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Energetics and Vibrational Analysis of Methyl Salicylate Isomers

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Energetics and vibrational analysis study of six isomers of methyl salicylate in their singlet ground state and first excited triple state is put forward in this work at the density functional theory level and large basis sets. The ketoB isomer is the lowest energy isomer, followed by its rotamer ketoA. For both ketoB and ketoA their enolized tautomers are found to be stable as well as their open forms that lack the internal hydrogen bond. The calculated vibrational spectra are in excellent agreement with IR experiments of methyl salicylate in the vapor phase. It is demonstrated that solvent effects have a weak influence on the stability of these isomers. The ionization reaction from ketoB to ketoA shows a high barrier of 0.67 eV ensuring that thermal and chemical equilibria yield systems containing mostly the ketoB isomer at normal conditions.

Introduction

Methyl salicylate (MS), $C_8H_8O_3$, is a semivolatile compound well-known for its signaling properties in nature.[1,2] MS is released into the atmosphere by certain plants when under stress or when being attacked and is used as an additive to enhance aroma in many commercial products. MS is also used in small amounts in foods to add a wintergreen taste, which gives rise to its alternative name of oil of wintergreen. MS is photoluminescent and is considered to be a surrogate to study certain biological and chemical threats.[3]

More recently, MS is being used in Forster's resonance energy transfer (FRET) systems and as the fluorescence component in optical bar code systems.[3,4] MS has an interesting dual fluorescence with peaks at 340 and 450 nm. Weller first proposed that the dual fluorescence is due to an excited state intermolecular proton transfer (ESIPT).[5] On the basis of gas phase, solution, and supersonic jets, several authors have since proposed that two different rotamers ketoA and ketoB of methyl salicylate exist in equilibrium[6−9] and that MS has open forms of the ketoA and ketoB rotamers.[10,11] Both ketoA and ketoB structures contain an internal hydrogen bond, which is absent in the open forms. The most recent theories suggest that the short wavelength fluorescence of MS is due to the ketoA form while the long wavelength fluorescence is due to the ketoB form undergoing an ESIPT to the enol form.[12−17]

Despite the experimental interest on MS, theoretical calculations are very scarce. A recent density functional calculation demonstrates that both ketoA and ketoB are indeed stable isomers of MS.[18] Measurements of the IR spectra and a Hartree−Fock frequency calculation for ketoA were reported in ref 19. The work in this paper focuses on computing the structure, energetics, and vibrational analysis of six stable isomers, ketoA, ketoB, $\mathrm{ketoA_{open}}$, $\mathrm{ketoB_{open}}$, enol, and "enolized" ketoA (ekA), in their singlet and triplet states. Results from these calculations are important for supporting empirical predictions on the phase equilibria between isomers. This paper is organized as follows. The second section on energetics describes the methodology used and presents the results of the geometry optimization, energy calculations, and other physical properties of the six isomers in their lowest singlet and triplet states. The following section provides the vibrational analysis of the six isomers, including a comparison with experimental IR spectra when available. The next section gives a discussion of the isomerization reaction from ketoB to ketoA, the transition state structure and potential energy along the reaction coordinate. This work is concluded in the last section.

Energetics of Methyl Salicylate

All-electron density functional theory (DFT) and the hybrid Becke−Perdew−Wang 1991 (B3PW91) approach were used throughout this study, which includes local and nonlocal correlation functionals.[20−22] Calculations of the MS isomers were obtained using the Gaussian 03 package[23] and a triple-ζ basis set with s, p, d polarization functions and extra diffuse d-functions (6-311++G).[24,25] A multitude of molecular structures from an unrestricted Monte Carlo and small basis sets simulation were used as initial conditions for the structural optimization. These molecular structures were subsequently minimized using the Berny optimization algorithm with redundant internal coordinates.[26] The vibrational frequencies were calculated to ensure for the presence of a minimum. The convention in this paper for designating a singlet or triplet state will be a superscript (1 or 3) preceding the isomer name.

The geometries of ketoA, ketoB, $\mathrm{ketoA_{open}}$, $\mathrm{ketoB_{open}}$, enol, and ekA isomers of MS were identified as stable in both the singlet and triplet states. Although there has been experimental hints on the existence of the first five isomers, the ekA form has not been predicted experimentally yet. The ground state of all isomers are singlet states. The optimized singlet geometries of the six different isomers are shown in Figure 1. Table 1 provides the detailed geometric parameters of ketoB in its singlet state, which is the most stable isomer. Geometries of all other isomers are provided as Supporting Information to this paper. The molecular symmetry of all isomers is low since they belong to the C_1 point group in either their singlet or triplet states. The singlet states of all isomers have planar geometries (excluding the hydrogens in the CH_3 group), whereas the triplet states are nonplanar geometries. Both the $^3\mathrm{ketoA_{open}}$ and $^3\mathrm{ketoB_{open}}$ forms are notably nonplanar, with the carbonyl group bending above the benzene ring plane and the phenol oxygen bending below

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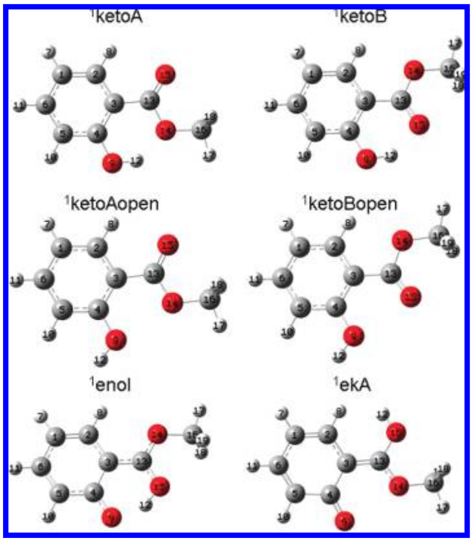

Figure 1. Geometries of the six MS isomers.

TABLE 1: Geometry of ¹ketoB Ground State

bond	distance (Å)	bond	angle (deg)	dihedral bond	angle (deg)
C_1-C_2	1.385	(2,1,6)	119.5	(6,1,2,3)	0.0
C_1-C_6	1.404	(2,1,7)	120.2	(6,1,2,8)	−180.0
C_1-H_7	1.082	(6,1,7)	120.3	(7,1,2,3)	180.0
C_2-C_3	1.408	(1,2,3)	120.8	(7,1,2,8)	0.0
C_2-H_8	1.081	(1,2,8)	120.9	(2,1,6,5)	0.0
C_3-C_4	1.416	(3,2,8)	118.4	(2,1,6,11)	180.0
C_3-C_{13}	1.456	(2,3,4)	119.1	(7,1,6,5)	−180.0
C_4-C_5	1.399	(2,3,13)	121.8	(7,1,6,11)	0.0
C_4-O_9	1.366	(4,3,13)	119.0	(1,2,3,4)	0.0
C_5-C_6	1.386	(3,4,5)	119.8	(1,2,3,13)	−180.0
C_5-H_{10}	1.081	(3,4,9)	122.8	(8,2,3,4)	180.0
C_6-H_{11}	1.083	(5,4,9)	117.5	(8,2,3,13)	0.0
O_9-H_{12}	0.991	(4,5,6)	120.0	(2,3,4,5)	0.0
$C_{13}-O_{14}$	1.359	(4,5,10)	118.1	(2,3,4,9)	180.0
$C_{13}-O_{15}$	1.254	(6,5,10)	121.9	(13,3,4,5)	180.0
$O_{14}-C_{16}$	1.463	(1,6,5)	120.8	(13,3,4,9)	0.0
$C_{16}-H_{17}$	1.085	(1,6,11)	119.8	(2,3,13,14)	0.0
$C_{16}-H_{18}$	1.089	(5,6,11)	119.4	(2,3,13,15)	−180.0
$C_{16}-H_{19}$	1.089	(4,9,12)	110.0	(4,3,13,14)	−180.0
		(3,13,14)	114.8	(4,3,13,15)	0.0
		(3,13,15)	124.0	(3,4,5,6)	0.0
		(14,13,15)	121.2	(3,4,5,10)	−180.0
		(13,14,16)	117.1	(9,4,5,6)	−180.0
		(14,16,17)	104.6	(9,4,5,10)	0.0
		(14,16,18)	110.1	(3,4,9,12)	0.0
		(14,16,19)	110.1	(5,4,9,12)	180.0
		(17,16,18)	111.1	(4,5,6,1)	0.0
		(17,16,19)	111.1	(4,5,6,11)	−180.0
		(18,16,19)	109.6	(10,5,6,1)	180.0
				(10,5,6,11)	0.0
				(3,13,14,16)	180.0
				(15,13,14,16)	0.0
				(13,14,16,17)	−180.0
				(13,14,16,18)	60.5
				(13,14,16,19)	−60.5

the ring plane. The ³enol structure is nonplanar with the hydrogen from the OH radical attached to the phenol oxygen and popping above the ring plane. The ³ekA form has the $COOCH_3$ group rotated quite noticeably out of the ring plane with the H_{12} atom sticking out at an angle almost normal to the ring plane.

The total energies of the different isomers in their lowest singlet and triplet states are compiled in Table 2. The ¹ketoB geometry was determined to have the lowest total energy of −14.562 keV. This finding is in agreement with a previous DFT calculation with smaller basis set.[18] Therefore, the ¹ketoB isomer is the global minimum structure and all energies reported in Table 2 are relative to the energy of this isomer. The ¹ketoA isomer is the next lowest energy at 0.082 eV above the ¹ketoB. This result was checked against an all-electron ab initio MP2 (same basis set) calculation that yields 0.128 eV as the difference in energy between the two optimized rotamer structures. In supersonic jet experiments at various temperatures an estimate of 0.11 eV was reported for the energy difference between ¹ketoB and ¹ketoA rotamers.[7] Although our DFT result is about 25% lower than the experiment and the MP2 result 16% higher than experiment, we believe that thermal excitation of the vibrations in these two rotamers during the experiment accounts for such discrepancy. The ¹ketoA rotamer is theorized to coexist in equilibrium with ¹ketoB.[6,8,7] However, an energy barrier between these two isomers may not allow chemical equilibrium to occur at room or medium-to-high temperatures, as discussed in a later section. Both open-form isomers have considerably higher energy structures about 0.57 eV above ¹ketoB. The geometry of the ¹enol is similar to the ¹ketoB due to the proton transfer from the carbonyl to the phenol groups and this isomer is 0.764 eV above the ¹ketoB. Previous DFT studies using smaller basis sets were unable to find the singlet enol optimized structure.[18] The ekA is new to the literature and is the highest energy of all six isomers.

First excited triplet states of the six isomers are reported in Table 2. These triplet states may or may not be the lowest excited state for each isomer. Although the DFT approach used in this paper ensures that the reported triplet states are indeed the lowest of all triplets, the approach is inadequate for calculation of other excited states. It is interesting to note that in the lowest triplet states, the energy ordering of the six isomers is altered when compared to the ordering in the ground state. The ³enol isomer is the lowest, followed by the ³ketoB and ³ketoA. Table 2 provides values of the zero point energy ϵ_0 for both singlets and triplets of the six MS isomers showing that this quantity does not change much across the different isomers.

In addition, calculated dipole and quadrupole moments of the MS isomers are reported in Table 2, showing that the ¹ketoA is the least polar of all isomers. Our results of the ¹ketoB and ¹ketoA dipole moments are in agreement with the 3.1 and 0.8 D ab initio values obtained at the MP2 level. The hydrogen bond lengths in ketoB, ketoA, and enol are 1.75, 1.73, and 1.51 Å, respectively. These bond lengths compare well with the MP2 values of 1.75 Å (ketoB) and 1.78 Å (ketoA). Rotational constants for the six isomers are similar. For the singlet states these constants in GHz are 2.14358, 0.82490, 0.59792 (2.15870, 0.83002, 0.60179 with MP2) for ketoB, and 2.24913, 0.82585, 0.60637 (2.24933, 0.82818, 0.607639 with MP2) for ketoA. For the other isomers rotational constants in GHz are 2.09378, 0.82141, 0.59216 ($\text{ketoB}_{\text{open}}$), 2.22137, 0.81777, 0.59998 ($\text{ketoA}_{\text{open}}$), 2.21092, 0.82402, 0.60258 (enol), and 2.23019, 0.81010, 0.59755 (ekA). Rotational constants for the most stable isomer ketoB are in agreement with experimental measurements.[18]

In the liquid phase, solvent effects may induce structural shifts in the solute molecular constituents. Therefore, properties such as the binding energy, dipole moments, and quadrupole moments will change. We considered a mixture of ketoB and ketoA in the liquid phase and used the polarized continuum model (PCM)[28] to calculate molecular properties of the solute. Considering one ¹ketoB molecule in an MS solvent with relative dielectric constant, $\epsilon = 9.0$ (ketoB value[29]), the solvent

TABLE 2: Total Electronic Energy, Zero Point Energy (ϵ_0), Dipole and Quadrupole of the MS Isomers[a]

	singlet					triplet				
isomer	state	*E* (eV)	ϵ_0 (eV)	dipole (D)	quadrupole (D/Å)	state	*E* (eV)	ϵ_0 (eV)	dipole (D)	quadrupole (D/Å)
ketoB	^{1}A	0	4.027	3.1	49, 68, 67, 1, 0, 0	^{3}A	3.117	3.887	1.4	50, 70, 67, −9, 0, 0
ketoA	^{1}A	0.082	4.026	0.8	47, 71, 67, 7, 0, 0	^{3}A	3.240	3.904	3.0	52, 66, 67, −0, 0, 0
ketoA$_{\text{open}}$	^{1}A	0.566	4.001	3.4	50, 61, 67, 1, 0, 0	^{3}A	3.825	3.879	4.2	53, 59, 67, −3, −1, 2
ketoB$_{\text{open}}$	^{1}A	0.573	4.004	2.9	48, 62, 67, 10, 0, 0	^{3}A	3.829	3.879	3.3	50, 60, 68, 9, 1, 2
enol	^{1}A	0.765	3.997	4.3	46, 71, 67, 0, 0, 0	^{3}A	2.861	3.917	2.7	50, 67, 67, −0, 0, 0
ekA	^{1}A	1.926	3.983	5.7	47, 67, 67, −0, −1, −0	^{3}A	3.536	3.896	3.6	50, 66, 66, −2, −3, −4

[a] Total energies *E* are relative to the ^{1}ketoB ground state energy of −14.561723 keV.

destabilizes ^{1}ketoB by 0.085 eV, zero-point energy decreases 0.005−4.022 eV, the dipole moment increases to 3.9 D from 3.1 D, and the quadrupole changes very little to 47, 68, 67, 0, 0, 0 D/Å. The total energy for ^{1}ketoA increased 0.062 eV, the zero-point energy decreased only 0.004 to 4.022 eV, the dipole moment changed from 0.8 to 0.9 D, and the quadrupole also showed little change to 44, 72, 67, −9, 0, 0 D/Å.

Vibrational Analysis

The calculated vibrational spectra of ketoB and ketoA in the singlet electronic states are reported in Table 3 and compared to IR experimental results in the gas phase.[19,30] Reported frequencies are the calculated frequencies scaled by a factor of 0.977, which gives the smallest error when the most prominent frequencies with IR intensity higher than 50 are compared to experimental data in ref 30. Additionally, this table contains the calculated intensity of the different lines and their summarized assignment. The scaled vibrational spectra for the other four isomers in their singlet electronic states and for all six isomers in the triplet states are reported in Table 4.

In the high frequency range, a modestly intense absorption line in the experiment is seen at about 3200 cm^{-1}.[30] This absorption is likely due to the OH stretch in the phenol. From our calculations, both ^{1}ketoB and ^{1}ketoA isomers have strong IR intensities due to the contribution of the OH stretching to the normal mode vibrations at 3262 and 3387 cm^{-1}, respectively. The calculated OH stretch for ^{1}enol is the second most intense feature of its vibrational spectrum and is located at a significantly red-shifted 2978 cm^{-1}. The calculated OH stretching of ^{1}ketoA$_{\text{open}}$ and ^{1}ketoB$_{\text{open}}$ isomers are located at 3615 cm^{-1} and their IR-active intensity is weak. In the triplet state of ^{3}ketoA the OH stretching appears in two modes at 2979 and 2993 cm^{-1} while in ^{3}ketoB it appears in only one mode at 2424 cm^{-1}, both cases displaying a dramatic red shift. However, the OH stretching in the ^{3}ketoA$_{\text{open}}$ and ^{3}ketoB$_{\text{open}}$ is shifted by only a few wavenumbers to 3590 and 3589 cm^{-1}. The ^{3}enol isomer was calculated to have a strong OH stretching at 3004 cm^{-1}. The ^{1}ekA and ^{3}ekA have OH stretching modes shifted to the blue at 3644 and 3622 cm^{-1}, respectively. The experimental less intense lines at 2850−3100 cm^{-1} are due to CH stretches and CH$_3$ symmetric and asymmetric stretches.

One of the two strongest absorption lines in ref 30 is at 1698 cm^{-1} (Table 3). This intense line is almost always seen in carboxylic acid derivatives.[31,32] In aromatic esters, the rule of three bands (RTB)[31] places the C=O stretching line within 1715−1730 cm^{-1}. Our calculation shows a strong C=O stretching vibration at 1647 cm^{-1} (1686 cm^{-1} without scaling) for ^{1}ketoB and at 1655 cm^{-1} (1694 cm^{-1} without scaling) for ^{1}ketoA. The ^{1}ketoB$_{\text{open}}$ C=O stretch is also in the vicinity at 1656 cm^{-1} and for ^{1}ketoA$_{\text{open}}$, ^{1}enol, ^{1}ekA the calculated line lies considerably lower at 1625, 1638, 1646 cm^{-1}, respectively. The other strong line reported in ref 30 is at 1310 cm^{-1}. Again from the RTB, the C−C−O stretch of aromatic esters is in the 1250−1310 cm^{-1} range. The calculated C−C−O stretching mode is located at 1308 cm^{-1} in ^{1}ketoB and at 1269 cm^{-1} in ^{1}ketoA. In the open forms ^{1}ketoB$_{\text{open}}$, ^{1}ketoA$_{\text{open}}$ and in ^{1}enol, ^{1}ekA this mode appears at 1245, 1316, 1334, and 1357 cm^{-1}, respectively. The third vibration frequency from RTB for aromatic esters is the O−C−C stretch, which typically falls in the 1000−1130 cm^{-1} range. Experimental work locates this O−C−C stretch absorption line at 1094,[30,19] which coincides well with our calculations at 1091 cm^{-1} for ^{1}ketoB and a rather intense line at 1077 cm^{-1} for ^{1}ketoA. The calculated O−C−C stretching mode in ^{1}ketoB$_{\text{open}}$ is very strong at 1067 cm^{-1}, in ^{1}ketoA$_{\text{open}}$ is intense at 1124 cm^{-1}, and appears rather intense in ^{1}enol at 1100 cm^{-1} and ^{1}ekA at 1053 cm^{-1}, respectively. This O−C−C stretch is strong in both ^{3}ketoB at 1076 cm^{-1} and ^{3}ketoA at 1057 cm^{-1}. All four isomers ^{3}ketoB$_{\text{open}}$ and ^{3}ketoA$_{\text{open}}$, ^{3}enol and ^{3}ekA show the O−C−C stretch as their most intense lines at 1086, 1087, 1068, and 1085 cm^{-1}, respectively. All three RTB calculated lines agree very well with the experimental values listed in Table 3.

In ^{1}ketoB, the umbrella mode is located at 1444 cm^{-1} and the in-plane OH bend at 1385 cm^{-1}. Two prominent experimental absorption lines[30] are located at approximately 754 and 705 cm^{-1}. Since MS has an ortho-substituted benzene ring, then the first line is due to out-of-plane CH motion while the latter is due to aromatic ring bending vibrations. The calculated out-of-plane CH bending vibrations for the different isomers have the following wavenumbers: ^{1}ketoB at 786 cm^{-1}, ^{1}ketoA at 790 cm^{-1}, ^{1}ketoA$_{\text{open}}$ at 757 cm^{-1}, ^{1}ketoB$_{\text{open}}$ at 759 cm^{-1}, ^{1}enol at 770 cm^{-1}, ^{1}ekA at 746 cm^{-1}, ^{3}ketoA at 808 and 667 cm^{-1}, ^{3}ketoB at 808 and 681 cm^{-1}, ^{3}ketoA$_{\text{open}}$ at 774 and 642 cm^{-1}, ^{3}ketoB$_{\text{open}}$ at 773 and 640 cm^{-1}, ^{3}enol at 735 cm^{-1}, and ^{3}ekA at 758 cm^{-1}. Except for ^{3}enol and ^{3}ekA, isomers in the triplet states show a CH out-of-plane motions into two different modes because only some of the CH bonds participate in one mode while the rest move in the other mode.

The calculated aromatic ring bending vibrations appear at the following wavenumbers: ^{1}ketoA at 662 cm^{-1}, ^{1}ketoB at 680 cm^{-1}, ^{1}ketoA$_{\text{open}}$ at 673 cm^{-1}, ^{1}ketoB$_{\text{open}}$ at 667 cm^{-1}, ^{1} enol at 674 cm^{-1}, ^{1} ekA at 655 cm^{-1}, ^{3}ketoA at 600 cm^{-1}, ^{3}ketoB at 594 cm^{-1}, ^{3}ketoA$_{\text{open}}$ at 609 cm^{-1}, ^{3}ketoB$_{\text{open}}$ at 613 cm^{-1}, ^{3}enol at 617 cm^{-1}, and ^{3}ekA at 683 cm^{-1}.

ketoB to ketoA Isomerization Reaction

With the calculated normal-mode frequencies, a harmonic analysis of several thermodynamic functions is feasible within the canonical ensemble.[33] For example, the free-energy, internal energy, and vibrational specific heat were calculated for all six isomers as a function of temperature. By inspecting the temperature dependence of the Helmholtz free energy of each MS isomer in their singlet and triplet states, we estimate that these structures will not undergo thermal isomerization up to

TABLE 3: Calculated Vibrational Spectra of ^{1}ketoB and ^{1}ketoA Isomers and Comparison with Experiments in Ref 30 and Table 2 of Ref 19[a]

^{1}ketoB			^{1}ketoA		experiment			
ν (cm^{-1})	intensity	assignment	ν (cm^{-1})	intensity	ref 30 (cm^{-1})	ref 19 (cm^{-1})	ref 19 (cm^{-1})	ref 19 (cm^{-1})
3262	244	ν O−H	3387	305	3262	3188		
3151	8	ν_s ring C−H	3147	10				
3145	7	ν_a ring C−H	3140	11				
3126	14	ν_a ring C−H	3125	8				
3115	11	ν_a CH_3	3114	9		3010		
3108	6	ν_a ring C−H	3109	6	3078	2954	3081	2977
3080	17	ν_a CH_3	3086	14		2920	2964	2931
2988	32	ν_s CH_3	2992	31	2966	2850	2854	2874
1647	200	ν C=O, ν ring C−C, ρ Ph H	1655	234	1698	1682	1683	1647
1593	136	ν C=O, ν ring C−C	1633	248	1618	1616	1620	
1579	30	ν C=O, ρ Ph H	1587	32		1586	1590	1562
1490	70	ρ ring C−H	1494	17	1482			1509
1487	28	σ CH_3	1488	6				
1473	14	τ CH_3	1484	122				
1463	10	ρ ring H	1472	15				
1444	78	ω CH_3	1442	14	1450	1488	1472	1449
1385	135	ρ Ph H	1386	17	1410	1442	1437	
1357	40	ν ring C−C	1343	23				1350
1308	273	ν C−CH_3O, ρ ring H	1269	320	1310	1339	1337	1277
1253	50	ν C−Ph O, ρ ring H	1247	32	1254	1307		
1222	291	ρ Ph H	1214	90	1214	1255	1255	
1179	38	σ ring H	1178	10		1218	1203	
1174	79	τ CH_3	1168	38	1166	1159	1162	
1139	27	σ ring H	1137	1		1137	1143	
1136	1	τ CH_3	1116	64				
1091	81	ν O CH_3	1077	162	1094	1092	1068	
1034	15	ω ring CH	1035	59		1034	1039	
992	0	ω ring CH	997	1				
981	2	ω ring CH	985	2				
941	8	ν O CH_3	934	14		965	965	
874	0	ω ring CH	876	0				
835	20	ring breath, ν C−Ph O	844	2	854	850	858	874
786	28	ω ring CH	790	30	754	802	814	
784	1	σ C(=O)−O	765	20				
748	8	ω C−C/C−H/O−H	751	35		760		
728	208	ω OH	693	104	706	702		735
680	2	ω ring	662	80				
671	12	ring breath	661	6		667	671	
563	4	ring breath	556	8			566	
529	7	ω ring	531	5	530	563	517	523
507	12	ρ O_9H_{12}−O_{15}	528	4		511		
437	0	ω out-of-plane	441	0				
431	5	ρ in-plane	387	8			442	432
342	19	ρ O_9H_{12}−O_{15}	351	3			346	345
323	8	ρ in-plane	312	12				
259	2	ω full molecule	256	1			267	219
174	3	ω full molecule	183	2			190	
166	2	ρ CH_3	176	2				
128	2	τ CH_3	108	0				
86	1	τ CH_3	85	0				
74	0	τ CH_3	62	6				

[a] Symbols: υ, stretching; ω, wagging; ρ, rocking; τ, twisting; σ, scissoring; Ph, phenyl; s symmetric; a, asymmetric. Calculated frequencies are scaled by a 0.977 factor.

temperatures of about 2000 K. More so, at temperatures above 2000 K, the ^{1}ketoA isomer becomes more stable than ^{1}ketoB and a crossing of the free energy curves occurs.[34] At even higher temperatures the ^{1}ketoA$_{\text{open}}$ is the most stable isomer. The harmonic approximation of the thermodynamic functions is very accurate at lower energies. However, we believe that as a first estimate, the high temperature results provide a qualitative description of a given process. Therefore, our findings are indicative that at $T = 300$ K thermal fluctuations would not be responsible for an isomer structural transition. On the basis of this fact, extra energy of about 0.3 eV is needed to isomerize ketoB into ketoA, and chemical equilibrium would strongly favor a high relative concentration of about 100% ketoB versus ketoA. This result is consistent with previously proposed chemical equilibrium in which MS vapor at room temperature is mainly ketoB and only 1/70 of its concentration is ketoA.[7]

On the basis of the harmonic estimate of the isomer transition, we additionally investigated the isomerization reaction of ketoB → ketoA at the DFT level of calculation. A transition state was found at 0.67 eV above the ketoB energy, which has the lowest positive and one negative frequencies at +85 and −125 cm^{-1}. The transition state geometry was discovered with the synchronous transit-guided quasi-Newton method[26,27] letting relax all bond lengths and angles. This structure has the $COOCH_3$ group

TABLE 4: Vibrational Frequencies of ^{1}ketoB$_{open}$, ^{1}ketoA$_{open}$, ^{1}enol, and ^{1}ekA and of All Six Isomers in Their Triplet Electronic States[a]

^{1}ketoA$_{open}$ (cm^{-1})	^{1}ketoB$_{open}$ (cm^{-1})	^{1}enol (cm^{-1})	^{1}ekA (cm^{-1})	^{3}ketoB (cm^{-1})	^{3}ketoA (cm^{-1})	^{3}ketoA$_{open}$ (cm^{-1})	^{3}ketoB$_{open}$ (cm^{-1})	^{3}enol (cm^{-1})	^{3}ekA (cm^{-1})
3615	3615	3142	3644	3158	3157	3590	3589	3149	3622
3145	3163	3136	3135	3151	3145	3147	3154	3143	3140
3129	3131	3123	3125	3132	3131	3141	3145	3127	3125
3113	3113	3119	3122	3106	3107	3108	3107	3106	3115
3110	3105	3098	3094	3103	3101	3102	3098	3106	3108
3087	3089	3090	3085	3064	3075	3079	3080	3070	3101
3070	3068	2995	3046	2978	2993	3059	3058	3004	3068
2982	2981	2978	2991	2424	2979	2975	2974	2981	2973
1625	1656	1638	1646	1592	1550	1556	1550	1570	1536
1621	1619	1571	1595	1542	1536	1507	1518	1504	1527
1590	1600	1543	1540	1508	1506	1489	1492	1491	1490
1511	1512	1524	1508	1489	1493	1472	1471	1489	1482
1486	1490	1485	1482	1470	1472	1470	1465	1473	1478
1471	1472	1474	1477	1455	1471	1445	1447	1459	1448
1460	1455	1464	1466	1441	1437	1431	1431	1445	1410
1439	1441	1446	1448	1425	1427	1390	1394	1420	1381
1359	1357	1386	1396	1376	1407	1381	1381	1385	1350
1316	1313	1357	1357	1337	1332	1312	1293	1370	1270
1293	1269	1334	1281	1288	1291	1276	1282	1266	1250
1243	1245	1254	1239	1265	1272	1207	1209	1243	1213
1185	1185	1202	1184	1198	1173	1167	1168	1213	1171
1181	1174	1173	1173	1169	1161	1156	1161	1166	1170
1169	1168	1163	1152	1149	1149	1132	1135	1146	1126
1133	1137	1142	1126	1131	1137	1101	1104	1129	1096
1124	1121	1132	1114	1121	1109	1087	1086	1081	1085
1086	1067	1100	1053	1076	1057	1063	1061	1068	1036
1048	1050	1008	1005	1012	967	973	963	1002	1014
1010	999	998	1000	956	942	923	932	953	960
974	971	981	948	949	910	909	912	931	924
938	944	924	910	937	898	842	852	890	914
860	861	855	848	892	849	814	790	829	855
844	828	838	842	808	819	774	773	819	833
795	799	770	761	804	808	736	736	811	758
777	774	746	746	741	714	684	683	735	694
757	759	738	711	681	667	642	640	715	683
673	667	723	655	594	600	609	613	617	603
662	667	674	617	587	598	560	554	605	557
558	564	629	547	549	528	527	515	545	529
536	537	554	538	511	519	470	480	535	505
527	499	544	512	505	516	450	443	483	459
453	448	521	461	423	393	391	401	447	383
372	391	451	401	408	371	381	390	408	350
338	353	417	387	355	358	334	335	345	323
295	329	370	341	321	352	312	307	328	313
292	292	316	301	314	298	270	262	319	267
247	256	243	224	222	221	180	183	226	200
168	170	174	161	151	182	152	147	164	181
156	164	158	139	141	119	128	139	148	124
110	111	119	112	101	100	111	107	119	102
94	94	86	65	85	77	78	66	98	64
26	24	81	60	75	57	49	58	59	41

[a] Reported frequencies are scaled by a 0.977 factor.

rotated ±90° with respect to the ring plane and away from its position in the ketoB structure. For comparison, the transition state geometry was recalculated at the MP2 level and the energy difference with respect to the MP2 optimized structure of ketoB yields 0.71 eV. Adding the solvent effect with PCM reduces the transition barrier to 0.5 eV. Next, the transition state geometry and the computed force constants were used as input for calculating the MS energy along the intrinsic reaction coordinate path (IRC)[35] shown in Figure 3. The IRC path was followed by relaxing the mass-weighted internal coordinates of atoms 14, 13, 3, 2 (Figure 1) that participate in the pertinent dihedral angle, which changes from 0° (ketoB) to 180° (ketoA) along the reaction.

Conclusion

The full energetics and vibrational analysis study of six isomers of MS is presented in this paper. We predict that at the BPW91/6-311++G level of calculation all six isomers in their ground state are singlets and report structures and energies of both the ground state and first excited triplet state. The ketoB isomer is the global minimum followed in energy by its rotamer ketoA. Our calculation for ketoB and ketoA confirms an earlier DFT study with smaller basis sets.[18] The structure and energy of the open forms of the ketoB and ketoA isomers, the tautomer with ring-inserted carbonyl radical (enol), and the enolized ketoA are new to the literature. We also provide the full

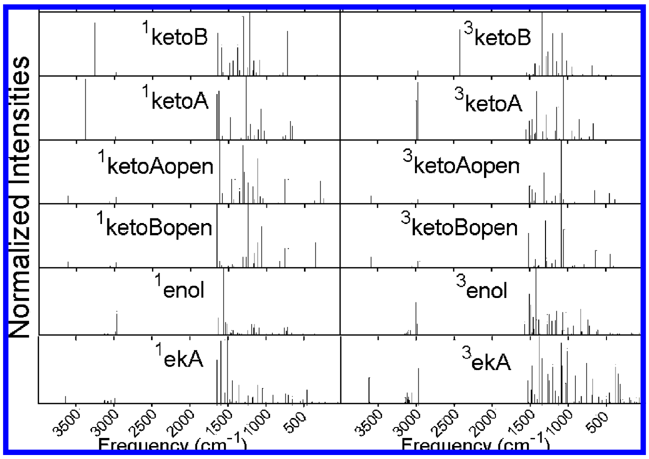

Figure 2. IR active spectra of the six MS isomers in the ground state and first excited triplet. state.

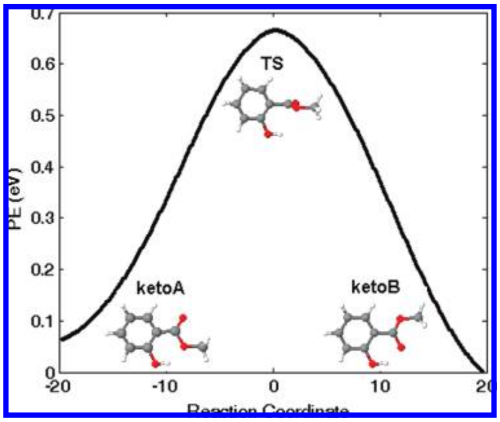

Figure 3. IRC isomerization reaction path following the O14−C13−C3−C2 dihedral angle changes.

calculated vibrational spectra of these six isomers in their ground state and first triplet state. The calculated vibrational lines of ^{1}ketoB correspond quite well to the peaks of the experimental spectrum.[30,19] Specifically, the calculated lines corresponding to the OH and CH stretching vibrations in the 3000−3500 cm^{-1} region correlate well with the experiments. The match of C═O stretching vibrations near 1700 cm^{-1} is less well-defined. However, the C−C−O and O−C−C calculated stretching vibrations lie close to the experimental bands. One intense line calculated at approximately 727 cm^{-1} is due to the aromatic ring bending vibration and might be correlated to either of the observed lines at 754 or at 705 cm^{-1}.

The isomerization reaction between the rotamers ketoB and ketoA was followed in detail, showing the existence of an energy barrier of 0.67 eV. Estimates of the liquid phase of MS by assuming each molecule in a solvent of all the others depletes the isomerization barrier by 0.17 eV. The high value of this barrier to the internal rotation of the −COOCH$_3$ group is indicative that at room temperature the isomerization reaction is unlikely to occur. However, since the reverse isomerization energy (ketoA to ketoB) barrier of 0.59 eV is almost as high, then it is likely that any ketoA species that are present in a sample will remain ketoA at room temperature.

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Supporting Information Available: Table of atomic parameters for the geometry of six isomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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