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# The Quantum Mechanical Calculations of the Vibration Spectra of the 1- Fluorofulvene and the 2-Fluorofulvene Molecules

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## Abstract

The thirty fundamental vibration modes along with their corresponding IR absorption intensities for both of 1- and 2—fluorofulvene molecules were calculated using the method based on the MINDO/3-FORCES MO model .The assignments of all of these vibration modes were , also, carried out .The effect of the fluorine atom on the vibration spectra of the two molecules were studied. It was shown that there is an effect on the values of the frequencies and the corresponding IR absorption intensities of the fundamental vibration modes associated with the methylene group .In 1-fluorofulvene , any one of these normal modes has the higher frequency and, in some cases, the lower IR absorption intensity values than the corresponding one in the 2-fluorofulvene. In addition, the thermodynamic functions, $U^o$, $H^o$, $S^o$, $G^o$ , and $A^o$ for the two molecules were calculated.

**Key words:MINDO/3-FORCES ,1- and 2-fluorofulvene molecules, vibration spectra.**

## الخلاصة

تم حساب الأنماط الأهتزازية الأساسية الثلاثين برفقة شدد امتصاص الأشعة تحت الحمراء المقابلة لهذه الأنماط ألاهتزازية لكل من الجريئتين 1- فلوروفولفين و 2- فلوروفولفين وذلك باستخدام طريقة نعتمد على اسلوب الميندو-3-فورسيز. أيضا تم تشخيص جميع هذه الأنماط الأهتزازية . وتمت دراسة تاثير ذرة الفلور على الطيف الأهتزازي في الجزيئتين . ووجد إن هناك تأثيرا على قيم الترددات الاهتزازية الأساسية وعلى شدد امتصاص الأشعة تحت الحمراء المصاحبة لها في مجموعة المثلين. في جزيئة 1- فلوروفولفين , أي واحد من هذه الأنماط الأعتيادية يمتلك التردد الأعلى , وفي بعض الحالات , شدة امتصاص الأشعة تحت الحمراء الأقل مقارنة مع ما يناظرها في جزيئة 2- فلوروفولفين . اضافة لذلك ,تم حساب الدوال الثرموداينمكية $U^o$, $H^o$, $S^o$, $G^o$ , $A^o$ للجريئتين المذكورتين.

## Introduction

Fulvenes are a cross-conjugated molecules with some unique properties (1-3). Their structure and electronic distribution were investigated theoretically(4) and experimentally(5). The halogenated substituted fulvenes were used to improve the octane quality of a fuel for an internal combustion engines(6) The fluorosubstituted fulvenes is relatively common ligand in the organometalic ; the low-valent titanium-pentafulvene complexes have been prepared(7).

The 1- and 2-fluorofulvene molecules, Fig.1, were studied theoretically(8) , but there is no reported study concerning their vibration spectra.

a b

**Fig.1:- a ,1-fluorofulvene and b, 2-fluorofulvene molecules**

The aim of this study is to calculate the vibration spectra of the 1-and 2-fluorofulvene molecules , investigate the effect of the fluorine on the fundamental vibration frequencies, and their corresponding IR absorption intensities, associated with the methylene group, and, finally, calculate the thermodynamic functions of these two molecules.

The present study is based on MINDO/3-FORCES model(9) which was developed and applied to the treatment of organic molecules (10-12). Such treatment yields the equilibrium geometry and energy values of the molecules in addition to their fundamental vibration frequencies (3N-6) and IR absorption intensities.

MINDO/3-FORCES model adopts the pulay forces method(13) to evaluate the force constants of molecules which are introduced then to the Wilson Secular equation of the following form(14),

$$\sum_j L_j (F_{ij} - M_{ij}\lambda) = 0$$

Solution of this equation yields vibration frequencies ($\lambda = 4\pi^2 \nu^2 C^2$) and vibration mode eigen vector coefficients, $L_j$ .These coefficients are utilized in evaluating the atomic partial participation values (APP) (the partial contribution of each atom to the molecular vibration), the ir absorption intensities and in doing the graphical representation of each of vibration mode.(10-12).

## Results and Discussion

The optimized geometric parameters of both of 1- and 2-fluorofulvene molecules were listed along with their heats of formation, $\Delta H_f$ , and with some other physical properties, table -1 .From this table, it was shown that the 2-fluorofulvene is slightly less stable than the other molecule. On the other hand, the character table shows that both molecules belong to $C_s$ point group and the thirty fundamental vibration al frequencies are distributed among the following symmetry species,

$$\Gamma_{30} = 21\bar{A} + 9\bar{\bar{A}}$$

Where $21A^-$ are in-plane modes and $9A^=$ are out of plane . Also, all these vibration modes are IR and Raman active.

The thirty fundamental vibrations of each one of the two molecules were listed, tables 2 and 3. Among of these vibrations, seven modes are associated with the methylene group. These are the symmetric and antsymmetric $CH_2$ st., the rocking and scissoring in plane bending , the wagging and twisting out of plane bending, and finally, the $C{=}CH_2$ stretching vibration. In the absence of any experimental data, our calculated results were compared well with that obtained by the MINDO/3(15) and the scaled frequencies were ,in most cases, close to that of PM3 (16) ones, tables 2 and 3.The C-F frequency is not pure mode; it mixed slightly with the ring( $\delta CCC$ )

motion in 2-fluorofulvene and with ring($\delta$CH ) motion in the second molecule. Also, some of ring($\delta$CH ), ring($\gamma$CH ), and ring($\delta CCC$ ) modes , in both of the molecules, are coupled with the other vibration motions. The C-C st. vibrations are not completely pure and they localized along C-C bonds .On the others hand, the C-H vibrations are localized along the C-H bonds.

In this study, we , also, investigated the effect of the fluorine atom on the values of the frequencies and their corresponding IR absorption intensities of the fundamental vibrations, associated with the methylene group, in the 1- and 2-fluorofulvene molecules. The correlation of the fundamental vibrations, associated with the methylene group, in the two molecules, was listed in table-4. From this table, it was shown that each vibration mode, in the 2-fluorofulvene, has the lower frequency and, in some cases, the higher IR absorption intensity than the corresponding mode in the 1-fluorofulvene.This may be attributed to the inductive effect caused by the withdrawing F substituent atom. Due to the closer of F atom to the methylene in the 1-fluorofulvene molecule, the inductive effect is the greater compared with that in the second molecule. The inductive effect causes to draw the electrons towards the F atom, so, this leads to increase the energy required for vibration transitions.

The thirty fundamental vibration frequencies for each one of the two molecules along with the rotational constants A, B, and C , obtained in this study, were used to calculate the vibration and rotation contributions to the thermodynamic functions according to the following statistical thermodynamic equations, (17) ,

$$U^{o}_{vib} = \sum_{i=1}^{30} \frac{RTX_i}{e^{x_i} - 1} \quad ,$$

$$U^{o}_{rot} = 1.5RT$$

$$S^{o}_{vib} = R\sum_{i=1}^{30} \left[\frac{X_i}{e^{X_i} - 1} - \ln(1-e^{-X_i})\right]$$

$$S^{o}_{rot} = R\left[\frac{3}{2} + \ln \frac{8\pi^2 (8\pi^3 I_x I_y I_z)^{1/2} (kT)^{3/2}}{\hbar^3 \sigma}\right]$$

$$X_i = \frac{1.44\nu^{-}}{T} \; , \; \sigma = 1$$

These two contributions along with the others contributions, for the translation, electronic, and nuclear motions, were used to calculate $U^o$ ,$H^o$ ,$S^o$ , $A^o$, and $G^o$ thermodynamic functions of the two molecules,table5.From this table it was obvious that the more stable molecule; 1-fluorofulvene, has the lower $S^o$ than that of the second molecule. There is no available experimental data in order to compare our calculated $S^o$ , However the isomer fluorobenzene(18), which is more stable than the two molecules, $\Delta H_f$, =-90.643 kJ $mol^{-1}$, has the value of 0.303 kJ $mol^{-1}.deg^{-1}$ for $S^o$

**Table -1: The geometric parameters for 1- and 2-fluorofulvene molecules. Bond lengths in angstrom and bond angle in degree: See fig.1**

| Geometric parameter | MINDO/3-FORCES$^*$ | |
|---|---|---|
| | 1-fluorofulvene | 2-fluorofulvene |
| $C_1 – C_2$ | 1.353 | 1.353 |
| $C_2$- $C_3$ | 1.479 | 1.467 |
| $C_3$- $C_4$ | 1.360 | 1.358 |
| $C_4$- $C_5$ | 1.505 | 1.506 |
| $C_5$- $C_1$ | 1.497 | 1.507 |
| $C_5 – C_6$ | 1.336 | 1.338 |
| $C_3 – H_3$ | 1.094 | 1.086 |
| $C_4 – H_4$ | 1.098 | 1.100 |
| $C_6 – H_5$ | 1.101 | 1.101 |
| $C_1 – F(C_2\text{-}F)$ | 1.365 | 1.370 |
| $\angle C_1 C_5 C_4$ | 99.7 | 103.1 |
| $\angle C_5 C_4 C_3$ | 109.7 | 110.4 |
| $\angle C_4 C_3 C_2$ | 111.5 | 107.0 |
| $\angle C_3 C_2 C_1$ | 103.4 | 111.4 |
| $\angle C_2 C_1$ C5 | 115.5 | 107.8 |
| $\angle C_5 C_1F(C_5C_1H_1)$ | 118.7 | 123.8 |
| $\angle C_5 C_4 H_4$ | 122.4 | 123.2 |
| $\angle C_1 C_2 H_2(C_1C_2F)$ | 128.9 | 126.9 |
| $\angle C_4 C_3 H_3$ | 125.6 | 128.1 |
| $\angle C_6 C_5 C_1$ | 130.4 | 128.4 |
| $\angle C_5C_6H_6$ | 124.1 | 124.6 |
| $\angle H_6C_6H_6$ | 110.2 | 110.5 |
| $\Delta H_f$ , kJ mol$^{-1}$ | 71.156 | 72.180 |
| Dipole moment, ( $\mu$ in Debye) | 1.658 | 2.253 |
| HOMO-LUMO, eV | 8.556, 0.100 | 8.788,0.042 |

* calculated in this work

**Table: 2 The calculated thirty fundamental vibration frequencies ($\nu^{-}$ in $cm^{-1}$) along with the corresponding infrared absorption intensities (IR intensities in km. $mol^{-1}$) , for the 1-fluorofulvene molecule. The scaled frequencies and the others calculated frequencies, for the molecule ,were ,also, shown.**

| No | MINDO/3-FORCES* Freq,** $cm^{-1}$; IR intensity, km $mol.^{-1}$ | PM3 Freq. $cm^{-1}$ Ref.16 | MINDO/3 Freq. $cm^{-1}$ Ref.15 | $X_i$$ | Assignments |
|---|---|---|---|---|---|
| | $a^{-}$(in plane) | | | | |
| $\nu_1$ | 3586(3105) 10.28 | 3157 | 3585 | 14.997 | ring (CH st.) |
| $\nu_2$ | 3547(3071) 27.05 | 3148 | 3545 | 14.833 | $CH_2$ as. st |
| $\nu_3$ | 3540(3066) 47.2 | 31.22 | 3539 | 14.809 | ring(CH st.) |
| $\nu_4$ | 3528(2963) 17.37 | 3133 | 3527 | 14.312 | CH2 s.st. |
| $\nu_5$ | 3518(3046) 20.52 | 3127 | 3517 | 14.713 | ring (CH st.) |
| $\nu_6$ | 1854(1626) 30.02 | 1329 | 1853 | 7.854 | C $=CH_2$ st |
| $\nu_7$ | 1738(1524) 39.44 | 1875 | 1737 | 7.361 | ring(C=C st.) |
| $\nu_8$ | 1671(1465) 28.44 | 1739 | 1670 | 7.076 | ring(C=C st.) |
| $\nu_9$ | 1349(1349) 27.31 | 1518 | 1349 | 6.516 | $\delta_s$ $CH_2$ + ring(C-C st.) |
| $\nu_{10}$ | 1353(1353) 7.611 | 1397 | 1332 | 6.535 | ring (CCC st.) |
| $\nu_{11}$ | 1309(1309) 13.52 | 1345 | 1308 | 6.322 | ring (C-C st.) + $\delta_s$ $CH_2$ |
| $\nu_{12}$ | 1181(1181) 6.79 | 1298 | 1179 | 5.704 | ring ($\delta$ CCC)+ring(C-F st.) |
| $\nu_{13}$ | 1091(1189) 2.54 | 1178 | 1091 | 5.743 | ring($\delta$ CH)(clock-anticlockwise) |
| $\nu_{14}$ | 1067(1163) 6.5 | 1102 | 1067 | 5.617 | ring($\delta$ CH) |
| $\nu_{15}$ | 1008(1008) 1.14 | 1071 | 1008 | 4.868 | ring($\delta$ CH) +C-F st. |
| $\nu_{16}$ | 893(893) 0.89 | 954 | 891 | 4.313 | $\rho_{CH2}$+ring($\delta$ CCC) |
| $\nu_{17}$ | 829(829) 4.85 | 888 | 826 | 4.004 | ring ($\delta$ C-F)+ $\rho_{CH2}$ |
| $\nu_{18}$ | 637(687) 0.46 | 798 | 637 | 3.318 | ring($\delta$ CCC)(ring elongation) |
| $\nu_{19}$ | 478(515) 0.2 | 621 | 473 | 2.487 | ring ($\delta$ CCC) |
| $\nu_{20}$ | 352(379) 1.01 | 474 | 352 | 1.830 | $\delta$ ring |
| $\nu_{21}$ | 191(191) 1.99 | 280 | 189 | 0.922 | ring ($\delta$ CF) |
| | $a^{=}$(out of plane) | | | | |
| $\nu_{22}$ | 917(1010) 1.15 | 1039 | 918 | 4.878 | $\omega_{CH2}$ |
| $\nu_{23}$ | 824(898) 0.34 | 975 | 824 | 4.337 | ring ($\gamma$ CH.) |
| $\nu_{24}$ | 757(825) 0.0 | 907 | 758 | 3.984 | ring($\gamma$ CH.) |
| $\nu_{25}$ | 738(804) 7.2 | 800 | 739 | 3.883 | ring($\gamma$ CH.) |
| $\nu_{26}$ | 645(645) 5.15 | 692 | 647 | 3.115 | $\tau_{CH2}$+ ring ($\gamma$ CH.) |
| $\nu_{27}$ | 575(575) 3.49 | 614 | 576 | 2.777 | ring ($\gamma$ CH.)+ $\tau_{CH2}$ |
| $\nu_{28}$ | 408(408) 4.05 | 461 | 412 | 1.970 | ring($\gamma$ CC.) |
| $\nu_{29}$ | 265(265) 1.68 | 317 | 264 | 1.28 | ring($\gamma$ C-F.)+ ring($\gamma$ CC) |
| $\nu_{30}$ | 139(196) 1.4 | 161 | 140 | 0.946 | $CH_2$ tor. |

s: symmetric, st: stretching, $\delta$ : in plane bending, as: antsymmetric, $\gamma$ : out of plane bending, tor: torsion, $\rho$ :rocking, $\omega$ : wagging,: $\tau$ :twisting , $:$X_i = \frac{1.44\nu^{-}}{T}$

* calculated in this work , ** The value between brackets is the scaled frequency(15)

**Table 3: The calculated thirty fundamental vibration frequencies ($\bar{\nu}$ in $cm^{-1}$) along with the corresponding infrared absorption intensities (ir intensities in km $mol^{-1}$) , for the 2-fluorofulvene molecule. The scaled frequencies and the others calculated frequencies, for the molecule ,were ,also, shown.**

| No | MINDO/3-FORCES$^{*}$<br>Freq,$^{**}$ $cm^{-1}$; | ir intensity, km $mol.^{-1}$ | PM3 Freq. $cm^{-1}$ Ref.16, | MINDO/3 ref.15 | $X_i^{\$}$ | Assignments |
|---|---|---|---|---|---|---|
| | $a^{-}$(in plane) | | | | | |
| $\nu_1$ | 3581(3101) | 7.37 | 3158 | 3579 | 14.978 | ring (CH st.) |
| $\nu_2$ | 3569(3091) | 20.76 | 3152 | 3568 | 14.930 | ring (CH st.) |
| $\nu_3$ | 3542(3067) | 32.08 | 3140 | 3541 | 14.814 | $CH_2$ as st.) |
| $\nu_4$ | 3527(2963) | 18.02 | 3136 | 3526 | 14.312 | CH2 s.st. |
| $\nu_5$ | 3516(3045) | 24.23 | 3131 | 3515 | 14.708 | ring (CH st.) |
| $\nu_6$ | 1836(1610) | 13.10 | 1920 | 1835 | 7.776 | C =$CH_2$ st |
| $\nu_7$ | 1735(1521) | 37.19 | 1872 | 1733 | 7.346 | ring(C=C st.) |
| $\nu_8$ | 1673(1467) | 3.330 | 1743 | 1672 | 7.086 | ring(C=C st.) |
| $\nu_9$ | 1403(1230) | 68.72 | 1524 | 1401 | 5.941 | ring(C-C st.) |
| $\nu_{10}$ | 1330(1448) | 0.590 | 1402 | 1330 | 6.994 | $\delta_s$ $CH_2$ |
| $\nu_{11}$ | 1299(1299) | 12.18 | 1343 | 1298 | 6.274 | ring (C-C st.) |
| $\nu_{12}$ | 1162(1267) | 12.82 | 1268 | 1161 | 6.119 | ring ($\delta$ CH) |
| $\nu_{13}$ | 1094(1192) | 0.44 | 1184 | 1094 | 5.757 | ring($\delta$ CH) |
| $\nu_{14}$ | 1035(1128) | 0.49 | 1084 | 1035 | 5.448 | ring($\delta$ CH) |
| $\nu_{15}$ | 968(1043) | 5.82 | 1069 | 966 | 5.037 | ring($\delta$ CCC)(ring elongation) |
| $\nu_{16}$ | 946(946) | 4.50 | 997 | 942 | 4.569 | ring($\delta$ CCC)+ring(C-F)st. |
| $\nu_{17}$ | 873(988) | 1.49 | 927 | 873 | 4.772 | $\rho_{CH2}$ |
| $\nu_{18}$ | 594(640) | 0.64 | 726 | 594 | 3.091 | ring($\delta$ CCC)(ring elongation) |
| $\nu_{19}$ | 478(515) | 1.32 | 620 | 473 | 2.487 | ring ($\delta$ CCC) |
| $\nu_{20}$ | 344(541) | 0.46 | 463 | 344 | 2.613 | $\delta$ ring |
| $\nu_{21}$ | 218(218) | 1.88 | 307 | 215 | 1.052 | ring ($\delta$ CF) |
| | $a^{=}$(out of plane) | | | | | |
| $\nu_{22}$ | 891(981) | 2.46 | 1043 | 893 | 4.738 | $\omega_{CH2}$ |
| $\nu_{23}$ | 826(900) | 0.03 | 970 | 826 | 4.437 | ring ($\gamma$ CH.) |
| $\nu_{24}$ | 782(852) | 9.33 | 908 | 782 | 4.115 | ring($\gamma$ CH.) |
| $\nu_{25}$ | 711(711) | 1.01 | 808 | 712 | 3.434 | ring ($\gamma$ CC.)+ $\tau_{CH2}$ |
| $\nu_{26}$ | 607(607) | 0.64 | 638 | 610 | 2.931 | $\tau_{CH2}$+ ring ($\gamma$ CC) |
| $\nu_{27}$ | 571(571) | 2.17 | 609 | 571 | 2.758 | ring ($\gamma$ CC)+ $\tau_{CH2}$ |
| $\nu_{28}$ | 498(498) | 4.89 | 546 | 500 | 2.405 | ring($\gamma$ CC)+ ring($\gamma$ C-F.) |
| $\nu_{29}$ | 243(243) | 2.68 | 292 | 243 | 1.173 | ring($\gamma$ C-F.)+ ring($\gamma$ CC) |
| $\nu_{30}$ | 134(134) | 0.07 | 155 | 134 | 0.912 | $CH_2$ tor. |

For abbreviations and symbols, see table 2.

**Table 4:-The correlation of the fundamental vibration frequencies, $\nu^{-}$, cm$^{-1}$ and their corresponding ir intensities, km mol$^{-1}$ associated with the methylene group in 1-and 2-fluorofulvene molecules.**

| Type of vibration mode | 1-fluorofulvene<br>$\nu^{-}$, cm$^{-1}$ ( ir , km mol$^{-1}$) | 2-fluorofulvene<br>$\nu^{-}$, cm$^{-1}$ ( ir , km mol$^{-1}$) |
|---|---|---|
| $\rho_{CH2}$ | $\nu_{16}$, 893(0.89) | $\nu_{17}$, 873(1.49) |
| $\omega_{CH2}$ | $\nu_{22}$,917(1.15) | $\nu_{22}$, 891(2.46) |
| $\tau_{CH2}$ | $\nu_{26}$,645(5.15) | $\nu_{26}$ ,607(0.64) |
| $\delta_{s}$ $CH_2$ | $\nu_{9}$,1349(27.31) | $\nu_{10}$,1330(0.59) |
| CH2 as. st. | $\nu_{2}$,3547(27.05) | $\nu_{3}$,3542(32.08) |
| CH2 s.st. | $\nu_{4}$,3528(17.37) | $\nu_{4}$,3527(18.02) |
| C=CH2 st. | $\nu_{6}$,1854(30.02) | $\nu_{6}$,1836(13.02) |
| CH2 tor. | $V_{30}$,139(1.4) | $V_{30}$,134(0.07) |

**Table 5: The calculated standard thermodynamics functions at 298.12$^{o}$ K for 1- and 2-fluorofulvene molecules**

| Thermodynamics function | 1-fluorofulvene | 2-fluorofulvene |
|---|---|---|
| U$^{o}$ , kJ mol$^{-1}$ | 15.801 | 16.298 |
| H$^{o}$, kJ mol$^{-1}$ | 18.279 | 18.776 |
| S$^{o}$, kJ mol$^{-1}$.deg$^{-1}$ | 0.430 | 0.435 |
| G$^{o}$, kJ mol$^{-1}$ | -109.986 | -110.832 |
| A$^{o}$, kJ mol$^{-1}$ | -112.464 | -113.311 |

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