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# Relative Studies of Vibrational and Quantum Chemical Calculations on Some α, β-Unsaturated Esters and Related Molecule

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## Abstract

The paper presents a study on the vibrational spectra of four different compounds, namely, methyl acrylate (MA), methyl methacrylate (MMA), methyl trans crotonate (MTC), and methyl-3-methoxy-2-propenoate (MMP), in their electronic ground state using the Hartree-Fock and Density Functional Theory calculations with extended basis sets and polarization functions. The study compares the outcomes of the possible conformers in terms of their frequency, form, and intensity of vibrations, as well as the potential energy distribution across the symmetry coordinates in the ground state. Moreover, the study examines the relationship between bond length and bond order.

*Keywords*: Ab initio calculation; Vibrational analysis; Atomic population; Bond order.

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## 1. Introduction

Some conformational studies by spectroscopic and quantum chemical methods on methyl acrylate [1-4], methyl methacrylate [4-9], and methyl trans crotonate [7-9] rotational isomerism about the carbon-carbon single bond leading to s-*cis* and s-*trans* conformers have been reported in the literature. However, uncertainty continues regarding the relative stability of the two conformers in each case. Vibrational spectra studies of methyl acrylate [1,2] have shown a preference for the *trans* conformer, microwave [3], electron diffraction, and quantum chemical [5] studies have predicted the s-*cis* conformer to be more stable. Based on electron diffraction, vibrational spectra, and *ab initio* calculations, Takemasa *et al*. [6] have concluded that the molar fraction of the s-*trans* conformer in the mixture of the s-*trans* and s-*cis* conformers is 0.64. However, based on angle-resolved electron energy loss spectra (EELS) and *ab initio* calculations, Rocco *et al*. [7] suggest that the s-*cis* and s-*trans* conformers are nearly equally populated at room temperature. Based on *ab initio* calculations involving Moller-Plesset correction at the MP2 level, Hollauer *et al.* [8] conclude that s-*cis* conformer is more stable than s-*trans* by 1.61 kcal/mol. Further, the *ab initio* CI and MP2-based calculations [9] lead to different inferences about the relative stability of the two conformers.

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Previous research has investigated the conformational behavior of three different esters, namely methyl acrylate [1-4], methyl methacrylate [5-9], and methyl trans crotonate [10-13]. These studies have focused on the rotational isomerism around the carbon-carbon single bond, resulting in two possible conformers: s-cis and s-trans. However, despite extensive research, the relative stability of each conformer remains uncertain. Vibrational spectra studies of methyl acrylate [1,2] have shown a preference for the trans conformer, while other methods such as microwave [3], electron diffraction, and quantum chemical [12] studies have predicted the s-cis conformer to be more stable. Takemasa *et al*. [5] concluded that the molar fraction of the s-trans conformer in the mixture of s-trans and s-cis conformers is 0.64 based on electron diffraction, vibrational spectra, and ab initio calculations. However, Rocco *et al.* [6] suggest that the two conformers are nearly equally populated at room temperature based on angle-resolved electron energy loss spectra and ab initio calculations. Hollauer *et al.* [7] used ab initio calculations involving Moller-Plesset correction at the MP2 level. They found that the s-cis conformer is more stable than s-trans by 1.61 kcal/mol. In contrast, the ab initio CI and MP2 [8] based calculations lead to different inferences about the relative stability of the two conformers. This study aims to fill the gap in the literature by conducting a comparative study of the vibrational spectra and the relationship between the bond length and bond order of these esters.

Based on the temperature dependence of the infrared and Raman bands in the vapor [9], solution [1], and liquid [2] states, it was inferred that the s-*trans* conformer of methyl *trans* crotonate is more stable than its s-*cis* conformer. These results were confirmed by Vsetecka *et al.* [13] from CNDO/2 calculations. However, based on 4-31G level *ab initio* SCF MO calculations, Dulce *et al*. [14] have contradicted these findings and suggested that the s-*cis* conformer is more stable than s-*trans*.

Our previous results [15] shed light on the relative stability of the s-cis and s-trans conformers and contribute to a better understanding of the conformational behavior of these important molecules. The conformers of esters have been extensively studied in the literature using spectroscopic and quantum chemical methods. However, there is a lack of comparative studies investigating the relationship between the vibrational spectra and these compounds' bond length and order. To address this knowledge gap, we aim to perform quantum chemical studies on a series of esters and investigate the relationship between the vibrational spectra and the bond length and order. By doing so, we hope to provide a deeper understanding of the conformations of esters and contribute to developing new theoretical models that can predict the vibrational spectra and structural properties of these important compounds.

## 2. Methodology

Torsion potential energy curves for these molecules' ground (S0) and excited (S1) electronic states are obtained by ab initio SCF-RHF calculations using 6-31G** extended basis sets. The primary calculations predict the existence of two stable conformers in all these esters. Fully optimized geometries of the stable conformers are used in our calculations. Calculated and scaled vibrational frequencies, intensities, and assignments of the fundamental vibrational bands of all the conformers are obtained by RHF/6-31G** and DFT/6-311G** methods. All the calculations are performed by using the software GAMESS [16].

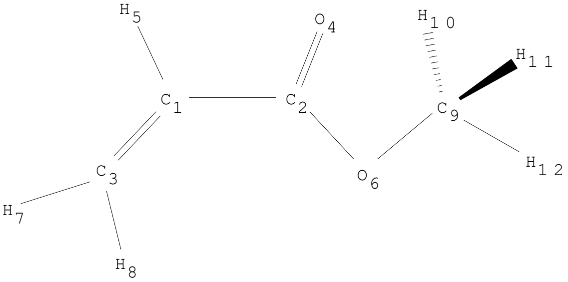

Fig. 1. Numbering of atoms of methyl acylate.

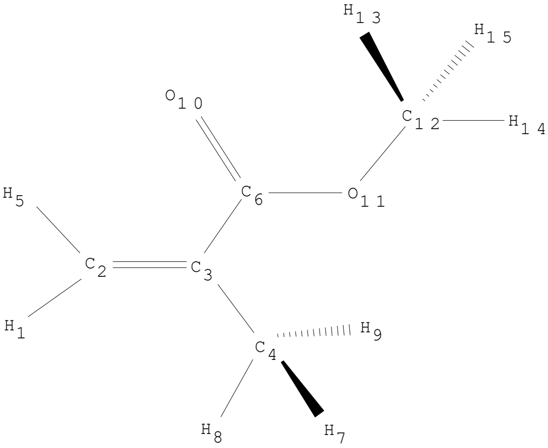

Fig. 2. Numbering of atoms of methyl methacrylate.

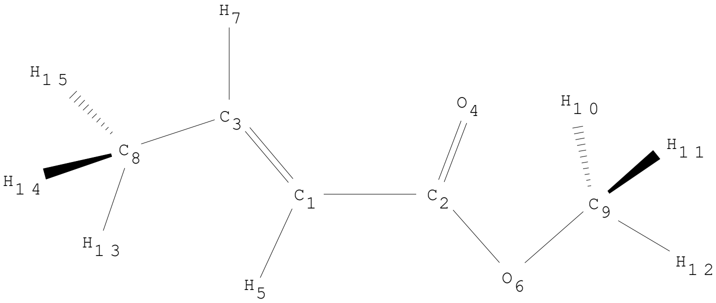

Fig. 3. Numbering of atoms of methyl trans crotonate.

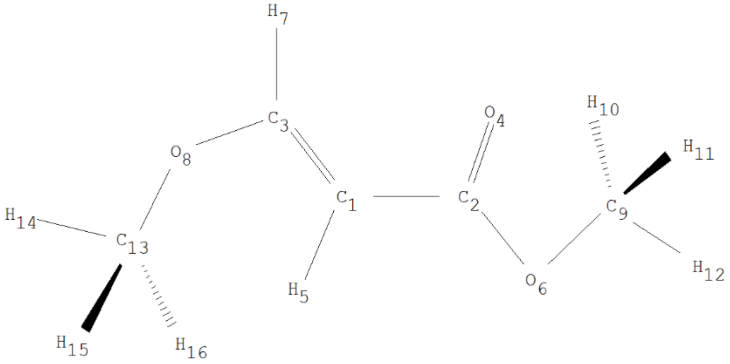

Fig. 4. Numbering of atoms of methyl-3-methoxy-2-propenoate.

## 3. Conformational Notations

Conformations with respect to dihedral angle φ(C=C-C=O) (Figs. 1-4) are denoted by a capital C (*cis* or syn, = 0°) or T (*trans* or anti, φ = 180°). Conformations with respect to the dihedral angle φ (O=C-O-C) are represented by lower case letter c (*cis* or syn, φ = 0°) or t (*trans* or anti, φ = 180°) following the capital letter C or T. Rotation of the methyl groups about the C-C and O-C bonds may give rise to either eclipsed or staggered conformations relative to the carbonyl group. However, in the present case, only the staggered conformations are found to be stable, and no separate notations are used for the purpose

## 4. Results and Discussion

### 4.1. *Vibrational studies*

Both the conformers of α, β-unsaturated esters belong to Cs point group. Symmetry coordinates corresponding to A′ and A″ species are calculated. Frequencies obtained from RHF calculations are found to be much higher than the experimental values due to the neglect of anharmonicity and correlational effects and therefore scaled using factors suggested by Baker *et al*. [17]. Since the DFT methods account for the correlational effects to a large extent, the calculated frequencies from DFT/6-311G** method are much closer to the experimental values. These have been scaled using the expression suggested by Yoshida *et al.* [18,19].

$$\upsilon_{obs}/\ \upsilon_{calc} = 1.0087 - 0.0000163\ \upsilon_{calc}$$

An analysis of the vibrational spectra of the presently studied unsaturated esters on the basis of *ab initio* calculations by RHF and DFT methods using extended double zeta and triple zeta basis sets with polarization functions and diffuse functions lead to some important conclusions about the structures of the molecules, the influence of structural changes on the frequencies and intensities of the vibrational bands and their correlation with the nature of the bonds and the substituents. Correcting some of the earlier assignments for the different vibrational bands and identifying characteristic bands of the various conformational forms has also been possible. Both the RHF and DFT methods are known to give higher values for the vibrational frequencies, mainly due to the neglect of anharmonicity effects. DFT is, however, known to include long-range electron correlation effects. Therefore, the calculated frequencies from RHF and DFT were suitably scaled by appropriate scaling techniques. It is found that although the assignments based on both methods are identical, the DFT frequencies and intensities are much closer to the experiment; the average difference between the experiment and calculated frequencies is ± 20 $cm^{-1}$.

A strong band in the unsaturated esters' spectra may be assigned to the carbonyl stretch mode. The position of this band in aldehydes, ketones, and acid halides is known [20-21] to depend on the nature of the substituent in the vicinity of the carbonyl group. Thus, in aldehydes, it appears near 1710 $cm^{-1}$ in ketones such as methyl vinyl ketone (having a methyl group in the vicinity of the carbonyl group), it appears near 1730 $cm^{-1}$ and in acid halides, it shifts to higher frequencies up to 1830 $cm^{-1}$, depending upon the electronegativity of the halogen atom. In the present case of unsaturated esters, this band appears in a narrow range of 1730-1755 $cm^{-1}$, close to the range in analogous ketones suggesting that the effect of a methoxy or methyl group in the vicinity of the carbonyl is almost identical. The change in conformation is found to appreciably affect the intensity of this band without changing its frequency significantly. Thus, it is found that in all the molecules, the intensity of the C=O stretch band of the *trans* conformer is more than that of the *cis* conformer. A direct relationship is found to exist between the bond order and frequency of the carbonyl bond; an increase in the bond order is associated with an increase in the frequency.

The C=C stretch (Table 1) bands in the presently studied molecules lie in a narrow range of 1630-1670 $cm^{-1}$. Change of conformation also does not affect the position of this band, although it considerably changes its intensity. In all cases, the intensity of this band in the *cis* conformer is more than in the *trans* conformer. This is in accordance with the general observation that the C=C band intensity decreases with an increase in symmetry. It is further observed that the ratio of intensities of the C=O and C=C stretch modes in the series of molecules is more in the *trans* conformers than in the *cis* conformers. Thus, it has values 16.23, 10.47, 12.73, and 1.62 in the *trans* conformers of methyl acrylate, methyl methacrylate, methyl *trans* crotonate, and methyl-3-methoxy-2-propenoate, respectively, and 6.74, 4.69, 1.60 and 0.44 in their *cis*.

Table 1. Comparison of the calculated experimental frequencies, intensities, and bond order of conformers having major stretching modes (C=O, C=C, C-C, C-O, and O-C) of MA, MMA, MC, and MMP.

| Molecule | C=O stretch | | C=C stretch | | C-C stretch | | C-O stretch | | O-C stretch | |
|---|---|---|---|---|---|---|---|---|---|---|
| MA | Cc | Tc | Cc | Tc | Cc | Tc | Cc | Tc | Cc | Tc |
| Calc. | 1754.21 | 1753.61 | 1661.00 | 1653.19 | 864.93 | 856.43 | 1208.45 | 1275.09 | 1012.36 | 979.98 |
| Intensity | 189.09 | 254.07 | 28.05 | 15.65 | 10.83 | 12.39 | 292.24 | 308.64 | 17.38 | 22.78 |
| Exp. | 1755 | 1755 | 1642 | 1642 | 855 | 855 | 1209 | 1209 | 964 | 964 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Bond order | 1.870 | 1.868 | | | | | | | | |
| MMA | Tc | Cc | Tc | Cc | Tc | Cc | Tc | Cc | Tc | Cc |
| Calc. | 1734.90 | 1744.30 | 1660.22 | 1659.81 | 1323.67 | 1297.86 | 840.66 | 831.01 | 1032.88 | 1022.89 |
| Intensity | 232.63 | 169.70 | 22.20 | 36.18 | 125.72 | 147.20 | 5.84 | 9.27 | 14.16 | 18.58 |
| Exp. | 1735 | 1741 | 1636 | 1646 | 1325 | 1301 | 833 | 820 | 1028 | 1017 |
| Bond order | 1.769 | 1.771 | | | | | | | | |
| MC | Cc | Tc | Cc | Tc | Cc | Tc | Cc | Tc | Cc | Tc |
| Calc. | 1742.20 | 1740.24 | 1676.55 | 1670.57 | 909.83 | 852.63 | 1200.24 | 1273.05 | 1034.75 | 1054.84 |
| Intensity | 192.71 | 322.23 | 119.91 | 25.30 | 4.94 | 21.54 | 182.88 | 387.24 | 37.40 | 80.97 |
| Exp. | 1723 | 1729 | 1662 | 1650 | 841 | 841 | 1198 | 1278 | 1026 | 1026 |
| Bond order | 1.752 | 1.741 | | | | | | | | |
| MMP | c′Cc | c′Tc | c′Cc | c′Tc | c′Cc | c′Tc | c′Cc | c′Tc | c′Cc | c′Tc |
| Calc. | 1735.04 | 1734.74 | 1639.77 | 1640.50 | 1335.28 | 1294.22 | 930.13 | 866.29 | 1037.85 | 1061.44 |
| Intensity | 215.75 | 389.13 | 488.79 | 240.62 | 108.39 | 139.14 | 52.19 | 79.65 | 17.33 | 114.79 |
| Exp. | 1730 | 1730 | 1638 | 1638 | 1341 | 1341 | 936 | 936 | 1060 | 1060 |
| Bond order | 1.740 | 1.737 | | | | | | | | |

C-C and C-O stretch bands are found to be non-characteristic in all the presently studied systems, and their calculated values appear in a broad range of 830-1335 cm$^{-1}$ (820-1341 cm$^{-1}$ experimental). Both the frequency and intensity of these bands are greatly influenced by the conformation change. However, no uniformity in these changes could be observed. As against these bands, the frequency of O-$CH_3$ stretch mode lies in a narrow range of 1012-1038 cm$^{-1,}$ which shifts by about 30 cm$^{-1}$ with the change of conformation. The other skeletal mode vibrations, like the C-O-C and C=C-C bend, appear in the far infrared region 140-350 cm$^{-1}$. While a change of conformation has an insignificant effect on the position of the C-O-C deformation band, it shifts the C=C-C band by about 15 cm$^{-1}$.

Four sets of bands at 3018 ± 3, 2922 ± 2, 1475 ± 2 and 1450 ± 4 cm$^{-1}$ (Table 2) observed in all the spectra of esters presently studied may be assigned to the asymmetric and symmetric stretch and the corresponding deformation modes of the methyl group. Being attached to an oxygen atom with a higher electronegativity than carbon, the symmetric deformation band experiences a higher frequency shift of about 80 cm$^{-1}$ from its normal position of about 1370 cm$^{-1}$ in alkanes. It appears as a band of medium to strong intensity in contrast to the asymmetric deformation band at 1475 ± 2 cm$^{-1}$ which has a weak intensity. In addition to the above set of absorption bands, an absorption peak of medium to strong intensity appears at 1195 ± 10 cm$^{-1}$ in all the spectra and may be assigned to the methyl rock mode. The frequencies and intensities of bands of the methyl group do not experience any major change with the change in molecular conformation.

Table 2. Comparison of the calculated experimental frequencies, intensities, and bond order of conformers having major stretch and bending mode ($CH_3$) of MA, MMA, MC, and MMP.

| Molecule | $CH_3$ asym. Stretch | | $CH_3$ sym. stretch | | $CH_3$ asym. bend | | $CH_3$ sym. bend | | $CH_3$ rock | |
|---|---|---|---|---|---|---|---|---|---|---|
| MA | Cc | Tc | Cc | Tc | Cc | Tc | Cc | Tc | Cc | Tc |
| Calc. | 3020.94 | 3019.73 | 2922.85 | 2922.72 | 1475.42 | 1477.44 | 1450.20 | 1452.10 | 1188.19 | 1195.62 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Intensity | 18.30 | 16.19 | 29.48 | 30.41 | 7.73 | 7.97 | 24.05 | 23.71 | 126.75 | 7.59 |
| Exp. | 2963 | 2963 | 2859 | 2859 | 1468 | 1468 | 1443 | 1443 | 1078 | 1078 |
| MMA | Tc | Cc | Tc | Cc | Tc | Cc | Tc | Cc | Tc | Cc |
| Calc. | 3018.47 | 3019.74 | 2923.12 | 2924.17 | 1476.33 | 1475.35 | 1451.64 | 1454.36 | 1199.88 | 1203.85 |
| Intensity | 16.27 | 17.17 | 31.99 | 32.16 | 9.17 | 3.19 | 8.69 | 9.53 | 114.40 | 198.39 |
| Exp. | 3030 | 3033 | 2913 | 2913 | 1467 | 1467 | 1454 | 1448 | 1204 | 1210 |
| MC | Cc | Tc | Cc | Tc | Cc | Tc | Cc | Tc | Cc | Tc |
| Calc. | 3018.48 | 3016.76 | 2922.64 | 2921.97 | 1475.23 | 1476.39 | 1447.33 | 1449.62 | 1185.51 | 1194.06 |
| Intensity | 19.54 | 17.62 | 33.89 | 34.60 | 6.81 | 8.34 | 12.62 | 19.76 | 175.16 | 13.06 |
| Exp. | 3023 | 3023 | 2952 | 2952 | 1469 | 1469 | 1444 | 1444 | 1181 | 1181 |
| MMP | c′Cc | c′Tc | c′Cc | c′Tc | c′Cc | c′Tc | c′Cc | c′Tc | c′Cc | c′Tc |
| Calc. | 3016.42 | 3015.59 | 2922.06 | 2921.73 | 1476.25 | 1477.57 | 1446.32 | 1448.95 | 1193.44 | 1193.43 |
| Intensity | 20.03 | 18.55 | 37.00 | 37.45 | 8.53 | 7.59 | 2.91 | 24.66 | 0.122 | 20.75 |
| Exp. | 3023 | 3023 | 2952 | 2952 | - | - | - | - | - | - |

Infrared spectra of the unsaturated esters have a number of vibrational frequencies in the 60-200 cm$^{-1}$ range, which may be ascribed to torsional modes about C-C, O-C, and C-O bonds (Table 3). The lowest frequency absorption bands in the 60-100 cm$^{-1}$ region may be assigned to asymmetric torsion of the molecule about the C-C bond. The asymmetric torsional modes of the Cc conformers appear at a higher frequency than those of the Tc conformer (c′Cc and c′Tc in case of MMP). Further, the asymmetric torsional frequencies of the Cc and Tc conformers of MMA are the lowest due to the mass effect of the methyl group at α-position to the carbonyl bond. The torsional frequencies of the methoxy group about the C-O bond and the methyl group about the O-C bond appear in 113-200 cm$^{-1}$ and 90-160 cm$^{-1}$ regions, respectively. The frequencies of both these bands are sensitive to the polarity of the neighboring substituent and appear at a lower value when the substituent is more polar. Thus, in the Cc conformer of MC, the torsional band of the methyl group closer to the C=O bond appears at 160 cm$^{-1}$ the other while that of one closer to the C=C bond appears at 219 cm$^{-1}$. Similar is the situation with its Tc conformer and also in the c′Cc and c′Tc conformers of MMP. Identically, in the c′Cc and c′Tc conformers of MMP, the torsional frequencies of the methoxy group closer to the C=O bond are predicted at 117.91 and 120.08 cm$^{-1}$ and those away from it and closer to the C=C bond at 362.27 and 351.56 cm$^{-1}$, respectively.

Table 3. Comparison of the calculated experimental frequencies, intensities, and bond order of conformer having torsion about single bonds (C-C, C-O, and O-CH$_3$) of MA, MMA, MC, and MMP.

| Molecule | C-C torsion | | C-O torsion | | O-CH$_3$ torsion | |
|---|---|---|---|---|---|---|
| MA | Cc | Tc | Cc | Tc | Cc | Tc |
| Calc. | 96.71 | 95.31 | 200.78 | 179.92 | 121.69 | 130.12 |
| Intensity | 3.20 | 0.36 | 4.44 | 6.52 | 0.17 | 0.04 |
| Exp. | 87 | 87 | 203 | 203 | 185 | 185 |
| MMA | Tc | Cc | Tc | Cc | Tc | Cc |
| Calc. | 61.02 | 69.23 | 113.53 | 113.37 | 147.65 | 160.67 |
| Intensity | 0.61 | 1.50 | 1.46 | 0.86 | 3.34 | 3.86 |
| Exp. | - | - | - | - | - | - |
| MC | Cc | Tc | Cc | Tc | Cc | Tc |

| | | | | | | |
|---|---|---|---|---|---|---|
| Calc. | 88.69 | 89.60 | 162.17 | 144.63 | 113.95 | 123.21 |
| Intensity | 3.63 | 0.70 | 0.51 | 1.99 | 0.02 | 0.03 |
| Exp. | - | - | 191 | 191 | 160<br>(219) | 160<br>(219) |
| MMP | c′Cc | c′Tc | C′Cc | c′Tc | C′Cc | C′Tc |
| Calc. | 86.82 | 77.34 | 117.91 | 120.68 | 96.41 | 91.70 |
| Intensity | 0.05 | 3.191 | 0.36 | 0.03 | 2.08 | 2.04 |
| Exp. | - | - | -<br>(362.27) | -<br>(351.56) | - | - |

An inverse relationship has been observed between the bond lengths and orders of the corresponding bonds, both in the case of change of conformation and electronic excitation. Thus, in all unsaturated molecules, the bond orders of the C=O and C=C bonds decrease with increased lengths on electronic excitation. Likewise, a decrease in the length of the C-C single bond between the carbonyl and vinyl double bonds leads to a corresponding increase in its bond order on electronic excitation.

## Conclusion

In conclusion, our quantum chemical studies on methyl acrylate, methyl methacrylate, methyl trans crotonate, and methyl-3-methoxy-2-propenoate have provided valuable insights into the vibrational spectra and the relationship between bond length and bond order. Our findings, based on DFT/6-311G** and RHF/6-31G** calculations, support the correctness of our vibrational assignments, as evidenced by the close agreement between the experimental infrared data and the calculated data. These results may have implications for future studies on these esters and the broader field of vibrational spectroscopy.

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