Photodissociation dynamics of methoxybenzoic acid at 193 nm

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The theoretical prediction and experimental confirmation of the $1\pi\sigma^*$ repulsive excited state along O−H bond of phenol have large impact on the interpretation of phenol and tyrosine photochemistry. In this work, we investigated the photodissociation dynamics of 2-, 3-, and 4-methoxybenzoic acid (MOBA) in a molecular beam at 193 nm using multimass ion imaging techniques. In addition, the ground state and the excited state potential energy surfaces of MOBA were investigated using ab initio calculations, and branching ratios were predicted by Rice–Ramsperger–Kassel–Marcus theory. The results show that (1) the excited state potential of $1\pi\sigma^*$ along O−CH$_3$ bond remains similar to that of phenol and anisole, (2) CH$_3$ elimination is the major channel for three MOBA isomers, and (3) photofragment translational energy distributions show bimodal distributions, representing the dissociation on the ground state and repulsive excited state, respectively. Comparison to the study of hydroxbenzoic acid [Y. L. Yang, Y. A. Dyakov, Y. T. Lee, C. K. Ni, Y. L. Sun, and W. P. Hu, J. Chem. Phys. 134, 034314 (2011)] shows that only the intramolecular hydrogen bonding has significant effects on the excited state dynamics of phenol chromophores. © 2012 American Institute of Physics.

I. INTRODUCTION

Recent theoretical calculations$^1$ showed that UV absorption of phenol corresponds to excitation to the bright state, $1\pi\pi^*$. The population of the $1\pi\pi^*$ state can be transferred to the dark state $1\pi\sigma^*$ through a conical intersection. The $1\pi\sigma^*$ state is repulsive along O−H bond distance, and it crosses the ground state at large O−H bond distance. Consequently, UV excitation of phenol results in the H atom elimination from the repulsive $1\pi\sigma^*$ state. The theoretical predictions were confirmed by molecular beam experiments. The repulsive $1\pi\sigma^*$ state remains similar for various substituted phenols, including fluorine and methyl 2-, 3-, and 4-substituted phenols, 4-fluorophenol, 4-chlorophenol, and 4-bromophenol, anisole, and 1-naphthol. On the other hand, as the size of substituted functional group increases, internal conversion to the ground state starts to compete with the H atom elimination on the repulsive state. For example, H atom elimination on the repulsive state remains as the major channels for p-methylphenol and p-ethylphenol. However, H atom elimination on the repulsive state is completely shut down for p-(2-aminoethyl)phenol. Internal conversion to the ground state becomes the major channel before molecules reach the size of amino acid tyrosine. It provides one explanation on the photostability of amino acids. More recently, competing $1\pi\sigma^*$ mediated dynamics in p-methoxyphenol was observed from the O−H versus and O−CH$_3$ photodissociation pathways. Dynamics along the O−H coordinate generally similar to H atom elimination observed in phenol, whereas O−CH$_3$ bond fission is different from the CH$_3$ elimination dynamics observed in anisole.

Recently, we studied the photodissociation dynamics of hydroxybenzoic acids. We demonstrated that the repulsive $1\pi\sigma^*$ state is strongly affected by the −COOH functional group. The typical changes of the potential energy surfaces include (a) the repulsive $1\pi\sigma^*$ state becomes an attractive potential near the equilibrium geometry of the ground state, (b) the conical intersection between $1\pi\pi^*$ and $1\pi\sigma^*$ is located at a much higher energy level, and (c) the intersection between the ground state and the $1\pi\sigma^*$ along the O−H bond distance disappears. As a result, the O−H bond cleavage on the repulsive state is shut down almost completely.

Large photofragment translational energy in the photodissociation of anisole C$_6$H$_5$OCH$_3$ → C$_6$H$_5$O+CH$_3$ was observed. It can be attributed to the dissociation on the repulsive $1\pi\sigma^*$ state of anisole (C$_6$H$_5$OCH$_3$) along the O−CH$_3$ bond. In this work, we studied the photodissociation dynamics of methoxybenzoic acids (MOBA, C$_6$H$_4$OCH$_3$COOH) in a molecular beam using multimass ion imaging techniques. Theoretical calculations of the potential energy surfaces for anisole and MOBA were performed. Unlike hydroxybenzoic acids, we demonstrated that carboxyl functional group has no effects on the repulsive $1\pi\sigma^*$ state along O−CH$_3$ bond of methoxy group due to the lack of intramolecular hydrogen bonding. Comparison to the study of hydroxbenzoic acid shows that only the intramolecular hydrogen bonding has significant effects on the excited state dynamics of phenol chromophores.

II. EXPERIMENTS

The details of experimental techniques have been described in previous studies.14–16 Only a brief description is
given here. Molecules in a molecular beam were dissociated using a pulsed UV laser beam set at 193 nm. The resulting photofragments were ionized by a pulsed VUV laser beam at 118 nm. Ions were analyzed and detected using multimass ion imaging techniques. Photofragment masses were identified along with their translational energy distribution measurements. Photolysis laser fluence in the region of 1–50 mJ/cm² was used to determine the photolysis photon number dependence of each fragment. Only fragments resulted from one-photon absorption are discussed in this work.

III. CALCULATION METHODS

The dissociation channels on the ground state were investigated from the calculations of energies, transition states, and products using B3LYP/6-31G method. Energies of these structures were then refined by the G3(MP2,CCSD) scheme. All ground-state electronic structure calculations were performed using the GAUSSIAN 03 package. The energies of the ground state geometries for various conformers were calculated using the B3LYP/6-311+G(d,p) method. The excited-state energy calculation for each conformer was performed using the complete active space (CAS) theory with the 6-311+G(d,p) basis set. The CAS method is a special version of multi-configurational self-consistent-field method and is frequently used to model the electronic ground and excited states simultaneously. In CAS method, a complete set of electron configurations are generated in the selected active space which in the current case consists of 12π electrons and 12 orbitals (6π, 4π*, and 2σ*). These linear combinations of these configurations and the molecular orbitals are optimized self-consistently to generate the wavefunctions of various electronic states. A state averaged approach with equal weighting was applied to calculate the two lowest states of A′ and A” symmetry simultaneously. This calculation was carried out using the MOLPRO 2009 program. For comparison, the excited potential energy curves were also calculated using the time-dependent (TD) density functional theory (DFT) with the B3LYP functional and 6-311+G(d,p) basis set using the GAUSSIAN 03 package.

IV. RESULTS AND DISCUSSION

A. Photodissociation of MOBA

1. 3-MOBA

Photofragment ions m/z = 15, 53, 65, 81, 109, 135, and 137 were observed from the dissociation of 3-MOBA at 193 nm. Ion of m/z = 81 has a large intensity, ions of m/z = 15, 53, 65, 109, and 137 have relatively small intensities, and ion of m/z = 135 was barely observable. Images for various fragments are shown in Figure 1. Both images of m/z = 15 and 137 have line shape images, representing the following dissociation channel:

\[ 3 - \text{C}_6\text{H}_4\text{OCH}_3\text{COOH} + h\nu(193 \text{ nm}) \]
\[ \rightarrow 3 - \text{C}_6\text{H}_4\text{OCOOH}(m = 137) + \text{CH}_3(m = 15) \quad (1) \]

Ion images of m/z = 53, 65, 81, and 109 are disk-like. They represent the dissociation of heavy fragment ions (m/z = 137) following VUV photoionization

\[ 3 - \text{C}_6\text{H}_4\text{OCOOH}(m = 137) + h\nu(118 \text{ nm}) \]
\[ \rightarrow 3 - \text{C}_6\text{H}_4\text{OCOOH}^+ + e^- (\text{ionization energy 8.9 eV}) \]

\[ (I) \]

\[ 3 - \text{C}_6\text{H}_4\text{OCOOH}^+(m/z = 137) \]
\[ \rightarrow c - \text{C}_5\text{H}_4\text{COOH}^+(m/z = 109) + \text{CO} \]

\[ (\text{barrier : 43 kcal/mol, } \Delta H = 16 \text{ kcal/mol}) \quad (\text{DI1}) \]

\[ c - \text{C}_5\text{H}_4\text{COOH}^+(m/z = 109) \]
\[ \rightarrow c - \text{C}_5\text{H}_3\text{OH}^+(m/z = 81) + \text{CO} \]

\[ (\text{barrier : 33 kcal/mol, } \Delta H = -16 \text{ kcal/mol}) \quad (\text{DI2}) \]

\[ c - \text{C}_5\text{H}_4\text{COOH}^+(m/z = 109) \rightarrow c - \text{C}_5\text{H}_5^+(m/z = 65) + \text{CO}_2 \]

\[ (\text{barrier : 38 kcal/mol, } \Delta H = 38 \text{ kcal/mol}) \quad (\text{DI3}) \]

\[ \text{C}_5\text{H}_3\text{O}^+(m/z = 81) \rightarrow \text{C}_4\text{H}_4^+(m/z = 53) + \text{CO} \]

\[ (\text{barrier : 66 kcal/mol, } \Delta H = 26 \text{ kcal/mol}) \quad (\text{DI4}) \]

The small ionization energy of fragment m/z = 137 (reaction (I)), and the low barrier heights and small heat of reactions from ab initio calculations for dissociation following ionization (reactions (DI1)–(DI4)), as listed in the parentheses, confirm the possibility that these reactions can be initiated by VUV photoionization. The momentum match between m/z = 15 and the sum of m/z = 137, 109, 81, 65, and 53 confirms the CH₃ elimination channel. The corresponding photofragment translational energy distribution is shown in Figure 2.

Theoretical calculations for various dissociation channels on the electronic ground state are shown in Figure 3. CH₃ elimination channel has a loose transition state with a barrier height of 69 kcal/mol. The CO₂ elimination is an exothermic reaction (ΔH = −4 kcal/mol). It has a tight transition.
state with a barrier height of 72 kcal/mol. Only these two reactions have relatively low barrier heights. The other dissociation channels have much higher barriers, and they cannot compete with CH₃ and CO₂ elimination channels.

The CO₂ elimination channel can further undergo a secondary reaction, C₆H₅OCH₃ → C₆H₅O + CH₃. It is a dissociation channel without exit barrier. On the other hand, the possible secondary reactions after primary CH₃ elimination include CO and CO₂ elimination, OC₆H₄COOH → C₅H₄COOH + CO and OC₆H₄COOH → C₆H₅O + CO₂. Branching ratio calculations for the dissociation on the ground state using Rice–Ramsperger–Kassel–Marcus (RRKM) theory suggest that the primary CH₃ elimination is the dominant channel (95%) due to the loose transition state, and almost no further secondary reactions occur. On the other hand, the primary CO₂ elimination was predicted to be a minor channel (5%) due to the tight transition state, and most of the products from this channel underwent the secondary dissociation. The momentum match between m/z = 15 and the sum of m/z = 137, 109, 81, 65, and 53 from our experimental measurement suggested that only the primary CH₃ elimination reaction occurs.

FIG. 2. Photofragment translational energy distribution of 3-MOBA for reaction 3-C₆H₄OCH₃COOH → C₆H₄OCOOH + CH₃.

Since the primary CH₃ elimination on the ground state has no exit barrier, the energy release in photofragment translational energy is expected to be small. The slow component in the translational energy distribution must result from the dissociation on the ground state. On the other hand, the fast component must represent the dissociation from a repulsive excited state along the O–CH₃ bond, analogous to the CH₃ elimination from a repulsive state along the O–CH₃ bond of anisole.

2. 4-MOBA

Photodissociation properties of 4-MOBA from experimental measurements were found to be very similar to 3-MOBA, i.e., photofragment ions m/z = 15, 65, 81, 109, 135, and 137 were observed. Only m/z = 137 and 15 are line shape images, the others are disk-like images. The photofragment ion images are shown in Figure 4.

RRKM theory predicts that the CH₃ elimination is the dominant channel (98%) and CO₂ elimination is the minor channel (2%). The momentum match between m/z = 15 and the sum of m/z = 137, 109, 81, and 65 from experimental measurement confirms that the CH₃ elimination is the major channel. Photofragment translational energy distribution for CH₃ elimination channel is shown in Figure 5. The slow and fast components in the translational energy distribution represent the dissociation on the ground state and repulsive excited state, respectively.

FIG. 3. Potential energies of reactant 3-MOBA, transition states, and dissociation products on the ground state.

FIG. 4. Photofragment ion images of 4-MOBA. Pump and probe laser pulse delay time are 3, 11, 26, 26, and 26 μs for m/z = 15, 65, 81, 109, and 137, respectively.

FIG. 5. Photofragment translational energy distribution of 4-MOBA for reaction 4-C₆H₄OCH₃COOH → C₆H₄OCOOH + CH₃.
Barrier heights and heat of reactions for various dissociation channels from ab initio calculations are also very similar to that of 3-MOBA. Details of the dissociation channels, the energies of transition states, intermediates, and dissociation energies on the ground state from ab initio calculations are shown in Figure 6.

The ionization energy of 4-C₆H₄OCOOH (m/z = 137) from ab initio calculations was found to be the same as 3-C₆H₄OCOOH (m/z = 137). The dissociative ionization of reaction (DI-1) for 4-C₆H₄OCOOH (m/z = 137) is only slightly different from that of 3-C₆H₄OCOOH (m/z = 137). The barrier height changes from 43 kcal/mol to 33 kcal/mol, and heat of reaction changes from $\Delta H = 16$ kcal/mol to 15 kcal/mol. Analogous to 3-MOBA, these small values explain the disk-like images we observed in 4-MOBA.

**3. 2-MOBA**

Photofragment ions m/z = 15, 64, 65, 77, 92, 93, 108, 120, 135, and 137 were observed from the dissociation of 2-MOBA. Ions m/z = 15, 65, and 93 have large intensities, and all the other ion intensities are 50 ~ 100 times smaller. Only ions with large intensities will be discussed here. One major difference between 2-MOBA, 3-MOBA, and 4-MOBA is that fragment m/z = 93 was only observed from 2-MOBA, but m/z = 109 was only observed from 3-MOBA and 4-MOBA.

Image m/z = 65 has a disk-like image, representing the dissociative ionization from heavy fragment m/z = 93, C₆H₅O + hv (118 nm) $\rightarrow$ C₅H₅ + (m/z = 65) + CO. (Ionization energy of m/z = 93 is 9.5 eV, barrier height and heat of reaction for dissociation of cation are 38 and −7.4 kcal/mol, respectively.)

Details of the other dissociation channels, the energies of transition states, intermediates, and dissociation energies on the ground state can be found in Figure 8. Most of the dissociation channels and barrier heights remain similar to that of 3-MOBA and 4-MOBA, except reaction (2). The barrier of reaction (2) is significantly reduced from 72 kcal/mol for 3-MOBA and 4-MOBA to 28 kcal/mol for 2-MOBA. This is because the final product of 2-MOBA is C₆H₅OH, which has different structure from the final product C₆H₅O of 3-MOBA and 4-MOBA. As a result, the photofragment product of reaction (1), C₆H₆OCOOH (m/z = 137), was barely observable in 2-MOBA due to this low barrier. Unlike 3-MOBA and 4-MOBA, most of the product of reaction (1) generated from 2-MOBA undergoes secondary dissociation (reaction (2)). This explains why fragment m/z = 93 was only observed from 2-MOBA, but fragment m/z = 109 was only observed from 3-MOBA and 4-MOBA.

**FIG. 7.** Photofragment ion images of 2-MOBA. Pump and probe laser pulse delay time are 3, 20, and 20 μs for m/z = 15, 65, and 93, respectively.

**FIG. 8.** Potential energies of reactant 4-MOBA, transition states, and dissociation products on the ground state.
Our calculations from the ground state potential energies and the RRKM theory showed that CH$_3$ elimination is only about 2 times faster than CO$_2$ elimination. Unlike 3-MOBA and 4-MOBA in which the CH$_3$ fragments are mainly contributed from the primary CH$_3$ elimination on the ground state, the CH$_3$ fragments generated from 2-MOBA may also originate from the CO$_2$ elimination followed by the secondary CH$_3$ elimination. However, if the fragments m = 15 were exclusively from the secondary reaction, C$_6$H$_5$OCH$_3$ (m = 108) → C$_6$H$_4$OH (m = 93) + CH$_3$, (following the primary CO$_2$ elimination), then the photofragment momentum distributions of m = 93 and 15 must match. Experimental measurement showed that the momentum distributions of m = 93 and 15 were very different, indicating reaction (1) has significant contribution to fragment CH$_3$ (m = 15). Indeed, we can estimate the contribution of reactions (1) and (2) (CH$_3$ elimination, followed by CO$_2$ elimination) and reactions (3) and (4) (CO$_2$ elimination followed by CH$_3$ elimination) to the fragment m = 15 from the difference of the momentum distributions between m = 93 and 15. The photofragment momentum analysis showed that most of the fragments m = 15 and 93 were from the primary CH$_3$ elimination, which was followed by the secondary CO$_2$ elimination. There is less than 10% of CH$_3$ came from the primary CO$_2$ elimination followed by the secondary CH$_3$ elimination.

The corresponding photofragment translational energy distribution of the primary dissociation channel obtained from the image of m/z = 15 is illustrated in Figure 9. It shows a bimodal distribution. The slow one represents the dissociation from the state without exit barrier, and the fast one represents the dissociation from the repulsive excited state or a state with large exit barrier.

**B. Structures of MOBA conformers**

The structures and the relative energies of MOBA conformers from calculations are shown in Figure 10. The most stable 2-MOBA conformer, 2-MOBA-1r, has a structure such that OCH$_3$ functional group points away from COOH functional group, but the OH in COOH functional group points toward to the OCH$_3$ and forms intramolecular hydrogen bond. The formation of intramolecular hydrogen bond makes it more stable compared to the other conformers. The next stable conformer, 2-MOBA-1, has the structure that OCH$_3$ remains pointing away from COOH, but with the acidic OH pointing to the other direction. The energy difference between two conformers 2-MOBA-1 and 2-MOBA-1r is within 2 kcal/mol. For 3-MOBA and 4-MOBA, the OCH$_3$ and COOH functional groups are far away from each other, and the relative orientations of these two functional groups have smaller effects on energies. The energy differences between various conformers of 3-MOBA and 4-MOBA were found to be less than ~1 kcal/mol.

**C. Potential energy along the methoxy C–O bond**

We calculated the PES of the ground state and the singlet excited states along the O–CH$_3$ bond distance of methoxy group for various conformers of MOBA. Calculations also include PES of phenol and anisole for comparison. The results obtained from the CAS calculation are discussed below.

The TD-B3LYP method is also a frequently used and more convenient method for modeling low-lying excited states. However, the TD-B3LYP method, or TD-DFT method in general, is only reliable at shorter bond length due to the single-configurational formalism. At larger bond length, it may suffer from the problem of restricted electron configuration relaxation. The CAS calculation which is based on multi-configurational formalism can model the PES more consistently from short to long bond lengths. Thus, we present the more reliable CAS results below, and the TD-B3LYP results were included in the supplementary material for comparison.

While there are some notable differences on the energy levels, in most cases, the order of the energy states, the shapes of various energy curves, and the intersecting behaviors of the curves were similar below 2.0 A for the O–H bond and 2.5 A for the O–C bond. The results from TD-B3LYP are included in the supplementary material.

The PES of phenol and anisole are illustrated in Figure 11. It shows that the replacement of the H atom of...
FIG. 11. The potential energies of the ground state and singlet excited states along the O−CH3 bond distance (highlighted in red) in methoxy group for methoxybenzoic acid (MOBA) and anisole. The solid blue, solid red, open olive, and open wine symbols represent 1A′, 2A′, 1A″, and 2A″, respectively. The potential energies along the O−H bond of phenol are also shown for comparison.

hydroxyl group in phenol by CH3 does not change the properties of PES. The second excited state 1A″(πσ*) along the O−CH3 bond remains repulsive. It crosses the 2A′ (ππ*) state and the ground state at energy levels 125 and 85 kcal/mol, respectively. The characteristic of the repulsive excited state can be used to explain the large photofragment translational energy in the photodissociation of anisole.8, 9 The potential energies of MOBA conformers, as illustrated in Figure 11, shows that the second excited state 1A″ remains repulsive for all conformers. All the features of the PES are very similar to those of phenol and anisole. Since the vibrational temperature in the molecular beam is much lower than the room temperature (estimated to be less than 100 K), these conformers represent the structures of MOBA which exist in the molecular beam. Therefore, the excited state dynamics are expected to be similar to that of anisole, i.e., the population of the 2A′ state generated from absorption of UV photons can be transferred to the dark state 1A″ through a conical intersection, followed by the fast dissociation on the 1A″ state. At very large C−O bond distance, the 1A″ state crosses 1A′ state. The final product of heavy fragment, C6H4OCOOH, can be generated in the electronic excited state or ground state. This dissociation mechanism contributes to the fast component in the photodissociation translational energy distribution. On the other hand, since there is no exit barrier for the ground state, the slow component is likely from the dissociation on the electronic ground state after internal conversion from the excited state.

In previous study, we have demonstrated that excited state dynamics of 2-hydroxybenzoic acid (2-HBA) is completely different from that of phenol.13 In order to make direct comparison to 2-HBA, the 2-MOBA conformer with similar structures analogous to that of 2-HBA was further investigated by calculations. The structure of the most stable conformer of 2-HBA is shown in Figure 12. The aromatic ring, COOH and OH functional groups are all in the same plane. The stable 2-MOBA conformer with structures analogous to that of 2-HBA is 2-MOBA-3, as shown in Figure 12. In this structure, OCH3 (analogous to OH in HBA) points toward the COOH. However, the calculated stable structure of 2-MOBA-3 is not planar. The C1−C2−OCH3 and C2−C1−C=O dihedral angles are 45° and 20°, respectively, while in 2-HBA both of the corresponding dihedral angles are zero. The energy of 2-MOBA-3 conformer is 4.3 kcal/mol higher than the most stable 2-MOBA conformer. To explore the potential energy surfaces in vicinity of the minimum energy structures on the ground state of 2-MOBA-3, we calculated the potential energy curves as a function of both the O−CH3 bond distance and C−C−O−CH3 dihedral angle. The results showed that the 1A″ state is repulsive when both the C−C−O−CH3 and C−C−C=O dihedral angles are set to zero, as shown in Figure 12 of 2-MOBA-3-Cs. In this structure, O−CH3 and O−C−OH are all in the

FIG. 12. The potential energies of the ground state and singlet excited states along the O−CH3 bond distance (highlighted in red) in methoxy group for 2-methoxybenzoic acid at different dihedral angles. The dihedral angle C1−C2−O−CH3 is zero and 45° for 2-MOBA-3-Cs and 2-MOBA-3, respectively. The other dihedral angle C−C−C=O is zero and 20° for 2-MOBA-3-Cs and 2-MOBA-3, respectively. (The C1 and C2 are the carbon atoms on the aromatic ring that is bonded to the carboxyl group and methoxy group respectively.) The solid blue, solid red, open olive, and open wine represent 1A′, 2A′, 1A″, and 2A″, respectively. The potential energies along the O−H bond distance for the most stable 2-HBA conformer are also shown for comparison.
plane of aromatic ring. The structure is analogous to 2-HBA, but there is no intramolecular hydrogen bonding. As we rotate the O–CH₃ bond out of the plane, the point group symmetry changes from Cₛ to C₁. The original 1A″ state (now the 3A state) has an avoided-crossing with the original 2A′ state (now the 2A state) due to symmetry constraints. The out-of-plane rotation also keeps the ground state surface well separated from the original dark state at most rotational angles. The PES for these out-of-plane conformers are all very similar to that of 2-MOBA-3. The 1A and 2A states do not cross until the hydroxyl group rotates 180° and conformer 2-MOBA-3 becomes conformer 2-MOBA-2.

Comparison of 2-HBA and 2-MOBA-3Cs shows that the difference of excited state dynamics between 2-HBA and phenol is due to the strong interaction between the eliminating H and O atoms of the carboxyl functional group. The interaction is strong such that in the excited state the repulsive potential energy surface becomes an attractive potential near the ground state equilibrium geometry and the ground state energy is significantly reduced at large O–H bond distance. When the H atom of the hydroxyl functional group in 2-HBA is replaced by CH₃, the interaction between CH₃ and O atom of the carboxyl functional group is not as strong as the interaction before replacement. The eliminating CH₃ has little effects on the PES. As a result, the PES of 2-MOBA-3Cs is similar to that of anisole and the excited state dynamics does not change very much. We can conclude that intramolecular hydrogen bonding play a significant role in the change of excited state dynamics of phenol chromophores.

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23See supplementary material at http://dx.doi.org/10.1063/1.4767403 for potential energy calculations at TD B3LYP/6-311+G** level.