# Comparison of the Raman Spectra of 1,1,1 and 1,1,2Trichloroethane

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TABLE V.

| SUB-STANCE | a | b | $\Delta H/T_b$ | SUB-STANCE | a | b | $\Delta H/T_b$ |
|---|---|---|---|---|---|---|---|
| NH₃ | 8.1616 | 1266.08 | 24.179 | HF | 6.3739 | 1316.8 | 20.551 |
| ND₃ | 8.2800 | 1308.23 | 24.721 | DF | 6.2026 | 1261.6 | 19.766 |
| H₂O | 9.1582 | 2342.5 | 28.742 | HCl | 7.6192 | 891.30 | 21.696 |
| D₂O | 9.2854 | 2399.1 | 29.325 | DCl | 7.6125 | 906.59 | 21.665 |
| HCN | 7.795 | 1467 | 22.171 | HBr | 7.465 | 945.7 | 20.397 |
| DCN | 7.695 | 1440 | 21.728 | DBr | 7.517 | 956.5 | 20.630 |
|  |  |  |  | HI |  |  | 19.869 |
|  |  |  |  | DI |  |  | 19.932 |

vaporization are not equal, Trouton's rule is not obeyed. To test this further, the constant was calculated for each of a group of substances and these constants are presented in Table V.

The constants $a$ and $b$ are those giving the vapor pressure according to Eq. (7).

$$\log P_{(mm)} = a - b/T \qquad (7)$$

where $b = \Delta H/4.5787$. Correction to constant vapor concentration, as in the Hildebrand[7] modification, produces changes too small to alter the conclusion. For example, the difference between the Trouton's constants for the chlorides is increased in this manner by 0.03.

An interesting observation to be made from Table V is that an isotopic change produces the greatest shift in the value of the constant for those substances which are known to deviate most from Trouton's rule, water and ammonia.

[7] Hildebrand, J. Am. Chem. Soc. **37**, 970 (1915).

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# Comparison of the Raman Spectra of 1,1,1- and 1,1,2-Trichloroethane

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The Raman frequencies of 1,1,1- and 1,1,2-trichloroethane have been obtained. Comparison with CCl₄ indicates that the Cl₃C and Cl₂HC radicals have tetrahedral symmetry. The frequencies of Cl₃C·CH₃ and Cl₂HC·CH₂Cl are compared, and the combination frequencies and modes of vibration of the two molecules indicated.

THE Raman spectra of 1,1,1- and 1,1,2-trichloroethane have been up to the present time unknown. Among the compounds examined by Hanle,[1] are listed the Raman frequencies of $Cl_2C = CHCl$, obviously misnamed trichloroethane. Consequently it has seemed worth while to investigate the Raman spectra of both 1,1,1- and 1,1,2-trichloroethane, and to compare them with those of similar compounds.

Apparatus and experimental technique employed were similar to those described by Wood.[2] In the preliminary investigations a Hilger constant deviation spectrograph was used, having a dispersion of 25A/mm at λ4500. A Cooper-Hewitt Hg arc operated at 750 watts served as light source. The line chosen for excitation was λ4358. A filter consisting of a water solution of $NaNO_2$ was used to eliminate λ4047 and λ4078.

With this apparatus exposures ranged from 30–60 min. In the later work a spectrograph containing two 60° prisms and having a dispersion of 12A/mm at λ4500 was used. Two low pressure Hg arcs operated at 150 watts each served as light source. This apparatus, however, required exposure from 24 to 96 hours. The 1,1,1- and 1,1,2-trichloroethane were purchased from the Eastman Kodak Company and were fractionally distilled before use. The boiling range for the distilled $Cl_3C·CH_3$ was 74° to 75.5°C and for the distilled $Cl_2HC·CH_2Cl$ was 113° to 115°C, both at normal pressure. Both compounds decompose very slowly when exposed to light, necessitating redistillation half-way through each exposure. Measurements were made directly on the spectrograms and also on microphotometer traces (Koch-Goos). A Cu arc spectrum was used for comparison, and wavelengths of the Raman lines were calculated by the Hartmann formula.

[1] W. Hanle, Ann. d. Physik, [5] **15**, 345 (1932).
[2] R. W. Wood, Phil. Mag. [7] **6**, 729 (1928); Phys. Rev. **36**, 1421 (1930).

TABLE I. *1, 1, 1-trichloroethane.*

| | | | |
|---|---|---|---|
| 241 (7)* | 714 (7b) | 1242 (½b) | 1592 (½b) |
| 345 (10)* | {1071 (2) {1086 | {1361 (½) {1384 (½) | 2743 (½b) |
| 523 (9)* | 1175 (1) | {1424 (2) {1451 (2) | 2943 (7) |
| | | | 3011 (6) |

TABLE II. *1, 1, 2-trichloroethane.*

| | | | |
|---|---|---|---|
| 255 (4)* | 525 (1) | 1056 (1b) | 1575 (½b) |
| 283 (2)* | 638 (3) | 1207 (2) | 2960 (8) |
| 332 (10)* | 664 (5b) | 1260 (2) | 2996 (7) |
| 395 (3)* | {772 {781 (10) | 1304 (2) | 3021 (5b) |
| 441 (½)* | 931 (1) | 1428 (2) | |

\* Observed also as anti-Stokes lines.

In Tables I and II are tabulated the Raman frequencies in wave numbers for 1,1,1- and 1,1,2-trichloroethane. The numbers in parentheses are the relative intensities, obtained from the microphotometer traces.

## DISCUSSION

The striking resemblance between the first four Raman frequencies of $Cl_3C \cdot CH_3$ and $CCl_4$ indicates that the $Cl_3C$ radical also has tetrahedral symmetry. Consequently the frequency 241 can be ascribed to a bending of the $C-Cl$ bond and 523 to an expansion and contraction of the $Cl_3C$ radical as a whole. The frequency 714 does not correspond, however, to the doublet 760,793 of $CCl_4$. Following the method of Dadieu and Kohlrausch in calculation,[3] it is found that the frequency of vibration along the $C-C$ bond between $Cl_3C$ and $CH_3$ is 680. The frequency 714 must then be due to a stretching of this bond. A similar calculation for $Cl_2HC \cdot CH_2Cl$ gives a frequency of 443 which may be compared with the Raman frequency 441. This line is very weak, however. It is possible that the selection rules for $Cl_2HC \cdot CH_2Cl$ are such that the frequency 441

[3] A. Dadieu and K. W. F. Kohlrausch, Monatsh. f. Chem. **52**, 396 (1929).

TABLE III.

| Cl₃C·CH₃ | | MODE OF VIBRATION | Cl₂HC·CH₂Cl | |
|---|---|---|---|---|
| RAMAN | COMBINATION | | RAMAN | COMBINATION |
| 241(7) | | C—Cl bending | 255(4) | |
| 345(10) | | | 332(10) | |
| 523(9) | | Cl₃C and Cl₂HC expansion and contraction | 525(1) | |
| 714(7b) | | C—C stretching | 441(½) | |
| | | | 664(5b) | 2(332) |
| {1071(2) {1086 | 345+714 | | {772(10) {781 | 332+441 |
| | | | 1056(1b) | 2(525) |
| 1242(½b) | 523+714 | | | |
| {1361(½) {1384 | 345+2(523) | | | |
| {1424(2) {1451 | 2(714) | C—H bending | 1428(2) | |
| 1592(½b) | 3(523) | | 1575(½b) | 3(525) |
| 2743(½b) | 2[345+2(523)] | | | |
| 2943(7) | | C—H stretching | 2960(8) | |
| 3011(6) | | | 2996(7) | |
| | | | 3021(5b) | |

cannot give rise to a strong Raman line unless in combination with some other frequency. It may be noted that $332+441=773$ is nearly the mean of the doublet 772,781 (10). Since each radical in $Cl_3C \cdot CH_3$ is symmetrical, one would expect numerous instances of degeneracy which would not occur in $Cl_2HC \cdot CH_2Cl$. Consequently $Cl_2HC \cdot CH_2Cl$ should have more lines in its Raman spectrum than $Cl_3C \cdot CH_3$, as is found to be the case. A comparison of the Raman spectra of the two compounds is given in Table III, possible combination frequencies being indicated, as well as the modes of vibration responsible for certain lines.

It is interesting to note that the doublet 1424,1451 in the Raman spectrum of $Cl_3C \cdot CH_3$ can be ascribed both to the doubling of the fundamental frequency 714 and to the bending of the $C-H$ bond.

In conclusion the author wishes to express his indebtedness to Professor W. W. Watson for his many helpful suggestions during the course of this work, and to his father under whom the preliminary investigations were carried out at Dartmouth College.