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Ab initio studies on conformation, vibrational and electronic spectra of methyl methacrylate

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Abstract

A systematic quantum mechanical study of the possible conformations, their relative stabilities, vibrational and electronic spectra and thermodynamic parameters of methyl methacrylate (MMA) has been reported for the electronic ground (S_0) and first excited (S_1) states using Density Functional Theory (DFT) with B3LYP functionals and RHF methods in extended basis sets 6-31G, 6-31G**, 6-311G** and 6-311 + G** have been conducted. The molecule was considered as a two rotor system having internal rotation about C–C and C–O bonds with the possibility of hindered rotation of the methyl group. Rotation about C–O bond indicates that conformations having the carbonyl and methoxy groups in *cis* positions are the most stable, while the methyl group has staggered conformation relative to the carbonyl group. Plots of the potential energy curves for rotation about C–C bonds in the S_0 and S_1 states show two energy minima corresponding to the Tc and Cc conformations, separated by 0.365 and 1.104 kcal/mol, respectively, and indicate that the former is more stable than later in both the electronic states. Electronic excitation is found to substantially reduce rotation barrier between the two conformers, which may make their inter-conversion in the S_1 state easier. Fully optimized geometries of the two stable conformers in the S_0 and S_1 states are being reported; the later being reported for the first time. Based on suitably scaled RHF/6-31G** and DFT/6-311G** results, a complete assignment is provided to the fundamental vibrational bands of both the Tc and Cc conformers in terms of frequency, form and intensity of vibrations and potential energy distribution across the symmetry coordinates in the S_0 state. A complete interpretation of the electronic spectra of the Tc and Cc conformers of MMA has been provided by MP2/6-31G** calculations in terms of the nature, energy and intensity of electronic transitions.

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Keywords: Ab initio calculations; Methyl methacrylate; Conformational analysis; Vibrational analysis; Electronic transitions

1. Introduction

The structure of methyl methacrylate (MMA) is of some interest as being a two-rotor system it has possibilities of rotation about single C–C and C–O bonds and may exist in several conformational forms. Despite great technological utility of its polymeric

form poly(methyl methacrylate) as a resist in UV and X-ray lithographic techniques in micro-electronics and micro-fabrication, very little information is available about the structure, vibrational and electronic spectra of MMA. Experimental studies on the vibrational spectra by El-Bermani [1] and dipole moment measurements by Santhanam et al. [2] suggest that the molecule may exist in two conformational forms *trans* and *cis* with *trans* being more stable than the *cis*. Based on electron diffraction, vibrational spectra and

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ab initio calculations Takemasa et al. [3] have concluded 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. [4] suggest that the *s-cis* and *s-trans* conformers are nearly equally populated at room temperature. They have also attempted to assign the electron excitation spectrum of MMA. Baker et al. [5] have provided tentative assignment to absorption bands in the matrix isolation infrared spectra of MMA and have inferred that the *cis* conformer is more stable than the *trans*. Based on ab initio calculations involving Møller–Plesset correction at the MP2 level, Hollauer et al. [6] 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 [5,6] lead to different inferences about the relative stability of the two conformers. Finally, no conformational studies for the first excited $n\pi^*$ state of MMA are available in the literature. In order to resolve the situation and to search for possible higher energy conformers of MMA in its ground and first excited electronic states RHF and DFT calculations are being reported in these states. A complete assignment of the fundamental modes in the vibrational spectra of the stable conformers in the ground state and the electronic transitions have been attempted.

2. Method of calculation

Potential energy curves for asymmetric torsion of MMA about C_3-C_6 bond (Fig. 1) were obtained by calculating the variation of the total energy of the molecule with dihedral angle $\varphi(C_2C_3C_6O_{10})$ in interval of 20° (interval of 10° near the turning points) in the range 0° and 360° by ab initio SCF-HF calculations using 6-31G basis set for the ground and STO-3G for the first excited states (S_1).

Geometries of stable conformers of MMA were optimized in the ground state (S_0) by RHF calculations using the basis set 6-31G**. They were also optimized by Density Functional Theory (DFT) using B3LYP functionals and 6-31G** and 6-311 + G** basis sets. In the case of the first excited (S_1) state the geometries of the stable conformers were optimized using the extended

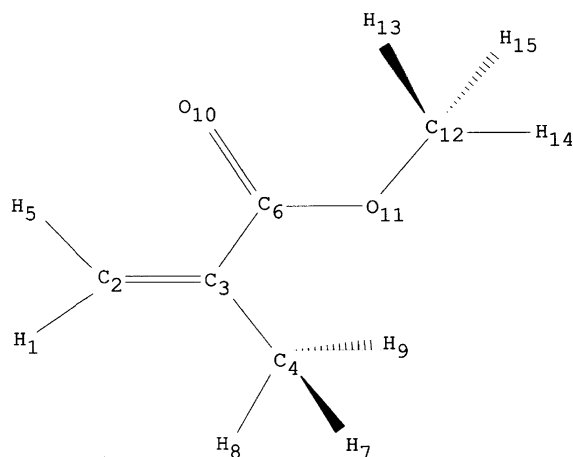


Fig. 1. Numbering of atoms of methyl methacrylate.

basis 6-31G** and correlational correction (MP2). In order to scale down the calculated frequencies from RHF method, the SQM [7,8] and direct scaling [9] procedure have been used. The later has also been used in DFT calculations. Yoshida et al. [10,11] have proposed wave number linear scaling procedure (WLS) and have given mathematical expressions to calculate scaled frequencies in DFT methods. Frequencies, forms and intensities of vibrational bands of the stable conformers of MMA presently reported for the S_0 state have been calculated using RHF/6-31G** and DFT/6-311G**. In either case the force fields and frequencies of vibration are scaled by appropriate [7–11] procedures mentioned above. Electronic transitions and oscillator strengths for the two stable conformers are calculated using RHF/6-31G**. Computer softwares Gaussian98 [12] and GAMESS [13] have been used for the calculations.

3. Conformational notations

The notations used for conformers of MMA are analogous to those used previously by Viridi et al. [14] in methyl acrylate. Conformations with respect to dihedral angle $\varphi(C_2C_3C_6O_{10})$ are denoted by a capital C (*cis* or *syn*, $\varphi = 0^\circ$) or T (*trans* or *anti*, $\varphi = 180^\circ$). Conformations with respect to the dihedral angle $\varphi(O_{10}C_6O_{11}C_{12})$ are represented by lower case letter c (*cis* or *syn*, $\varphi = 0^\circ$) or t (*trans* or *anti*, $\varphi = 180^\circ$).

following the capital letters C or T. Rotation of the methyl groups about the C_3-C_4 and $O_{11}-C_{12}$ 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.

4. Results and discussion

4.1. Conformational studies

Potential energy curves for rotation about C_3-C_6 bond for the ground (S_0) and first excited (S_1) electronic states, with the ester group in *cis* conformation, are given in Fig. 2. It may be seen that in both these states, the molecule has two potential minima at $\varphi(C_2C_3C_6O_{10}) = 0^\circ$ and 180° corresponding to the *cis* (C) and *trans* (T) conformations. Since in both the cases the molecule is found to have minimum energy for the *cis* conformation ($\varphi(C_{12}O_{11}C_6O_{10}) = 0^\circ$) relative to the C_6O_{11} bond the molecular conformation at these minima may be identified as Cc and Tc. As in the case of methyl acrylate [14], the methyl groups have staggered conformation relative to the carbonyl group. The relative energies of the stable conformations of MMA in the S_0 and S_1 states are

given in Table 1. It is found that in both the electronic states the Tc conformer is more stable than the Cc conformer; the enthalpy difference between them being 0.365 kcal/mol in the S_0 state and 1.104 kcal/mol in the S_1 state. This situation is different from that prevailing in similar compounds like acrolein [15] and methyl vinyl ketone [16], where $n\pi^*$ transition reverses the sequence of stability of the conformers and makes *cis* conformer more stable than *trans*. The enthalpy difference between the two conformers was also obtained by completely optimizing their geometries by RHF/6-31G**, RHF/6-311G**, DFT/6-31G**, DFT/6-311 + G** methods in the S_0 state and by RHF/STO-3G and MP2/6-31G** methods in the S_1 state. It is found that in the S_0 state the Tc conformer is more stable than the Cc conformer by an enthalpy difference of 0.319 kcal/mol in RHF/6-31G**, 0.449 kcal/mol in RHF/6-311G**, 0.067 kcal/mol in DFT/6-31G** and 0.237 kcal/mol in DFT/6-311 + G** (Table 1). Results of RHF and DFT calculations are close to the enthalpy difference of 0.52 kcal/mol reported by Rocco et al. [4] on the basis of ab initio calculations using Dunning–Huzinaga double zeta basis set. Our results are also supported by those of Takemasa et al. [3] based on electron diffraction studies. RHF/6-311G** calculations in S_0 state were also conducted after taking

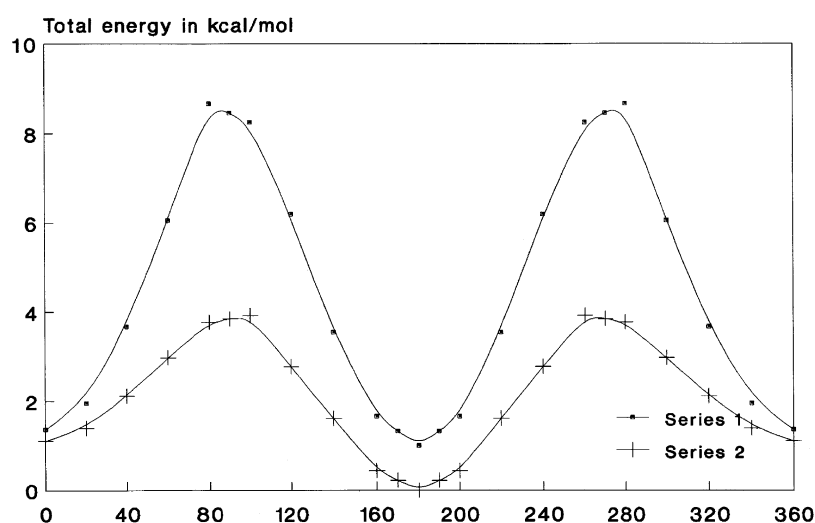


Fig. 2. Potential energy curves of methyl methacrylate for rotation about C_3-C_6 bond in S_0 (Series 1) and S_1 (Series 2) states. $\varphi(O_{10}C_6O_{11}C_{12}) = 0^\circ$ and $\varphi(C_6O_{11}C_{12}H_{14}) = 180^\circ$. The abscissa is the angle of rotation θ about C_3-C_6 bond relative to Cc conformation for which the dihedral angle $\varphi(O_{10}C_6C_3C_2) = 0^\circ$. The ordinates for Series are shifted by 1 kcal/mol above Series 2.

Table 1

Total energy, ionization potential and rotational barrier of different conformers of methyl methacrylate in ground (S_0) and excited (S_1) states

Basis sets	Conformation				Rotational barrier (kcal/mol)	
	Relative energy (kcal/mol)		Ionization potential (eV)		Tc/Cc	Cc/Tc
	Tc	Cc	Tc	Cc		
Ground state (S ₀)						
RHF/6-31G	0.0 ^a	0.365	10.229	10.170	7.665	7.360
RHF/6-31G**	0.0 ^b	0.319	10.188	10.112		
RHF/6-311G**	0.0 ^c	0.449	10.274	10.198		
DFT/6-31G**	0.0 ^d	0.067	7.279	7.214		
DFT/6-311 + G**	0.0 ^e	0.237	7.601	7.545		
MP2/6-311G**	0.067	0.0 ^f	10.170	10.100		
Excited state (S ₁)						
RHF/STO-3G	0.0 ^g	1.104	7.983	7.893	3.921	2.817
MP2/6-31G**	0.0 ^h	2.014	10.280	10.110		

^a Absolute value: −215654.01 kcal/mol.^b Absolute value: −215760.56 kcal/mol.^c Absolute value: −215807.68 kcal/mol.^d Absolute value: −217057.42 kcal/mol.^e Absolute value: −217116.33 kcal/mol.^f Absolute value: −216498.53 kcal/mol.^g Absolute value: −212987.25 kcal/mol.^h Absolute value: −216407.36 kcal/mol.

into account Møller–Plesset correlational correction at MP2 level. These results, however, provide Cc conformer to be more stable than Tc by an enthalpy difference of 0.067 kcal/mol (Table 1). It thus follows that the Møller–Plesset correction is significant enough to reverse the relative stability of the two conformers.

In the excited electronic state (S_1), RHF calculations in 6-31G** basis set with MP2 level correction predict an enthalpy difference of 2.014 kcal/mol between the two stable conformers Tc and Cc. No experimental data is, however, available in the literature for comparison purpose. It further follows from Table 1 and Fig. 2 that there is a significant decrease in the rotational barrier Tc/Cc and Cc/Tc from 7.665 and 7.360 kcal/mol in the S_0 state to 3.921 and 2.817 kcal/mol in the S_1 state, making the conformational isomerism more probable in the excited electronic state.

The ionization potentials of the Tc and Cc conformers of MMA in various basis sets are given in Table 1. In the S_0 state the RHF calculations provide values 10.229, 10.188 and 10.274 eV for

the Tc conformer and 10.170, 10.112 and 10.198 eV for the Cc conformer. These are close to the values (9.04 and 9.01 eV) reported by Hollauer et al. [6] from ROHF calculations. DFT calculations, however, provide much lower values of ~ 7 eV for the ionization potential. It also follows from Table 1 that there is no appreciable difference in the ionization potential in the S_0 and S_1 states.

5. Optimized geometries

Optimized geometries of the Tc and Cc conformers of MMA in the ground (S_0) and excited (S_1) electronic states were obtained from RHF/MP2 and DFT techniques using the basis functions 6-31G** and 6-311 + G**. The results are given in Tables 2 and 3 for the Tc and Cc conformers, respectively.

It may be seen that for the S_0 state the RHF and DFT methods give comparable geometries which differ from each other by not more than 0.01 Å in bond length and 2° in bond angle. The geometries of

Table 2

Optimized geometries of the Tc conformer of methyl methacrylate in the ground (S_0) and excited (S_1) states in different basis sets

Internal Coordinates	Ground state (S_0)					Excited state (S_1)	
	RHF/6-31G**	DFT/6-31G**	DFT/6-311 + G**	RHF/DZ-DH ^a	Exptl. ^b	RHF/STO-3G	MP2/6-31G**
H ₁ C ₂	1.075	1.086	1.085	1.072		1.078	1.075
C ₂ C ₃	1.321	1.338	1.336	1.335	1.341	1.323	1.336
C ₃ C ₄	1.505	1.505	1.504	1.511		1.529	1.510
C ₂ H ₅	1.072	1.083	1.082	1.070		1.078	1.072
C ₃ C ₆	1.495	1.495	1.496	1.490	1.494	1.460	1.446
C ₄ H ₇	1.084	1.095	1.093	1.082	1.106	1.087	1.085
C ₄ H ₈	1.083	1.092	1.091	1.082	1.106	1.084	1.082
C ₄ H ₉	1.084	1.095	1.093	1.082	1.106	1.087	1.085
C ₆ O ₁₀	1.211	1.216	1.220	1.222		1.316	1.280
C ₆ O ₁₁	1.324	1.353	1.350	1.351	1.348	1.421	1.363
O ₁₁ C ₁₂	1.416	1.436	1.438	1.452	1.433	1.438	1.408
C ₁₂ H ₁₃	1.081	1.093	1.091	–	1.106	1.094	1.084
C ₁₂ H ₁₄	1.080	1.090	1.088	1.078	1.106	1.091	1.079
C ₁₂ H ₁₅	1.081	1.093	1.091	1.074	1.106	1.094	1.084
H ₁ C ₂ C ₃	120.88	120.93	120.79	120.8		121.28	119.71
C ₂ C ₃ C ₄	124.18	124.00	123.77	124.4		122.56	122.74
C ₃ C ₂ H ₅	121.77	121.58	121.58	–		121.80	122.40
C ₂ C ₃ C ₆	120.93	121.30	121.23	120.5	121.2	121.71	120.63
C ₃ C ₄ H ₇	110.81	110.84	110.91	110.9		110.84	111.19
C ₃ C ₄ H ₈	110.54	110.91	110.66	110.9		110.27	110.16
C ₃ C ₄ H ₉	110.81	110.85	110.92	110.9		110.84	111.18
C ₃ C ₆ O ₁₀	122.92	123.41	123.42	123.5		122.30	122.17
C ₃ C ₆ O ₁₁	114.10	113.60	113.66	114.6		118.72	119.44
C ₆ O ₁₁ C ₁₂	116.76	115.11	115.84	119.5	116.8	118.17	118.90
O ₁₁ C ₁₂ H ₁₃	110.59	110.69	110.51	110.0		112.17	111.38
O ₁₁ C ₁₂ H ₁₄	105.85	105.65	105.43	105.1		106.48	105.66
O ₁₁ C ₁₂ H ₁₅	110.59	110.68	110.50	105.1		112.17	111.38
C ₂ C ₃ C ₆ O ₁₀	180.0	180.0	180.0	–		180.0	180.0
C ₂ C ₃ C ₆ O ₁₁	0.0	0.0	0.0	0.0		0.0	0.0
C ₃ C ₆ O ₁₁ C ₁₂	180.0	180.0	180.0	–		180.0	180.0

^a Ref. [4].^b Ref. [3].

the Tc and Cc conformers are also very close to those reported by Takemasa et al. [3] and Rocco et al. [4] based on electron diffraction and Dunning–Huzinaga double zeta basis set, respectively, differing from them by a maximum of 0.01 Å in bond length and 1° in bond angle. In going from Tc to Cc conformer bond lengths do not change significantly. However, a major change is observed in few bond angles; the bond angle C₂C₃C₆ increases by 4.08° (DFT), while the angle C₃C₆O₁₀ decreases by 2.29° (DFT) in S_0 state.

The optimized geometries of the Tc and Cc conformers of MMA in the first excited $n\pi^*$ electronic state (S_1) from RHF/STO-3G and RHF/6-31G** calculations are reported in Tables 2

and 3 and compared with their ground state geometries. In order to include electron correlational effects which become more prominent in the excited state, Møller–Plesset correction MP2 were also involved. The electronic excitation in Tc conformer results in a decrease in C₃C₆, C₆O₁₀, O₁₁C₁₂, bond lengths by about 0.05, 0.07 and 0.01 Å, respectively. On the other hand C₃C₄ and C₆O₁₁ bond lengths increase by about 0.01 Å each. More significantly, the angles C₃C₆O₁₁ and C₆O₁₁C₁₂ increase by about 5.8° and 3.1°, respectively. Also, the angle C₃C₆O₁₀ decreases by 1.25°. Similar situation is observed in case of Cc conformer in the S_1 state. However, in this case, the angle C₃C₆O₁₀ decreases by about 3.9°

Table 3

Optimized geometries of the Cc conformer of methyl methacrylate in the ground (S_0) and excited (S_1) states in different basis sets

Internal coordinates	Ground state (S_0)				Excited state (S_1)	
	RHF/6-31G**	DFT/6-31G**	DFT/6-311 + G**	RHF/DZ-DH ^a	RHF/STO-3G	MP2/6-31G**
H ₁ C ₂	1.075	1.085	1.084	1.072	1.077	1.073
C ₂ C ₃	1.321	1.338	1.336	1.335	1.326	1.339
C ₃ C ₄	1.507	1.506	1.506	1.510	1.528	1.515
C ₂ H ₅	1.073	1.084	1.083	1.071	1.078	1.073
C ₃ C ₆	1.498	1.498	1.500	1.492	1.460	1.441
C ₄ H ₇	1.085	1.095	1.093	1.082	1.087	1.083
C ₄ H ₈	1.083	1.093	1.091	1.081	1.085	1.083
C ₄ H ₉	1.085	1.095	1.093	1.082	1.087	1.083
C ₆ O ₁₀	1.210	1.215	1.210	1.222	1.317	1.273
C ₆ O ₁₁	1.325	1.355	1.353	1.349	1.419	1.363
O ₁₁ C ₁₂	1.416	1.436	1.440	1.452	1.438	1.408
C ₁₂ H ₁₃	1.081	1.092	1.090	–	1.094	1.084
C ₁₂ H ₁₄	1.080	1.089	1.088	1.074	1.091	1.079
C ₁₂ H ₁₅	1.081	1.092	1.090	1.078	1.094	1.084
H ₁ C ₂ C ₃	121.36	121.45	121.23	121.2	121.22	120.11
C ₂ C ₃ C ₄	124.11	123.99	123.72	124.3	122.42	122.22
C ₃ C ₂ H ₅	120.79	120.40	120.67	–	122.43	122.81
C ₂ C ₃ C ₆	117.05	116.97	117.15	117.5	122.80	123.30
C ₃ C ₄ H ₇	111.16	111.19	111.21	110.3	110.64	111.21
C ₃ C ₄ H ₈	110.24	110.66	110.42	111.0	110.13	109.20
C ₃ C ₄ H ₉	111.16	111.19	111.21	111.0	110.64	111.21
C ₃ C ₆ O ₁₀	124.97	125.65	125.71	125.4	121.95	121.71
C ₃ C ₆ O ₁₁	112.10	111.46	111.46	112.8	118.99	119.65
C ₆ O ₁₁ C ₁₂	116.89	115.11	115.85	109.7	118.14	118.63
O ₁₁ C ₁₂ H ₁₃	110.53	110.61	110.43	110.0	112.14	111.30
O ₁₁ C ₁₂ H ₁₄	105.90	105.72	105.52	105.1	106.50	105.71
O ₁₁ C ₁₂ H ₁₅	110.53	110.62	110.43	105.1	112.14	111.30
C ₂ C ₃ C ₆ O ₁₀	0.0	0.0	0.0	0.0	0.0	0.0
C ₂ C ₃ C ₆ O ₁₁	180.0	180.0	180.0	180.0	180.0	180.0
C ₃ C ₆ O ₁₁ C ₁₂	180.0	180.0	180.0	0.0	180.0	180.0

^a Ref. [4].

while angles C₃C₆O₁₁ and C₆O₁₁C₁₂ increase by about 8.2 and 2.8°, respectively.

6. Vibrational analysis

Both the Tc and Cc conformers of MMA belong to C_s point group and its 39 normal vibrational modes will span the irreducible representation 25A' + 14A''. Symmetry coordinates corresponding to A' and A'' species are listed in Table 4. Calculated and scaled vibrational frequencies, intensities and assignments of the fundamental vibrational bands of the Tc conformer of MMA by

RHF/6-31G** and DFT/6-311G** methods are given in Table 5. Corresponding results for the Cc conformer are given in Table 6. 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. [9]. 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

$$\nu_{\text{obs}}/\nu_{\text{calc}} = 1.0087 - 0.0000163 \nu_{\text{calc}}$$

Table 4
Symmetry coordinates for methyl methacrylate

S. no.	Species	Description	Symmetry coordinate
1	A'	C=C stretch	$S_1 = r_{2\ 3}$
2		C–C stretch	$S_2 = r_{3\ 6}$
3		C=O stretch	$S_3 = r_{6\ 10}$
4		C–O stretch	$S_4 = r_{6\ 11}$
5		O–CH ₃ stretch	$S_5 = r_{11\ 12}$
6		CH ₂ symmetric stretch	$S_6 = r_{2\ 5} + r_{1\ 2}$
7		CH ₂ asymmetric stretch	$S_7 = r_{2\ 5} - r_{1\ 2}$
8		C–C stretch	$S_8 = r_{34}$
9		(O)CH ₃ symmetric stretch	$S_9 = r_{12\ 14} + r_{12\ 13} + r_{12\ 15}$
10		(O)CH ₃ asymmetric stretch	$S_{10} = 2r_{12\ 14} - r_{12\ 13} - r_{12\ 15}$
11		(C)CH ₃ symmetric stretch	$S_{11} = r_{4\ 8} + r_{4\ 7} + r_{4\ 9}$
12		(C)CH ₃ asymmetric stretch	$S_{12} = 2r_{4\ 8} - r_{4\ 7} - r_{4\ 9}$
13		CH ₂ rock	$S_{13} = \alpha_{5\ 2\ 3} - \alpha_{1\ 2\ 3}$
14		CH ₂ scissoring	$S_{14} = 2\alpha_{5\ 2\ 1} - \alpha_{5\ 2\ 3} - \alpha_{1\ 2\ 3}$
15		C=C–CH ₃ bend	$S_{15} = \alpha_{2\ 3\ 4} - \alpha_{4\ 3\ 6}$
16		C=C–C(O) bend	$S_{16} = 2\alpha_{2\ 3\ 6} - \alpha_{2\ 3\ 4} - \alpha_{6\ 3\ 4}$
17		C=O in plane bend	$S_{17} = \alpha_{10\ 6\ 3} - \alpha_{10\ 6\ 11}$
18		C–C–O bend	$S_{18} = 2\alpha_{3\ 6\ 11} - \alpha_{3\ 6\ 10} - \alpha_{10\ 6\ 11}$
19		C–O–C bend	$S_{19} = \alpha_{6\ 11\ 12}$
20		(O)CH ₃ symmetric deformation	$S_{20} = \alpha_{14\ 12\ 13} + \alpha_{14\ 12\ 15} + \alpha_{13\ 12\ 15} - \alpha_{11\ 12\ 13} - \alpha_{11\ 12\ 14} - \alpha_{11\ 12\ 15}$
21		(O)CH ₃ asymmetric deformation	$S_{21} = 2\alpha_{13\ 12\ 15} - \alpha_{13\ 12\ 14} - \alpha_{15\ 12\ 13}$
22		(C)CH ₃ symmetric deformation	$S_{22} = \alpha_{8\ 4\ 7} + \alpha_{8\ 4\ 9} + \alpha_{7\ 4\ 9} - \alpha_{3\ 4\ 7} - \alpha_{3\ 4\ 8} - \alpha_{3\ 4\ 9}$
23		(C)CH ₃ asymmetric deformation	$S_{23} = 2\alpha_{9\ 4\ 7} - \alpha_{8\ 4\ 9} - \alpha_{8\ 4\ 7}$
24		(O)CH ₃ rock	$S_{24} = 2\alpha_{14\ 12\ 11} - \alpha_{11\ 12\ 13} - \alpha_{11\ 12\ 15}$
25		(C)CH ₃ rock	$S_{25} = 2\alpha_{3\ 4\ 8} - \alpha_{3\ 4\ 7} - \alpha_{3\ 4\ 9}$
26	A''	(O)CH ₃ asymmetric stretch	$S_{26} = r_{13\ 12} - r_{15\ 12}$
27		(C)CH ₃ asymmetric stretch	$S_{27} = r_{7\ 4} - r_{9\ 4}$
28		(O)CH ₃ asymmetric deformation	$S_{28} = \alpha_{14\ 12\ 13} - \alpha_{14\ 12\ 15}$
29		(C)CH ₃ asymmetric deformation	$S_{29} = \alpha_{8\ 4\ 7} - \alpha_{8\ 4\ 9}$
30		(O)CH ₃ rock	$S_{30} = \alpha_{11\ 12\ 13} - \alpha_{11\ 12\ 15}$
31		(C)CH ₃ rock	$S_{31} = \alpha_{3\ 4\ 7} - \alpha_{3\ 4\ 9}$
32		CH ₂ twist (C=C torsion)	$S_{32} = \tau_{2\ 3}$
33		C–C torsion	$S_{33} = \tau_{3\ 6}$
34		C–O torsion	$S_{34} = \tau_{6\ 1\ 1}$
35		O–CH ₃ torsion	$S_{35} = \tau_{11\ 12}$
36		C–CH ₃ torsion	$S_{36} = \tau_{4\ 3}$
37		CH ₂ wag	$S_{37} = w_1$
38		C–C out-of-plane bend	$S_{38} = w_2$
39		C=C out-of-plane bend	$S_{39} = w_3$

Abbreviations: *r*, stretching; α , bending; τ , torsion; *w*, out-of-plane. See Fig. 1 for atom numbering.

suggested by Yoshida et al. [10,11]. Tables 5 and 6 also contain the symmetry coordinates and potential energy distribution (PED) for the corresponding vibrations.

Baker et al. [5] have reported the matrix isolation infrared spectrum of MMA in argon matrix in the spectral region 400–4000 cm^{−1} and have provided an

incomplete and tentative assignment of the fundamental bands from MP2/6-31G** calculations. Based upon the frequencies and modes of vibrations expressed in terms of symmetry coordinates, potential energy distribution and intensity of vibration bands a complete assignments of vibrational bands of the Tc and Cc conformers of MMA is, therefore, being attempted.

Table 5

Fundamental vibrational frequencies and assignments of the Tc conformer of methyl methacrylate

Species	$\nu_{\text{expt.}}^{\text{a}}$ (cm^{-1})	DFT/6-311G**			RHF/6-31G**		Assignment	Symm. Coord. (PED)
		$\nu_{\text{calculated}}$ (cm^{-1})	ν_{scaled} (cm^{-1})	Intensity (kJ/Mole)	ν_{scaled} (cm^{-1})	Intensity ^b		
A'								
1	3116	3239.78	3096.88	4.539	3076.5	0.110	CH ₂ asym.str.	$S_7(0.99)$
2	3030	3153.10	3018.47	16.278	2984.2	0.638	CH ₃ asym. str.	$S_{10}(0.98)$
3	2999	3144.61	3010.78	9.960	2989.2	0.250	CH ₂ sym. Str.	$S_6(0.98)$
4	2964	3115.22	2984.13	16.810	2945.4	0.554	CH ₃ asym.str.	$S_{12}(0.99)$
5	2913	3048.04	2923.12	31.994	2888.9	0.865	CH ₃ sym.Str.	$S_9(1.0)$
6	2849	3035.40	2911.62	15.247	2873.2	0.571	CH ₃ sym. Str.	$S_{11}(0.99)$
7	1735	1770.59	1734.90	232.635	1726.0	7.361	C=Ostr.	$S_3(0.66)$
8	1636	1692.18	1660.22	22.200	1664.4	1.488	C=Cstr.	$S_1(0.53)$
9	1467	1499.96	1476.33	9.177	1479.7	0.158	(O)CH ₃ asym. def.	$S_{21}(0.62)$
10	1463	1491.58	1468.30	22.847	1468.7	0.452	(C)CH ₃ asym. def.	$S_{23}(0.77)$
11	1454	1474.25	1451.64	8.697	1458.7	0.135	(O)CH ₃ sym. def.	$S_{20}(0.68)$
12	1404	1437.18	1416.01	7.877	1428.1	0.015	CH ₂ sciss., (C)CH ₃ sym. def.	$S_{14}(0.38), S_{22}(0.33)$
13	1382	1415.40	1395.05	6.082	1400.9	0.305	(C)CH ₃ sym. def., CH ₂ sciss.	$S_{22}(0.23), S_{14}(0.15)$
14.	1325	1341.33	1323.67	125.725	1340.9	3.867	C–C str., C–C–O bend,C–C str., C–O str.	$S_2(0.23), S_{18}(0.11),$ $S_8(0.10), S_4(0.10)$
15.	1204	1213.22	1199.88	114.402	1204.9	0.713	(O)CH ₃ rock	$S_{24}(0.71)$
16.	1194	1185.40	1172.80	220.609	1169.0	0.073	CH ₂ rock, C–O str.	$S_{13}(0.46), S_4(0.32)$
17.	1028	1041.51	1032.88	14.164	1042.9	0.914	(O)CH ₃ str., C–C str.	$S_5(0.47), S_8(0.32)$
18.	988	1001.56	993.87	6.654	1029.1	0.652	(C)CH ₃ rock	$S_{25}(0.54)$
19.	933	938.09	931.90	11.324	930.0	0.358	C–C str., O–CH ₃ str.	$S_8(0.42), S_5(0.27)$
20.	833	844.95	840.66	5.843	827.5	0.157	C–O str., C–C–O bend, C–O–C bend	$S_4(0.26), S_{18}(0.20), S_{19}(0.13)$
21.	601	606.77	606.04	2.215	601.8	0.121	C=O in plane bend, C–C str.	$S_{17}(0.32), S_2(0.27)$
22.	–	496.20	496.50	2.222	492.2	0.070	C=C–C bend, C–C–O bend	$S_{16}(0.41), S_{18}(0.27)$
23.	–	370.80	371.78	0.874	372.1	0.066	C=C–C bend	$S_{15}(0.48)$
24.	–	338.94	340.01	18.866	347.8	0.447	C–O–C bend, C=C–C bend	$S_{19}(0.31), S_{15}(0.28)$
25.	–	211.14	212.23	2.563	227.0	0.077	C–C–O bend, C=C–C bend, C–O–C bend	$S_{18}(0.44), S_{16}(0.23), S_{19}(0.21)$
A''								
26.	2984	3119.88	2988.36	23.320	2960.0	0.728	(O)CH ₃ asym. Str.	$S_{26}(0.98)$
27.	2937	3087.56	2958.07	13.477	2922.2	0.535	(C)CH ₃ asym. Str.	$S_{27}(1.0)$
28.	1457	1481.82	1458.92	8.636	1467.9	0.452	(O)CH ₃ rock	$S_{30}(0.66)$
29.	1439	1473.10	1450.54	14.940	1451.3	0.122	(C)CH ₃ asym. def.	$S_{29}(0.66)$
30.	1167	1173.03	1161.01	0.781	1169.3	0.073	(C)CH ₃ asym. def.	$S_{28}(0.65)$
31.	1100	1073.24	1063.80	0.142	1073.4	0.001	(C)CH ₃ rock	$S_{31}(0.68)$
32.	945	972.30	965.34	33.559	978.9	0.600	C–C out-of-plane bend,CH ₂ wag	$S_{38}(0.37), S_{37}(0.20)$
33.	816	836.78	832.64	13.603	811.0	0.157	CH ₂ wag	$S_{37}(0.60)$
34.	642	657.15	655.82	9.498	689.4	0.416	CH ₂ twist	$S_{32}(0.58)$

Table 5 (continued)

Species	$\nu_{\text{expt.}}^a$ (cm^{-1})	DFT/6-311G**			RHF/6-31G**		Assignment	Symm. Coord. (PED)
		$\nu_{\text{calculated}}$ (cm^{-1})	ν_{scaled} (cm^{-1})	Intensity (kJ/Mole)	ν_{scaled} (cm^{-1})	Intensity ^b		
35.	-	394.13	395.02	3.567	419.2	0.003	C=C out-of-plane bend	$S_{39}(0.85)$
36.	-	163.80	168.74	1.871	170.7	0.003	(C)CH ₃ torsion	$S_{36}(1.0)$
37.	-	146.73	147.65	3.340	170.6	0.002	(O)CH ₃ torsion	$S_{35}(1.0)$
38.	-	112.80	113.57	1.465	111.1	0.134	C–O torsion	$S_{34}(0.83)$
39.	-	60.56	61.02	0.614	64.4	0.061	C–C torsion	$S_{33}(0.84)$

^a Ref. [5].^b Intensity in (debye)²/AMU-(Å)².

7. Tc conformer

7.1. Carbon hydrogen stretches

The experimental [5] vibrational bands at 3116 and 2999 cm^{-1} may be compared with the calculated bands at 3096.88 and 3010.78 cm^{-1} (DFT) and assigned to CH₂ asymmetric stretch (S_7 , 0.99) and symmetric stretch (S_6 , 0.98) modes, respectively. Numbers in parentheses represent potential energy distribution over the symmetry coordinates. Similarly, in agreement with Baker et al. [5] the absorption bands at 2937 and 2984 cm^{-1} may be assigned to asymmetric CH stretch modes of the methyl and methoxy groups, respectively, corresponding to symmetry coordinates S_{27} (1.0) and S_{26} (0.98) of A'' species. The corresponding bands of A' species appear at 3030 and 2964 cm^{-1} and may be correlated with the coordinates S_{10} (0.98) and S_{12} (0.99). The absorption band at 2913 and 2849 cm^{-1} may be correlated with calculated bands at 2923.12 cm^{-1} (DFT) and 2911.62 cm^{-1} (DFT) and may be assigned to the symmetric CH stretch modes of the methoxy (S_9 , 1.0) and methyl (S_{11} , 0.99) groups, respectively.

7.2. Carbon hydrogen bends

The three CH₃ deformations consist of two A' deformations—one symmetric and one asymmetric, and an asymmetric A'' mode. These vibrations in the case of methyl and methoxy groups are found to appear at slightly different frequencies; the methoxy group having vibrations at higher frequency. Thus, the experimental vibrational bands at 1382, 1463 and

1439 cm^{-1} may be assigned to methyl groups and those appearing at 1454, 1467 and 1457 cm^{-1} to the methoxy groups. The corresponding symmetry coordinates and PED are given in Table 5. The absorption band at 1382 cm^{-1} is found to have contributions both from the CH₃ symmetric deformations and CH₂ scissoring modes in agreement with Baker et al. [5].

The experimental band at 933 cm^{-1} has been assigned by Baker et al. [5] to CH₂ wag. However, our calculations show that it belongs to skeletal mode having contributions from C–C stretch (S_8 , 0.42) and O–CH₃ stretch (S_5 , 0.27) modes. Vibrational bands at 816 and 642 cm^{-1} may be assigned to CH₂ wag (S_{37} , 0.60) and CH₂ twist (S_{32} , 0.58) modes, respectively, with calculated values of 832.64 and 655.82 cm^{-1} in DFT. As against three possible rocking modes corresponding to the methyl and methylene groups Baker et al. have assigned five experimental bands at 1204, 1194, 1167, 988 and 945 cm^{-1} to these modes. These correspond to their six calculated frequencies (scaled 4-31G**) at 1232, 1201, 1157, 1052, 999, 928 cm^{-1} . Our calculations assign the experimental bands at 1204 and 988 cm^{-1} to the (O)CH₃ and (C)CH₃ rock modes and the band at 1194 cm^{-1} to CH₂ rock mode. In DFT calculations these correspond to the band at 1199.88 cm^{-1} (S_{24} , 0.71), 993.87 cm^{-1} (S_{25} , 0.54) and 1172.80 cm^{-1} (S_{13} , 0.46), respectively.

7.3. Skeletal modes

The heavy atom skeleton of MMA will give rise to 11A' fundamental and 4A'' vibrations. The A' vibrations will include six stretches and five skeletal deformations. The carbonyl stretch can readily be

Table 6

Fundamental vibrational frequencies and assignments of the Cc conformer of methyl methacrylate

Species	$\nu_{\text{expt.}}^{\text{a}}$ (cm^{-1})	DFT/6-311G**			RHF/6-31G**		Assignment	Symm. coord. (PED)
		ν_{calc} (cm^{-1})	ν_{scaled} (cm^{-1})	Intensity (kM/Mole)	ν_{scaled} (cm^{-1})	Intensity ^b		
A'								
1.	3116	3237.41	3094.72	2.781	3073.90	0.074	CH ₂ asym. Str.	S ₇ (1.00)
2.	3033	3154.50	3019.74	17.176	2985.30	0.682	CH ₃ asym. Str.	S ₁₀ (0.99)
3.	2999	3145.25	3011.36	7.899	2983.80	0.244	CH ₂ sym. str.	S ₆ (0.98)
4.	2957	3111.18	2980.45	21.552	2942.60	0.644	CH ₃ asym. Str.	S ₁₂ (0.99)
5.	2913	3049.20	2924.17	32.163	2889.81	0.916	CH ₃ sym. str.	S ₉ (1.0)
6.	2853	3034.20	2910.53	16.622	2872.80	0.591	CH ₃ sym. str.	S ₁₁ (0.99)
7.	1741	1780.46	1744.30	169.700	1727.40	4.924	C=O str.	S ₃ (0.74)
8.	1646	1691.75	1659.81	36.186	1669.34	1.384	C=C str.	S ₁ (0.58)
9.	1467	1498.94	1475.35	3.194	1478.98	0.083	(O)CH ₃ asym. def.	S ₂₁ (0.61)
10.	1463	1493.56	1470.19	37.803	1470.50	0.735	(C)CH ₃ asym. def.	S ₂₃ (0.83)
11.	1448	1477.08	1454.36	9.536	1457.07	0.079	(O)CH ₃ sym. def.	S ₂₀ (0.81)
12.	1401	1434.10	1413.05	11.039	1427.32	0.257	CH ₂ sciss., (C)CH ₃ sym. def.	S ₁₄ (0.36), S ₂₂ (0.33)
13.	1378	1411.43	1391.23	8.365	1395.22	0.424	(C)CH ₃ sym. def., CH ₂ sciss.	S ₂₂ (0.33), S ₁₄ (0.25)
14.	1301	1314.60	1297.86	147.203	1310.36	4.936	C–C str., C–C str.	S ₂ (0.22), S ₈ (0.15)
15.	1210	1217.42	1203.85	198.393	1205.16	1.575	(O)CH ₃ rock	S ₂₄ (0.68)
16.	1197	1188.50	1175.81	172.642	1170.22	0.076	CH ₂ rock, C–O str.	S ₁₃ (0.46), S ₄ (0.32)
17.	1017	1031.26	1022.89	18.581	1050.53	0.872	(O)CH ₃ str., C–C str.	S ₅ (0.47), S ₈ (0.40)
18.	1005	1016.57	1008.57	8.626	1027.28	0.366	(C)CH ₃ rock	S ₂₅ (0.61)
19.	941	945.20	938.86	2.556	925.04	0.155	C–C str., O–CH ₃ str.	S ₈ (0.40), S ₅ (0.27)
20.	820	835.12	831.01	9.279	810.31	0.214	C–O str., C–C–O bend, C–O–C bend	S ₄ (0.29), S ₁₈ (0.13), S ₁₉ (0.15)
21.	594	599.02	598.38	2.823	593.96	0.128	C=O in plane bend, C–C str.	S ₁₇ (0.31), S ₂ (0.26)
22.	–	491.17	491.50	6.195	479.75	0.223	C=C–C bend	S ₁₅ (0.48)
23.	–	384.20	385.13	3.423	388.45	0.104	C=C–C bend	S ₁₆ (0.64)
24.	–	338.73	339.80	11.410	347.60	0.281	C–O–C bend, C=C–C bend	S ₁₉ (0.51), S ₁₅ (0.24)
25.	–	207.04	208.14	2.485	227.74	0.066	C–C–O bend, C=C–C bend, C–O–C bend	S ₁₈ (0.48), S ₁₆ (0.23), S ₁₉ (0.19)
A''								
26.	2984	3121.54	2989.87	21.926	2961.11	0.710	(O)CH ₃ asym. str.	S ₂₆ (0.99)
27.	2937	3086.61	2958.17	15.339	2921.55	0.605	(C)CH ₃ asym. str.	S ₂₇ (1.0)
28.	1457	1481.62	1458.70	7.829	1467.98	0.090	(O)CH ₃ asym. def.	S ₂₈ (0.85)
29.	1443	1469.99	1447.55	10.514	1454.19	0.131	(C)CH ₃ asym. def.	S ₂₉ (0.66)
30.	1171	1172.45	1160.24	0.786	1166.67	10.429	(O)CH ₃ rock	S ₃₀ (0.65)
31.	–	1071.31	1061.92	0.076	1073.89	0.001	(C)CH ₃ rock	S ₃₁ (0.64)
32.	945	983.45	976.24	31.684	980.30	0.816	C–C out-of-plane bend, CH ₂ wag	S ₃₈ (0.37), S ₃₇ (0.25)
33.	825	835.73	831.61	9.279	810.31	0.610	CH ₂ wag	S ₃₇ (0.57)
34.	663	672.39	670.07	10.114	707.64	0.438	CH ₂ twist	S ₃₂ (0.59)
35.	–	403.80	404.65	0.079	423.82	0.000	C=C out-of-plane bend	S ₃₉ (0.85)
36.	–	183.87	184.91	0.982	174.25	0.002	(C)CH ₃ torsion	S ₃₆ (1.0)
37.	–	159.70	160.67	3.861	170.01	0.002	(O)CH ₃ torsion	S ₃₅ (1.0)
38.	–	112.60	113.37	0.862	116.30	0.116	C–O torsion	S ₃₄ (0.84)
39.	–	68.71	69.23	1.502	65.50	0.089	C–C torsion	S ₃₃ (0.89)

^a Ref. [5].^b Intensity in (debye)²/AMU-(Å)².

assigned to the most intense band in the IR spectrum [5]. It corresponds to the calculated bands at 1734.9 cm^{-1} in DFT having intensity 232.635 kJ/Mole and 1726.0 cm^{-1} in RHF having intensity $7.361\text{ (debye)}^2/\text{AMU}(\text{\AA})^2$. Another vibrational band of medium intensity having calculated values of 1660.22 cm^{-1} (DFT) and 1664.40 cm^{-1} (RHF) may be assigned to the C=C stretch mode. The remaining four stretch modes corresponding to C₃–C₆, O₁₁–C₁₂, C₆–O₁₁ and C₃–C₄ stretch may be assigned to the vibrational bands at 1325 cm^{-1} (*S*₂, 0.23), 1028 cm^{-1} (*S*₅, 0.47), 833 cm^{-1} (*S*₄, 0.26) and 933 cm^{-1} (*S*₈, 0.42), respectively. None of these bands may be treated as characteristic bands as they have contributions from other stretch modes (Table 5). All the five possible skeletal deformation modes appear in the spectral region below 600 cm^{-1} for which no experimental data is available. Comparison is, therefore, made with the experimental IR-bands of methyl acrylate [17] and RHF results of Baker et al. [5] for MMA. The calculated frequencies from DFT at 606.04, 496.50, 371.78, 340.01 and 212.23 cm^{-1} and the corresponding bands from RHF may be assigned to C=O in plane bend, C₂=C₃–C₆ bend, C₂=C₃–C₄ bend, C₆–O₁₁–C₁₂ bend and C₃–C₆–C₁₁ bend, respectively, having major contribution from symmetry coordinates *S*₁₇(0.32), *S*₁₆(0.41), *S*₁₅(0.48), *S*₁₉(0.31) and *S*₁₈(0.44), respectively. It may be noted that all these vibrations are heavily mixed and have contributions from different bending modes. Baker et al. [5] assign these vibrations to skeletal modes without identifying the contributions of individual stretch and bending modes.

The four A'' skeletal mode vibrations at 965.34 cm^{-1} (*S*₃₈, 0.37), 395.02 cm^{-1} (*S*₃₉, 0.85), 113.57 cm^{-1} (*S*₃₄, 0.83) and 61.02 cm^{-1} (*S*₃₃, 0.84) in DFT calculations and the corresponding bands in RHF calculations may principally be assigned to C₃–C₄ out-of-plane bend, C=C out-of-plane bend, torsional mode about C₆–O₁₁ bond and asymmetric torsion about C₃–C₆ bond, respectively. The calculated band at 965.34 cm^{-1} in the IR-spectrum has contribution also from CH₂ wag (*S*₃₇, 0.20) and has been assigned by Baker et al. [5] to CH₃/CH₂ rock. The present calculations assign a vibrational band at 61.02 cm^{-1} (DFT), which corresponds to the 64.4 cm^{-1} band in RHF, to the asymmetric torsional mode. No

experimental results are available to confirm these assignments. In case of methyl acrylate, Egawa et al. [17] assign an infrared absorption band at 87 cm^{-1} to asymmetric torsional band. Similarly, in case of methacryloyl halides [18–20] this band appears at about 60 cm^{-1} . This confirms the correctness of our assignment. Baker et al. [5], however, assign their calculated band at 138 cm^{-1} to this vibrational mode. The calculated bands at 168.74 and 147.65 cm^{-1} , both in DFT, may be assigned to C–CH₃ and O–CH₃ torsional modes. The later assignment is in agreement with Baker et al. [5].

8. Cc conformer

The calculated and experimental [5] vibrational frequencies and their assignments for the Cc conformer are given in Table 6. A satisfactory agreement between the scaled and experimental frequencies may be noted. A comparison of Tables 5 and 6 shows that the vibrational frequencies of the Cc conformer lie very close to those of the Tc conformer and their assignments are also mostly unchanged. The transition from Tc to Cc conformer is, however, found to significantly affect vibrations corresponding to the skeletal modes. Thus the vibrational bands at 1325 , 1028 and 833 cm^{-1} in the Tc conformer shift to 1301 , 1017 and 820 cm^{-1} , respectively, in the Cc conformer. Further, DFT and RHF calculations are able to predict the relative shifts in the frequency and intensity of the carbonyl stretch band in the two conformers, in agreement with the experiment [5].

9. Electronic spectral studies

The electronic transition energies and optical oscillator strengths (OOS) of the two conformers (Tc and Cc) of MMA have been obtained by RHF/6-31G**–CI calculations with MP2 correction and are given in Table 7. These are compared with the corresponding results from SAC (Symmetric adapted cluster)–CI method reported by Hollauer et al. [6] and transitions based on angle-resolved EELS experiment [4]. Transitions involving four higher energy occupied molecular orbitals and four lower energy unoccupied orbitals which fall in the energy range 5–9 eV and

Table 7

Electronic transitions and assignments in Tc and Cc conformers of methyl methacrylate

State	Transition energy, E ($f \times 10^{3a}$ eV, Oscillator strength)		Assignment
	SAC-CI ^b	MP2/6-31G**	
Tc conformer			
A''	5.38 (<10)	5.86 (0.1)	n- π^*
A'	7.37 (440)	7.63 (647.7) ^c	π - π^*
A'	7.93 (140)	8.53 (41.2)	n- π^*
A''	8.92 (100)	8.60 (27.4)	σ_{mix} - π^*
A'	9.39 (<10)	8.89 (1.8)	n- π^*
Cc conformer			
A''	5.34 (<10)	5.63 (0.1)	n- π^*
A'	7.10 (220)	6.40 (647.7)	π - π^*
A'	7.97 (140)	7.80 (41.2)	n- π^*
A''	8.95 (20)	8.32 (27.4)	σ_{mix} - π^*
A'	9.34 (60)	8.44 (1.8)	n- π^*

^a Optical oscillator strength.

^b Ref. [6].

^c Experimental value 6.7 eV from EELS [4].

appear in the UV and visible spectral regions have been included in Table 7.

In case of Tc conformer, the calculations predict five transitions at 5.86 eV (0.0001), 7.63 eV (0.6467), 8.53 eV (0.0412), 8.60 eV (0.0274) and 8.89 (0.0018) eV; the numbers in parentheses are optical oscillator strengths (OOS). Based on the analysis of the main configurations and mixing coefficients for the singlet ground and excited states, the weak transitions at 5.86, 8.53 and 8.89 eV may be assigned to n- π^* excitations. None of these bands have been reported in the EELS spectrum [4]. The other two transitions at 7.63 eV (0.6467) and 8.60 eV (0.0274) may be assigned to π - π^* and σ_{mix} - π^* excitations. The high intensity transition at 7.63 eV may be correlated with the experimental band at 6.7 eV in EELS [4]. CAS-SCF/CI (Complete active space self consistent field) calculations [4], however, predict this band at 8.0 eV. Further, in agreement with the assignment of Sjogren et al. [21] based on NEXAFS experiments, the calculations suggest that the first virtual orbital is the ethylenic anti-bonding π^* orbital.

The electronic transitions for Cc conformer, except those at 6.40 eV (0.6477) and 7.80 eV

(0.0412), are close to the transitions in Tc conformer and have the same assignment. These two transitions may be assigned to π - π^* and n- π^* excitations, respectively.

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