A Comparative study of the characteristic vibrations of methyl acrylate, methyl methacrylate, methyl *trans* crotonate and methyl -3-methoxy-2-propenoate

Ajit Virdi[1]
[1]Affiliation, Country, Email
[1] Model Institute of Engineering & Technology Kotbhalwal Jammu, Jammu & Kashmir 181122 India,
ajit.ash@mietjammu.in

ABSTRACT

A relative quantum chemical study of the vibrational spectra of of methyl acrylate (MA), methyl methacrylate (MMA), methyl *trans* crotonate (MTC) and methyl -3-methoxy-2-propenoate(MMP) in their electronic ground state has been reported. Based on the Hartree-Fock and Density Functional Theory with extended basis sets and polarization functions calculations the results of the possible conformers are compared in terms of frequency, form and intensity of vibrations and potential energy distribution across the symmetry coordinates in ground state. A relationship between the bond length and bond order is also studied.

Key words: Ab initio calculation, vibrational analysis, atomic population, bond order

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 to exist regarding the relative stability of the two conformers in each case. Vibrational spectra studies of methyl acrylate [1[,[2] have shown 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.

Based on the temperature dependence of the infrared and Raman bands in the vapour [10], 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. [11] from CNDO/2 calculations. However, based on 4-31G level *ab initio* SCF MO calculations, Dulce et al. [12] have contradicted these findings and suggested that the s-*cis* conformer is more stable than s-*trans*.

No comparative studies about the vibrational spectra and relationship between the bond length and bond order is reported in the literature. In order to fill the void in the literature we attempt to perform quantum chemical studies on these esters

1.1 METHODOLOGY

Torsion potential energy curves for the ground (S_0) and excited (S_1) electronic states of these molecules are obtained by ab initio SCF-RHF calculations using 6-31G extended basis sets. The primary calculations predict the existence of two stable conformer 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 the all the conformers are obtained by RHF/6-31G** and DFT/6-311G** methods. All the calculations are performed by using software GAMESS [13]
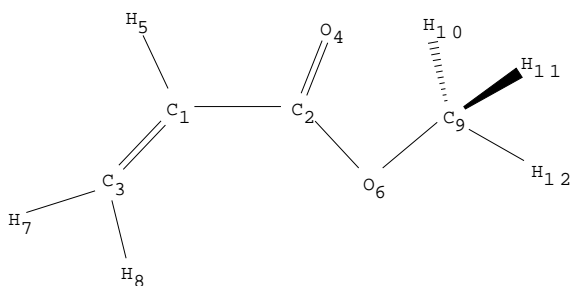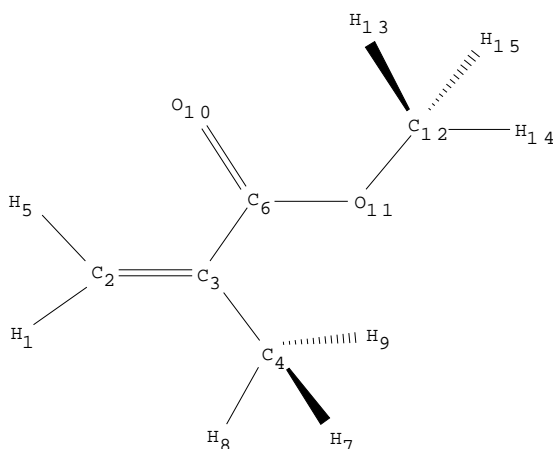
Figure 1: Numbering of atoms of methyl acylate
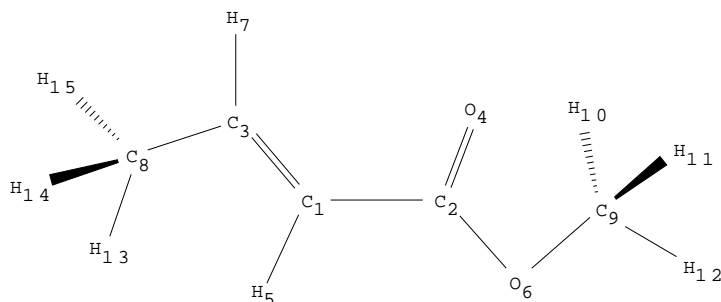

Figure 2: Numbering of atoms of methyl methacylate

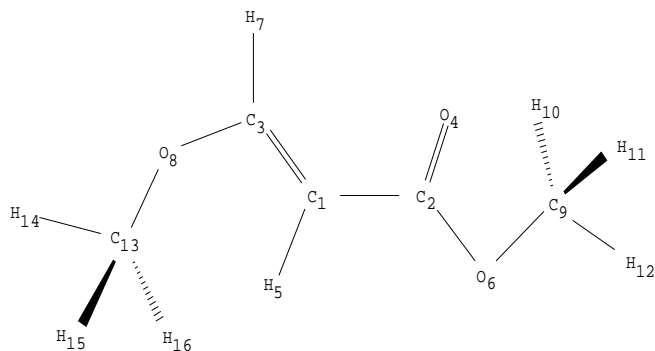**Figure 3:** Numbering of atoms of methyl trans crotonate

Figure 4 : Numbering of atoms of
methyl-3-methoxy-2-propenoate

1.2 CONFORMATIONAL NOTATIONS

Conformations with respect to dihedral angle ϕ(C=C-C=O) (Fig.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 is used for the purpose

2. RESULTS AND DISCUSSION

2.1 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. [14]. 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:

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

suggested by Yoshida et al. [15], [16].

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. It has also been possible to correct some of the earlier assignments for the different vibrational bands and to identify characteristic bands of the various conformational forms. 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. The calculated frequencies both from RHF and DFT were, therefore, suitably scaled by appropriate scaling techniques. It is found that although the assignments based on both the methods are identical, the DFT frequencies and intensities are much closer to the experiment; the average difference between the experiment and calculated frequencies being $\pm$ 20 cm^{-1}.

A strong band in the spectra of all the unsaturated esters may be assigned to the carbonyl stretch mode. The position of this band in aldehydes, ketones and acid halides is known [17]-

Table 1 : Atomic and bond population densities for different conformers of methyl acrylate, methyl *trans* crotonate, methyl-3-methoxy-2-propenoate, methyl methacrylate and methyl acetate in ground and excited states

Methyl acrylate

Internal Coordinates	Cc Bond order		Bond length/ Bond angle		Tc Bond order		Bond length/ Bond angle		Change in bond angle Cc to Tc	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
C_1-C_2	0.991	1.015	1.487	1.431	1.003	1.034	1.486	1.432		
C_1=C_3	1.870	1089	1.318	1.337	1.868	1.833	1.319	1.338		
C_2=O_4	1.763	1.712	1.186	1.263	1.751	1.680	1.186	1.270		
$C_2C_1C_3$			128.80	128.50			124.30	124.10	3.5	4.4
$C_1C_2O_6$			111.20	118.30			113.80	119.60	2.6	1.3
$C_1C_2O_4$			125.20	122.20			122.80	121.30	2.4	0.9
$C_2C_1H_5$			116.70	110.60			113.70	115.10	3.0	4.5

Methyl *trans* crotonate

Internal Coordinates	Cc Bond order		Bond length/ Bond angle		Tc Bond order		Bond length/ Bond angle		Change in bond angle Cc to Tc	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
C_1-C_2	1.002	1.028	1.482	1.456	1.017	1.049	1.481	1.456		
C_1=C_3	1.845	1.831	1.322	1.507	1.844	1.806	1.322	1.512		
C_2=O_4	1.752	1.702	1.187	1.190	1.741	1.667	1.191	1.193		
$C_2C_1C_3$			120.79	121.83			124.37	125.48	3.58	3.65
$C_1C_2O_6$			111.21	112.33			113.98	113.28	2.77	0.95
$C_1C_2O_4$			125.59	123.92			122.95	123.11	2.64	0.81
$C_2C_1H_5$			116.78	117.69			113.68	114.56	3.10	3.13

Methyl-3-methoxy-2-propenoate

Internal Coordinates	c'Cc Bond order		Bond length/ Bond angle		c'Tc Bond order		Bond length/ Bond angle		Change in bond angle c'Cc to c'Tc	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
C_1-C_2	1.021	1.044	1.471	1.437	1.034	1.063	1.470	1.438		
C_1=C_3	1.712	1.707	1.320	1.335	1.713	1.687	1.330	1.336		
C_2=O_4	1.740	1.693	1.189	1.279	1.737	1.661	1.188	1.276		
$C_2C_1C_3$			118.49	126.05			122.28	122.75	3.79	3.30
$C_1C_2O_6$			111.14	117.80			113.98	119.47	2.84	1.65
$C_1C_3H_7$			120.16	122.49			120.97	121.78	0.81	0.71
$C_1C_2O_4$			125.91	122.65			123.21	121.54	2.70	1.11
$C_2C_1H_5$			117.53	111.56			114.35	115.38	3.18	3.82

Methyl methacrylate

Internal Coordinates	Tc				Cc				Change in bond angle Tc to Cc	
	Bond order		Bond length/ Bond angle		Bond order		Bond length/ Bond angle			
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
C_3-C_6	0.978	1.008	1.495	1.446	0.971	0.999	1.498	1.441		
C_2=C_3	1.869	1.836	1.321	1.336	1.869	1.858	1.321	1.339		
C_6=O_{10}	1.769	1.705	1.211	1.280	1.771	1.712	1.210	1.273		
$C_2C_3C_6$			120.93	120.63			117.05	123.30	3.88	2.67
$C_3C_6C_{10}$			122.92	122.17			124.97	121.71	2.05	0.46
$C_3C_6O_{11}$			114.10	119.44			112.10	119.65	2.00	0.21

METHYL ACETATE

Internal Coordinates	Trans				Cis				CHANGE IN BOND ANGLE TRANS TO CIS	
	Bond order		Bond length/ Bond angle		Bond order		Bond length/ Bond angle			
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
C_1-C_2	0.890	0.901	1.504	1.499	0.885	0.889	1.515	1.506		
C_2=O_5	1.782	1.731	1.185	1.273	1.788	1.737	1.179	1.273		
C_2-O_3	0.883	0.876	1.321	1.374	0.830	0.827	1.330	1.370		
$C_1C_2O_3$			112.63	118.58			119.98	128.33	7.35	9.75
$C_2O_3C_4$			117.44	118.19			123.86	118.42	6.42	0.23
$O_3C_2O_5$			123.30	120.32			119.14	114.14	4.16	6.18

[18] 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 1730-1755 cm^{-1}, close to the range in analogous ketones suggesting that the affect 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 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 bands in the presently studied molecules lie in a narrow range 1630-1670 cm^{-1}. Change of conformation also does not affect the position of this band although it considerably changes its intensity. It is observed that in all the case 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 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*.

C-C and C-O stretch bands are found to be non characteristic bands 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 change of conformation. 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 1012-1038 cm^{-1} which shift by about 30 cm^{-1} with the change of conformation. The other skeletal mode vibrations like C-O-C bend and C=C-C bend appear in the far infrared region 140-350 cm^{-1}.

While a change of conformation has insignificant affect on the position of 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} 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, which has higher electronegativity than carbon, the symmetric deformation band experiences a higher frequency shifts of about 80 cm^{-1} from its normal position of about 1370 cm^{-1} in alkanes and 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.

Infrared spectra of the unsaturated esters have a number of vibrational frequencies in 60-200 cm^{-1} range which may be ascribed to torsional modes about C-C, O-C and C-O bonds. The lowest frequency absorption bands in the 60-100 cm^{-1} region may be assigned to asymmetric torsion of the molecule about C-C bond. The asymmetric torsional modes of the Cc conformers are found to appear at 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} region, 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.

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

3. CONCLUSION

Vibrational frequencies, intensities, forms of vibration and potential energy distribution over the symmetry coordinates as obtained from DFT/6-311G** and RHF/6-31G** calculations were used as the basis for the assignment of the vibrational bands of the two conformers of methyl acrylate, methyl methacrylate, methyl trans crotonate and methyl-3-methoxy-2-propenoate. A close agreement between the experimental infrared data and the calculated data support the correctness of our vibrational assignments.

REFERENCES

1. W.O. George, D.V. Hassid, W. C. Harris and W. F. Maddams. **Conformations of some α,β–unsaturated carbonyl compounds. Part III, Infrared solution spectra of methyl, $[2_{H_3}]$Methyl, ethyl, and $[2_{H_5}]$ ethyl acrylates and trans-crotonates**, *J. Chem. Soc. Perkin Trans*, Vol. II, pp. 400-404, 1972.
2. W. O. George, D. V. Hassid, W. C. Harris and W. F. Maddams. **Conformations of some α,β–unsaturated carbonyl compounds. Part V, Infrared solution spectra of methyl and $[2_{H_3}]$Methyl acrylates and trans-crotonates**, *J. Chem. Soc. Perkin Trans* , Vol. II, pp. 392-396, 1974.
3. T. Egawa, S. Maekawa, H. Fujiwara, H. Takeuchi, and S. Konaka. **Molecular structure and conformation of methyl acrylate. A gas electron diffraction study augmented by ab initio calculation and rotational constants**. *J .l Mol. Structure*, Vol. 352/353, 193-201, 1995.
4. J. I. Garcia, J. A. Mayoral, , L. Salvatella, X. Assfeld, and M. F. Ruiz-Lopez. **On the conformational preferences of α,β-unsaturated carbonyl compounds. An ab initio study,** *Journal. Molecular Structure (Theochem),* Vol. 362, pp. 187-197, 1996.
5. V. Santhanam, S. Singh and J. Sobhanadri. **Conformational analysis of some acrylates using dipole moment calculations by CNDO/force method**, *Tetrahedron,* Vol. 39 (24), pp. 4183-4187, 1983.
6. T. Takemasa, I. Harumasa, H. Takeuchi, and S. Konaka. **Molecular structure and conformation of methyl methacrylate deternined by gas electron diffraction**, *J. Molecular Structure*, Vol. 475, pp. 55-63, 1999.
7. M. L. M. Rocco, M. C. A. Lopes, C.A. Lucas, E. Hollauer, E. E. Monteiro and G.G. B. de Souza. **Excitation of the methyl methacrylate molecule in the UVV range by angle-resolve EELS**, *Chem. Phys.*, Vol. 223, pp 15-21, 1997.
8. E. Hollauer, M. L. M. Rocco, M. C. A. Lopes and G. G. B. de Souza. **An abinitio study of the valence excitation**

of methyl methacrylate as observed by EELS, *J.l Electron Spectroscopy Related Phenomenon*, Vol. 104, pp. 31-39, 1999.

9. B. L. Baker, M. Orgill, N.L. Owen, E. H. Stephenson, G. A. Williams, J. N. Macdonald and J. E. Boggs. **The molecular conformation of methyl methacrylate – An infrared and an ab initio study**, *J.   Molecular Structure*, Vol. 356, pp. 95-104, 1995.

10. A. J. Bowles, W. O. George, and D.B. Cunliffe-Jones. **Conformations of some α, β- unsaturated carbonyl compounds. Part II, Infrared and Raman spectra of methyl and ethyl acrylate and trans crotonate**, *J. Chemical Society*, Vol. B, pp. 1070-1075, 1970.

11. V. Vsetecka, , J. Pecka, and M. Prochazka. **(E-Z)-isomerisation   of   unsaturated   esters X-CH=CH-COOCH$_3$** , *Collection Czechoslovak Chem. Commun.*, Vol. 47, pp. 277-285, 1982.

12. M. Dulce, G. Faria , J. J. C. Teixeira-Dias and R. Fausto. **Vibration spectra and structure of methyl trans crotonate**, *Vibrational Spectr.*, Vol. 2, pp. 107-123, 1991.

13. M. W. Schmidt, , K. K. Baldridge, , J. A. Boatz, , S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K.A.Nguyen, T.L., Dupuis, J.   A. Montgomery. **Computer Program GAMESS,** *Journal Comput. Chem.,*Vol. 14, pp. 134713-134763, 1993.

14. J. Baker, A. A. Jarzecki and P. Pulay. **Direct scaling of primitives valence force constants. An alternative approach to scaled quantum mechanical force fields**, *J. Phys. Chem. A*, Vol. 102, pp. 1412-1424, 1998.

15. H. Yoshida, K. Takeda, J. Okamura, A. Ehara and H. Matsuura. **A new approach to vibrational analysis of large molecules by density functional theory : wavenumber-Linear scaling method**, *J. Phys. Chem. A,*   Vol. 106, pp. 3580-3586, 2002.

16. H. Yoshida, A. Ehara and H. Matsuura, **Density functional   vibrational   analysis   using wavenumber-linear scale factors,** *Chem. Phys. Lett.* Vol. 325, pp. 477-483, 2000.

17. S. Thakur, V. P. Gupta, and B. Ram. **Semi-empirical calculations and normal coordinate study of the conformation and electronic and vibrational spectra of acrolein**, *Spectrochimica Acta Part A*, Vol. 53**,** pp. 749-759, 1997.

18. S. Thakur and V. P. Gupta. **Quantum mechanical study of the electronic spectra, torsional potential and physico- chemical properties of rotational conformers of methyl vinyl ketone in different electronic states**, *Indian Journal of Pure and Applied Physics*, 75B Vol. 4, pp. 651-659, 1999.

Table 2: Comparison of the calculated and experimental frequencies and intensities of conformers of MA, MMA, MC and MMP

Molecule	C=O stretch		C=C stretch		C-C stretch		A. C-O stretch		O-C stretch	
MA	*B. 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								

Molecule	CH₃ asym. stretch		CH₃ sym. stretch		CH₃ asym. bend		CH₃ sym. bend		CH₃ 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	-	-	-	-	-	-

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 (219)	160 (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.	-	-	- (362.27)	- (351.56)	-	-