/\sqrt{6}(2s_1-s_2-s_3)$ | $\nu'_s(CBr_3)$ | A' |
| $S_{13}=1/\sqrt{2}(s_2-s_3)$ | $\nu_{as}(CBr_2)$ | A'' |
| $S_{14}=1/\sqrt{6}(\delta_1+\delta_2+\delta_3-\gamma_1-\gamma_2-\gamma_3)$ | $\delta_s(CBr_3)$ | A' |
| $S_{15}=1/\sqrt{6}(2\delta_1-\delta_2-\delta_3)$ | $\delta'_s(CBr_3)$ | A' |
| $S_{16}=1/\sqrt{2}(\delta_2-\delta_3)$ | $\delta_{as}(CBr_2)$ | A'' |
| $S_{17}=1/\sqrt{6}(2\gamma_1-\gamma_2-\gamma_3)$ | $r_s(CBr_3)$ | A' |
| $S_{18}=1/\sqrt{2}(\gamma_1-\gamma_2)$ | $r_{as}(CBr_2)$ | A'' |
| $S_{19}=\alpha$ | $\delta$(OH) | A' |
| $S_{20}=\tau_1$ | $\tau(CBr_3)$ | A'' |
| $S_{21}=\tau_2$ | $\tau$(OH) | A'' |

In order to carry out an assignment of the vibrational spectrum, we have classified the normal vibrations as: a) vibrations of $CBr_3$ group; b)Hydroxyl vibrations and c) other fundamentals.

a) Vibrations of $CBr_3$ group.

– Stretching vibrations:

Three frequencies are expected in the region 800–500 $cm^{-1}$ which can be atributed to the stretching vibrations of $CBr_3$ group.

The $\nu_s(CBr_3)$; A' vibration is assigned to the strong 450 $cm^{-1}$ band in Raman. In I.R. this band is at 484 $cm^{-1}$ with an isotopic shift of 2 $cm^{-1}$. The observed depolarization ratio confirms the assignment previously propossed for th above fundamental.

We have assigned the strong 632 $cm^{-1}$ band with an isotopic shift of 2 $cm^{-1}$ in I.R. to the $\nu_{as}(CBr_3)$; A". This fundamental has been assigned to the depolarized Raman band at 630 $cm^{-1}$. Finally, we have assigned the medium band at 748 $cm^{-1}$ and 749 $cm^{-1}$ with an isotopic shift of 4 $cm^{-1}$ in Raman and I.R. respectively, to the $\nu'_s(CBr_3)$; A'. This assignment agrees very well with the Travert and Lavalley's[6] counter part.

– Deformational frequencies

Five bands are expected in the region 100–400 $cm^{-1}$ whose origin can reasonably be attributed to the deformational modes of the $CBr_3$ group.

By considering that symmetric $CBr_3$ deformation arises at lower frequency than the antisymmetric $CBr_3$ deformation, the symmetric rocking vibration which must be at lower frequency than the antisymmetric rocking vibration. According with literature[20], we have assigned the strong band at 142 $cm^{-1}$ to $r_s(Br_3C)$; A', and the very strong 155 $cm^{-1}$ band to $r_{as}(CBr_3)$; A". The observed depolarization ratio confirms the assignment previously proposed for the fundamental.

The medium band at 184 $cm^{-1}$ and the very strong band at 218 $cm^{-1}$ are assigned to $\delta_s(CBr_3)$; A', and $\delta_s'(CBr_3)$ A' respectively, which results very similar to tribromoacetic acid[18] and Bromal[20].

The fundamental $\delta_{as}(CBr_3)$A'' has been assigned to the depolarized Raman band at 343 $cm^{-1}$ which appears at 344 $cm^{-1}$ in I.R counter part. Its observed depolarization ratio confirms the previous assignment, proposed for this fundamental.

Finally, the torsional vibration $t(Br_3C)$; A'' is expected to appear at very low frequency. Since in the case of the compound $Cl_3CCH_2OH$[7] it has been calculated at 42 $cm^{-1}$. In the present case, it was able to be assigned since it is out of range of the measurement equipment.

b) <u>Hydroxil vibrations</u>

These vibrations are $\nu(OH)$; A', $\delta(OH)$; A', $\gamma(OH)$; A'' and r(OH); A''.

The O–H stretching band for hydroxilyc groups with hidrogen bonding (inter or intramoleculaires) is broad and complex and appear at lower frequency than when there is not these class of bridges. A broad and strong band is recorded at 3294 $cm^{-1}$ in the I.R. spectra of 2,2,2 –Tribromoethanol as correspond with intramolecular hydrogen bridges between OH and others functional groups and with polymer structures. This vibration appears at 2456 $cm^{-1}$ in the deuterated specie where 1.34 is the shift factor.

The O–H deformation $\delta(OH)$; A'; has been assigned to the strong band that appears at 1395 $cm^{-1}$ in the I.R spectrum of normal compound. This band disappears for the deuterated specie. The assignment agrees very well with the assignment described by Travert and Lavalley[6] at 1389 $cm^{-1}$.

In addition, a new band at 902 $cm^{-1}$ appears in the deuterated specie that we have assigned to $\delta$(OD).

Around 650 $cm^{-1}$, a band for alifatic alcohols atributable to $\gamma$(OH) along with other band $\nu(CBr_3)$, are expected.

At 632 $cm^{-1}$ in the I.R spectrum of normal 2,2,2 –Tribromoethanol a band with a shoulder at 604 $cm^{-1}$, appears which remains in the deuterated compound counter part too, while the shoulder disappears. We have assigned the fundamental $\gamma$(OH)A'' to the shoulder at 604 $cm^{-1}$ and 610 $cm^{-1}$ in I.R and Raman respectively.

Finally, the $\tau$(OH) vibration has been assigned to the medium band at 290 $cm^{-1}$ in the I.R. an Raman spectra of the normal compound. This band appears at similar frequency in Trichloroethanol[1-7] and trifluoroethanol[8-12].

c) Other fundamentals

Corresponding to this group the following vibrations are expected:

The fundamental $\nu_{as}(CH_2)$;A'' has been assigned to the strong band at 2945 $cm^{-1}$ and 2939 $cm^{-1}$ in I.R. of the normal compounds and deuterated respectively.

The strong band at 2915 $cm^{-1}$ (2910 $cm^{-1}$ for the deuterated specie) in I.R. is assigned to $\nu_s(CH_2)$;A'. This assignment compares well with the Perttila's[7] assignment.

The absorption band at 1440 $cm^{-1}$ has been assigned to the $\delta_{as}(CH_2)$;A'' in the normal compound and at 1437 $cm^{-1}$ in the deuterated molecule.

On the other hand, the $\delta_s(CH_2)$A' has been assigned to the strong band at 1355 $cm^{-1}$ in the I.R. spectrum.

The $\delta_s(CH_2)$;A' vibration is assigned to the strong band at 1234 $cm^{-1}$ and to the medium band at 1231 $cm^{-1}$ in I.R. in the normal and deuterated compounds respectively.

We have assigned the strong band in I.R. at 1009 $cm^{-1}$ to $r(CH_2)$;A'' according with literature[7].

At 1086 $cm^{-1}$ in the I.R. spectrum of normal 2,2,2 Tribromoethanol a very strong band with a shoulder at 1075 $cm^{-1}$ appears. We have assigned the band at 1086 $cm^{-1}$ in the compound normal and deuterated to $\nu(CO)$;A' and the shoulder at 1075 $cm^{-1}$ to $\nu(CC)$;A', according to the interval of frequencies for this vibrations described in the literature[7].

Finally, the medium band at 445 $cm^{-1}$ in I.R. and 440 $cm^{-1}$ in Raman is assigned to $\delta(CCO)$;A'. Its observed depolarization ratio confirms the previous assignment, proposed for this fundamental.

<u>Overtones and combinations.</u>

In addition to the fundamental vibrations, we have assigned some overtones, combinations and difference bands which are shown in Table I.

## STRUCTURE

The structure of similar molecules has been determined by electron difraction[21] and theoreticaly[6-7], but in the case of the 2,2,2 –Tribromoethanol a complete structural analysis is not available yet. Then, we have performed Ab Initio calculations with the Gaussian 86(a) program in order to determine the minimum energy geometry. These calculations were performed using standard bond lengths and bond angles for the alcohol group and for the $CBr_3$ group the bromal molecular parameters[28].

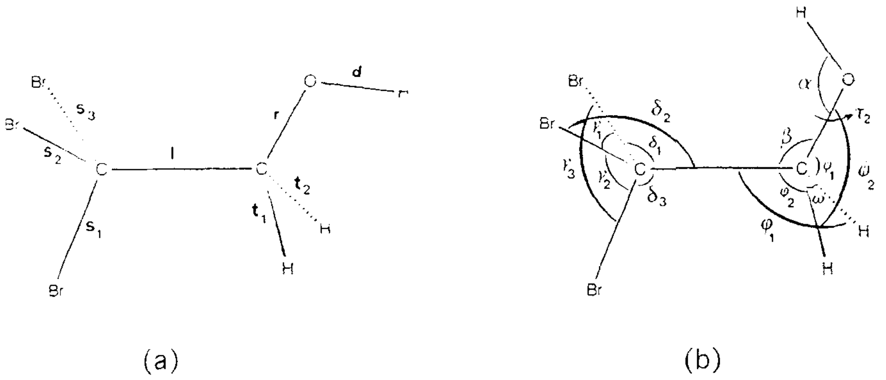

FIG. 1.– The conformers and internal coordinates of 2,2,2 –tribroethanol (a) trans, (b) gauche conformer.

TABLE 3.– The calculated bond lengths, bond angles and dihedral angles for 2,2,2 –tribromoethanol.

| Bond lengths | | Bond angles | | Dihedral angles | |
|---|---|---|---|---|---|
| C1–C2 | 1.5729 | | | | |
| C1–Br3 | 1.9450 | Br3–C1–C2 | 108.500 | | |
| C1–Br4 | 1.9450 | Br4–C1–C2 | 108.500 | Br4–C1–C2–Br3 | –120.0 |
| C1–Br5 | 1.9450 | Br5–C1–C2 | 108.500 | Br5–C1–C2–Br3 | 120.0 |
| C2–06 | 1.4393 | 06–C2–C1 | 114.117 | 06–C2–C1–Br4 | 60.0 |
| 06–H7 | 0.9896 | H7–06–C2 | 105.714 | H7–06–C2–Br3 | 0.0 |
| C2–H8 | 1.0963 | H8–C2–C1 | 108.150 | H8–C2–C1–Br3 | 60.0 |
| C2–H9 | 1.0963 | H9–C2–C1 | 108.150 | H9–C2–C1–Br3 | –60.0 |

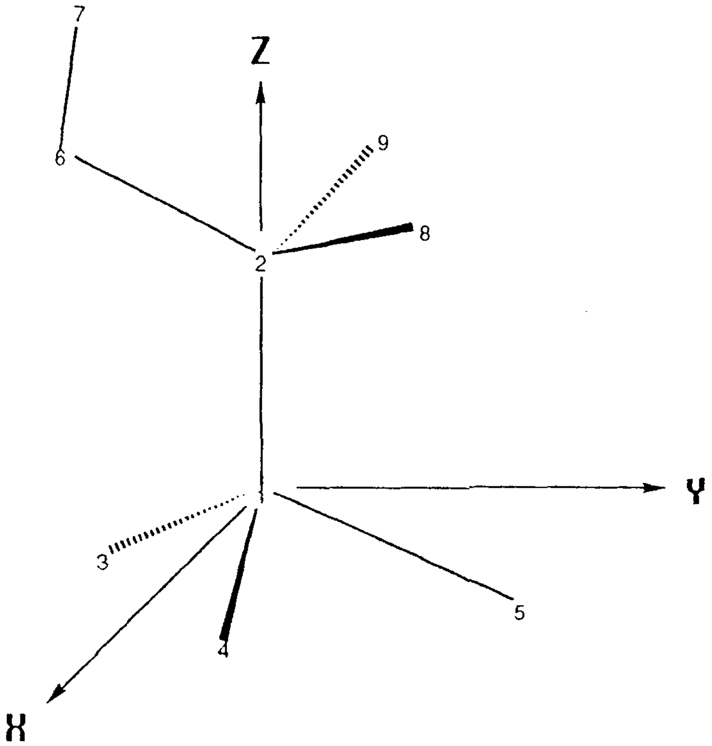

FIG. 2.– Numbering of atoms and the orientation of the cartesian axes in 2,2,2–tribromoethanol.

As a consequence of the rotation about the C–O bond, for the 2,2,2 –trihaloethanols two stable conformers exist: trans and gauche, as can be seen in figure 1. The formation of trans conformer should be favoured by the formation of intermolecular hydrogen bridges, but in most haloethanols the gauche component is found to prevail[6]. A possible explanation of this fact is that the intramolecular OH–Br interaction stabilizes the gauche conformer.In the case of 2,2,2 –tribromoethanol, we found that the trans conformer is more stable energeticaly and obtained the bond angles and the bond lengths as observed in Table 3. Figure 2 shows numbering of atoms and the orientation of the cartesian axes in 2,2,2 –tribromoethanol.

These parameters were obtained by the Roothaan's SCF–LCAO–MO non empirical method[25] on a VAX–STATION computer, with the GAUSSIAN–86 packacge. The STO–3G basis sets with standard exponents[26-27] have been used for the H, C, O, and Br. The Berny optimization process and a convergence criterium of $10^{-11}$ was used.

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