

Excited state photodissociation dynamics of 2-, 3-, 4-hydroxyacetophenone: Theoretical study

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ABSTRACT

Photodissociation of 2-, 3-, and 4-hydroxyacetophenone (2-, 3-, and 4-HAP) has been studied by analyzing excited-state potential energy surfaces (PES). For that, *ab initio* CASSCF(12,12)/6-31 + G(d,p) calculations of low-lying excited states have been performed. Molecular beam study of photodissociation of 2-, 3-, and 4-HAP under laser excitation at 193 nm revealed that there are three possible dissociation channels of HAP: separation of H atom, CH₃ and COCH₃ fragments. In 2-HAP isomer the H separation channel is quenched. In this study we explain the quenching mechanism of the H separation channel and suggest a new model of CH₃ and COCH₃ fragment elimination reactions. Calculations of the excited-state PES reveal that the most of H, CH₃ and COCH₃ fragments arise after relaxation into the second, optically “dark” ²A” state, while some of the reaction products result from the ¹A” state dissociation. Dissociation of 2-HAP through H separation in the ²A” state is deemed impossible, which explains the absence of deprotonated fragments in the 2-HAP mass spectrum. Breaking of intramolecular hydrogen bond in 2-HAP needs much more energy than the CH₃ detachment, which makes relaxation through the S₁ – S₀ conical intersection unfavorable.

1. Introduction

Photochemical processes in electronically excited aromatic heteroatomic molecules attract great attention due to their importance for understanding the mechanisms of absorption of ultraviolet radiation by biological systems. This class of substances has a high photostability. After the absorption of UV photon with wavelengths potentially dangerous for living systems, such compounds exhibit a very short lifetime of excited states (hundreds of femtoseconds) and weak fluorescence. Short lifetimes and the absence of fluorescence usually mean the presence of conical intersections (CI) between electronically excited and the ground (S₀) states, which provides radiationless transformation of electronic energy into the thermal (vibrational) excitations.

It was assumed [1–6] that the photostability of biomolecules is the important parameter for choosing the “building blocks” of biological tissues playing the key role in the evolution. By filling the insides of living cells, photostable molecules shield vital centers from damaging effects of ultraviolet radiation and prevent genetic mutations.

Finding conical intersections between electronic states in

biomolecules is an important problem of photochemistry. Since most of the biomolecules possess a complex structure and contain several functional groups, a typical way to study electronic properties of big molecules is to consider small elementary compounds having a simple structure, or containing a single functional group.

Some of the first works investigating electronic state structure and relaxation mechanisms of heteroatomic molecules were based on theoretical studies of photodissociation reactions of indole [5] and phenol [6]. It was found that the main dissociation channel in both cases is the detachment of hydrogen atom from NH and OH functional groups in the S₁ state through the predissociation mechanism.

After being excited to the optically bright electronic level corresponding to the bonding ¹ππ* orbital, molecules quickly relax to the anti-bonding ¹πσ* level through conical intersection arising due to increasing distances of N–H and O–H. Further increase in the distance leads either to the separation of the H-atom in the excited state, or the relaxation into the ground S₀ state through another CI.

Photodissociation of phenol molecule through deprotonation in an excited state has been also proved experimentally [3,7–10]. Since

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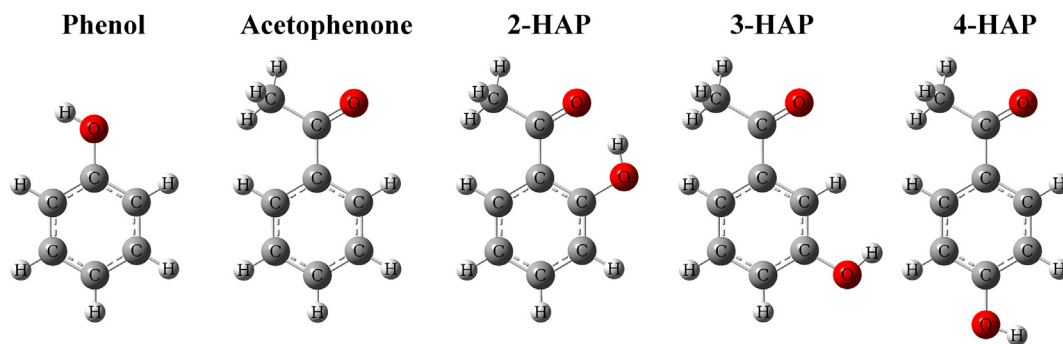


Fig. 1. Chemical structure of 2-, 3-, and 4-hydroxyacetophenone compounds (2-HAP, 3-HAP and 4-HAP). Structure of phenol and acetophenone molecules is provided for comparison.

phenol is a chromophore of amino acid tyrosine, and indole is the chromophore of the amino acid tryptophan, various substituted phenols [11–19] and indoles [20–22], as well as other amino acid chromophores, were also studied both experimentally and theoretically. It was found that H elimination reaction through the excited $^1\pi\sigma^*$ state plays an important role in the most of these species.

In particular, an interesting regularity has been revealed: probability of relaxation of molecules to the ground state increases with increasing molecular weight. In tryptophan, the large molecule, no dissociation products from the excited states were observed. It can indicate the existence of a low-lying CI between S_1 and S_0 electronic states, but whether this intersection occurs due to migration of the hydrogen atom, or by other mechanism, has not been clarified.

Experimental study of nitrogen-containing aromatic heteroatomic molecules – pyridine [23], pyrimidine [24], and triazine [25], which do not have H atoms bonded with nitrogen – has not detected any hydrogen elimination channels due to C–H bond breaking or after the H atom shift with formation of the NH group. Nevertheless, dissociation occurs from the ground electronic state through other channels. Theoretical calculations revealed that relaxation into the ground state occurs due to the ring opening and rotation of the end segments, which lead to intersection of S_1 and S_0 states. In this case, a metastable ring-opened biradical structure is formed, which can then either dissociate with fragmentation, or return to the initial S_0 closed ring configuration. This mechanism is clearly visible in the case of symmetric triazine $C_3N_3H_3$ molecule. Decay of closed-ring molecule should give a sharp velocity distribution of HCN molecules [25], but experiment [26] demonstrates a long tail of fragment speed data, which indicates, according to calculations [25], the dissociation from opened-ring structure.

Since most biomolecules have in their composition carboxyl (COOH) and acetyl (COCH₃) functional groups, it is very important to study conical intersections responsible for processes in these molecular fragments. During theoretical investigation of salicylic acid it was found that in the case of existence of intramolecular hydrogen bond between nearby OH and COOH groups, hydrogen atom can migrate from OH to the COOH group, forming energetically stable tautomer with HCOOH group. After turning by 90° with respect to HCOOH fragment, S_1 and S_0 electronic states intersect, providing radiationless relaxation of the excited salicylic acid molecule into the ground S_0 state [27]. This conical intersection point is energetically lower than the CI corresponding to the case of the increase of O–H distance at $^1\pi\sigma^*$ level, which should quench the hydrogen separation channel. Later this effect has been revealed experimentally [28]. In 2-hydroxybenzoic (salicylic) acid H separation was almost absent, while in 3- and 4-hydroxybenzoic acid isomers the deprotonation reaction was the major channel.

After substitution of the H atom in the OH group by the CH₃ group, the CH₃ fragment detachment in the excited state becomes the main dissociation channel for all three isomers of (2-, 3- and 4-) methoxybenzoic acid [29]. It means that the replacement of the hydrogen atom by CH₃ group either removes the conical intersection by the mechanism

described in [27], or makes this CI energetically higher than the CH₃ group detachment pathway.

2. Formulation of the problem

Experiments with photodissociation of 2-, 3-, and 4-hydroxyacetophenone (HAP) isomers [30] in molecular beam under 193 nm laser excitation revealed that these molecules demonstrate tendencies similar to isomers of salicylic acid. Photodissociation occurs mainly from the excited states, and mass-spectra of meta- and para-isomers have lines corresponding to H atom elimination, whereas ortho-isomer (2-HAP) does not exhibit this line.

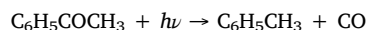
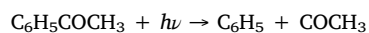
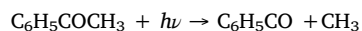
Details of dissociation reactions of HAP isomers in S_0 and T_1 states have been described recently [30]. According to the calculations, 2-HAP isomer in the ground electronic state decomposes by producing methane, while 3- and 4-HAP decompose through CH₃ elimination. In the T_1 state the only significant reaction channel for all isomers is related to CH₃ elimination. In the S_1 state the only predictable channel for all HAP isomers was due to the H atom separation without perceptible difference between the barrier heights for different isomers. Since the experimentally obtained mass spectrum had large differences from the calculated one, the questions of correct interpretation of the experimental results remained open.

In this paper the experimental molecular beam mass spectra of various isomers of HAP [30] is considered. For that, a detailed analysis of the electronic structure of HAP isomers is performed. The main task of this work is to search for alternative low-lying conical intersections between electronic states that determine electronic processes in the excited HAP molecules. We hope that the comparison of the barrier heights of main reaction channels will allow for a qualitative prediction of the yield of the final products.

2-, 3- and 4-HAP are the hydroxyl-substituted acetophenone moieties which can demonstrate properties of both phenol and acetophenone (Fig. 1). Investigations of photodissociation of phenol revealed [1,7–10] that the main dissociation channel there is H separation reaction occurring in the S_1 state.

A recent study of photodissociation induced by the laser excitation at 193 nm (148.1 kcal/mol) [31] revealed the formation of phenoxy radical in the second (B_2A^2) excited electronic state. This fact indicates that the reaction may proceed at a higher excited state than S_1 .

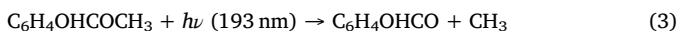
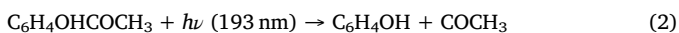
Experimental study of acetophenone photodissociation under excitation at 248 and 193 nm wavelengths [32] identified three possible decay channels:



The first two reaction channels are dominating, while the third one gives only a minimal contribution to the branching ratio of the reaction

products. A few years later, the photolysis of acetophenone by the method of ultrafast electron diffraction [33] revealed the same three main decay channels. The reactions occur simultaneously in several low-lying singlet and triplet electronic states: S_0 , S_1 , T_1 , and T_2 .

Study of the photodissociation reactions of HAP isomers in molecular beams [30] showed that the three most intense reaction channels for 3-HAP and 4-HAP correspond to the detachment of the H atom, CH_3 , and COCH_3 radicals, respectively:



Ortho-isomer (2-HAP) decomposes only through channels (2) and (3). Channel (1), corresponding to the H atom detachment, was completely absent in the list of possible reactions.

The main difference of 2-HAP isomer in comparison to others is that the OH group is adjacent to the COCH_3 group, and the H atom of the OH group is facing the oxygen of the COCH_3 group, creating an intramolecular hydrogen bond between the two groups. Since the formation of this intramolecular hydrogen bond can prevent the detachment of the hydrogen atom, in this work we will discuss in details the effect of this intramolecular bond on the photochemical properties of 2-HAP. Photodissociation reactions of other HAP isomers under the excitation by the UV radiation will also be considered.

3. Computational details

Ab initio calculations of the excited states of HAP isomers have been performed by MOLPRO-2012 [34] quantum chemical package using CASSCF method and 6-31 + G(d,p) basis set. For that, 12 electrons were distributed among 12 orbitals. In case of the C_s symmetry of the system, 6 electrons were distributed among 6 orbitals each corresponding to the irreducible representation. Molecular geometries were optimized for each electronic state.

Rate constants and branching ratios of products of chemical reactions have been obtained from statistical quasi-equilibrium RRKM theory [35–37]. For that it is assumed that vibrational energy of the molecule is uniformly distributed among all vibrational degrees of freedom. The rate constant of unimolecular reaction is given by the following equation:

$$k(E) = \frac{1}{h} \frac{W^\ddagger(E - E_0^\ddagger)}{\rho(E)}$$

where $W^\ddagger(E - E_0^\ddagger)$ and $\rho(E)$ denote the total number of states of the activated complex with activation energy E_0^\ddagger and the density of states of reactant with total internal energy E , respectively. Oscillator strengths indicating optical intensities of excited states were calculated by means

of TD-B3LYP/6-31 + G(d,p) method using Gaussian09 quantum chemical package [38].

4. Results

In the molecular beam experiment [30] strongly diluted molecular beam (i.e., in collisionless conditions) was irradiated by laser with photon energy below the ionization threshold (at the wavelength of 193 nm, or 148.1 kcal/mol). Absorption of photons induces electronic and vibrational excitations of the molecules, initiating photodissociation reactions terminated by reaction products. After that the molecular beam irradiation by the ionizing laser (at 118 nm, or 10.5 eV) causes separation to the reaction fragments. These fragments are analyzed as the final products in the mass-spectrometer. During this process, the masses of fragments, their velocity distributions and an approximate reaction sequence are estimated.

The ionization by a laser at a fixed wavelength is an essential drawback of this experimental scheme. Firstly, for some fragments, the ionization potential may be higher than the energy of the ionizing photons. Secondly, each fragment has its particular absorption coefficient at given wavelengths. Thirdly, many fragments after ionization undergo a secondary decay, which can substantially complicate the analysis of the mass spectrum. Therefore, for consideration of experimental results on molecular beams with laser ionization, it must be taken into account that the observed ratio of reaction products can vary significantly. Thus it makes sense to discuss only the presence of certain lines in the mass spectrum and the distribution of fragments in terms of velocities.

Here we will use the interpretation of the mass spectrum of HAP isomers, which has been proposed in [30]. According to the experimental observations, the main channel of photodissociation for 4-HAP is the reaction (1) – the detachment of the hydrogen atom. The other two reaction channels, (2) and (3), are due to the elimination of COCH_3 and CH_3 fragments. The translational energies of the fragments of reactions (2) and (3) show that at least some of the fragments are formed in the lowest excited electronic state.

4.1. Photodissociation of 4-HAP

Electronic state structure of *para*-isomer 4-HAP along the reaction coordinates (1), (2) and (3) is shown on Fig. 2. For calculations we assume that the system has C_s symmetry. Due to the fact that precision of the CASSCF method decreases strongly in calculations of high-lying electronic states, the accuracy of energy values of states $^3A'$ and $^2A''$ is lower than those for the lowest electronic states. So, the energy values of those states are shown in Fig. 2 only for estimation purposes of the relative positions.

The first two excited electronic levels are $^1A''$ and $^2A''$. However,

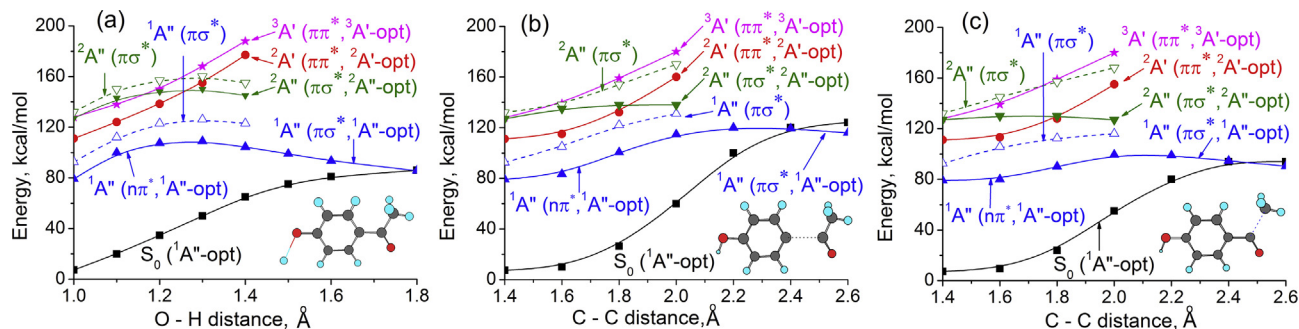


Fig. 2. Electronic state structure of 4-HAP and potential energy surfaces (PES) along the main dissociation reaction coordinates: (a) H atom separation from the OH group; (b) elimination of COCH_3 fragment; (c) elimination of CH_3 fragment. Ground S_0 and excited $^1A''$ state energies (solid line, filled squares and triangles) correspond to the $^1A''$ state optimization; dashed line and open triangles denote positions of $^1A''$ and $^2A''$ levels during ground state optimization; finally, energies of higher excited states $^2A''$, $^2A'$ and $^3A'$ (solid line, filled inverted triangles, circles and stars) are obtained by separate optimization of each corresponding state.

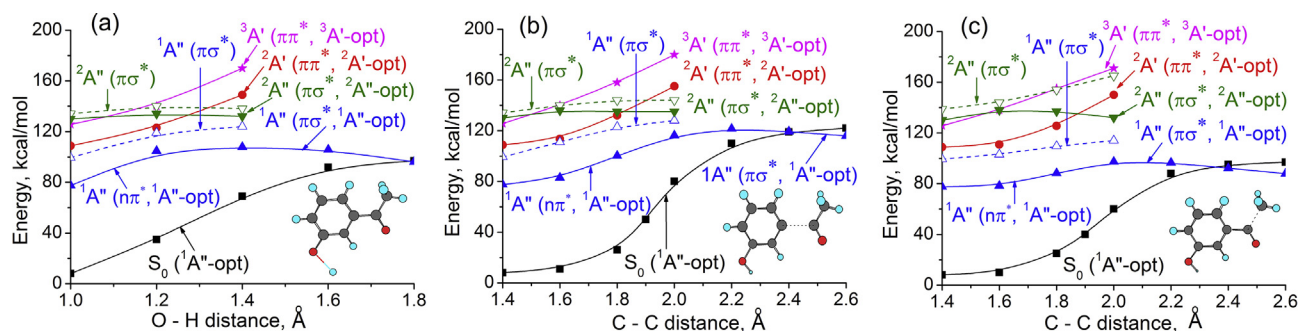


Fig. 3. Electronic state structure of 3-HAP and PES along the main dissociation reaction coordinates: (a) H atom separation from the OH group; (b) elimination of COCH₃ fragment; (c) elimination of CH₃ fragment. Ground S₀ and excited ¹A'' state energies (solid line, filled squares and triangles) correspond to the ¹A'' state optimization; dashed line and open triangles denote positions of ¹A'' and ²A'' levels during ground state optimization; finally, energies of higher excited states ²A'', ²A' and ³A' (solid line, filled inverted triangles, circles and stars) are obtained by separate optimization of each corresponding state.

levels ¹A'' and ²A'' are optically “dark”: the transition into these levels from the ground electronic state is unlikely, as indicated by the small oscillator strength of the respective transitions [30]. Optically “bright” are the transitions to levels ²A' and ³A', which are the local excitations of ππ* character.

The ³A' and ²A'' levels are the closest to the transition induced by the laser at 193 nm (148.1 kcal/mol). Calculations show the ³A' state to be several kcal/mol lower than the ²A'' state. However, with slight increase in O–H, C–CH₃, and C–COCH₃ bond lengths, excitation energy levels switch, and the ²A'' level becomes lower in energy than the ³A' one. It means that a conical intersection between these states, which enables nonadiabatic transition ³A' → ²A'', is expected.

The levels ²A'' and ¹A'' in the equilibrium geometry represent the excitation of the unpaired electron of the oxygen atom to one of the π-orbitals (nπ*–excitation with the charge transfer). When the lengths of the corresponding interatomic bonds increase, the states ²A'' and ¹A'' acquire the antibonding πσ* character, where the σ-orbital belongs to either the hydrogen atom, CH₃ or COCH₃ groups. Excitation to these orbitals results in elimination of the appropriate fragments.

When a photon is absorbed, transition into vibrationally excited electronic level ³A' occurs, and then the molecule subsequently relaxes to the ²A'' state, which easily decays through one of the channels (1), (2), or (3) listed above. The probability of decay via each channel is determined by the initial distribution of vibrational energy along the O–H, C–CH₃ and C–COCH₃ bonds.

The typical timescale of photodissociation reactions in excited states is in the order of tens of picoseconds, while the lifetimes of high-lying excited states are as small as tens and hundreds of femtoseconds. For example, formaldehyde and acetophenone exist in the S₁ state for approximately 25–50 picoseconds [33] before relaxation, whereas the lifetime of S₂ state of these compounds is less than 250 fs [39]. Probability of transition S₂ → S₁ is determined by the Franck-Condon overlap of the vibrational levels of the molecule. The closer the geometries of S₁ and S₂ levels, the shorter the transition time.

Electronic levels with the same orbital character of excitation (ππ* for ²A' and ³A', nπ* for ¹A'' and ²A'') have closer geometries than levels with different types of excitation. Therefore, the transition probabilities ³A' → ²A' and ²A'' → ¹A'' in the absence of conical intersections should be higher than the transition probabilities ³A' → ¹A'', ²A'' → ²A', and ²A' → ¹A''.

Moving along one of the reaction coordinates (Fig. 2) the molecule in the excited state ²A'' can relax to the state ¹A'' and either continue the decay in this state, or return to the equilibrium position and dissociate by one of the three possible channels: (1), (2) or (3) mentioned above.

The probability of decay via each channel is determined by the barrier height and the structure of the vibrational levels. For 4-HAP, the barrier height is 99 kcal/mol for the CH₃ separation, 109 kcal/mol for the deprotonation, and 119.5 kcal/mol for the COCH₃ group detachment. The RRKM calculations of the decay of 4-HAP in the ¹A'' state

give a probability of 99.5% for the CH₃ elimination channel, and 0.3% for the H separation channel.

Electronic state ²A' (ππ*) is involved in all three reaction channels and intersects neither with the state ¹A'' nor with the ground state S₀. Without intersection points, the processes of transition from one of them to another are slow. Therefore, the molecule being in the state ²A' either slowly moves to ¹A'', relaxes into the ground state S₀ as a result of the radiative transition, or goes over to a triplet state through the intersystem crossing.

The singlet-triplet transition is usually faster than the radiative relaxation. These transitions were observed, for example, in the photodissociation of acetophenone [33]. The most likely channel for the decay of 3-HAP and 4-HAP in the lowest triplet state T₁ is the detachment of the CH₃ fragment [30].

For large O–H and C–C bond distances (see Fig. 2), the ¹A'' level intersects with the ground electronic state S₀. Thus, the molecule can return from the intersection point to the equilibrium geometry in the S₀ state. This process competes with ²A' → S₀ relaxation. The experimental data [30] indicates that some of the 3-HAP and 4-HAP isomers decompose in the S₀ state, although this process is not dominant.

It is worthwhile to note that the simultaneous presence of photodissociation products in several electronic states is typical for heteroatomic molecules containing OH and NH functional groups [1–10]. The decay from the ground S₀ state assumes that the energy of the electronic excitation has been converted into the thermal energy of the oscillations, i. e., the molecule relaxes into the S₀ state without emitting a photon. In most cases, however, the specific mechanism of radiationless relaxation of molecules to the lowest electronic state remains unclear.

4.2. Photodissociation of 3-HAP

Potential energy surfaces of electronic states of the 3-HAP isomer along the reaction coordinates (1), (2), and (3) are shown in Fig. 3. The overall structure of electronic states of 3-HAP is similar to the case of 4-HAP. A small difference is the lower height of the CH₃ (97.5 kcal/mol) and H atom (107 kcal/mol) elimination barriers, whereas the height of COCH₃ detachment barrier is slightly higher (121.5 kcal/mol) compared to 4-HAP. The overall picture of the electronic transitions is the same for both isomers. The RRKM calculations of the 3-HAP decomposition from the ¹A'' state give 99.7% probability for CH₃ loss, and 0.3% for H atom loss channels.

4.3. Photodissociation of 2-HAP

The structure of the electronic states of the ortho-isomer 2-HAP, shown in Figs. 4 and 5, is qualitatively different from that of 3-HAP and 4-HAP. The principal difference between 2-HAP and other isomers is the presence of an intramolecular bond between the hydrogen atom of OH group and the oxygen of COCH₃ group. As a result, the direct

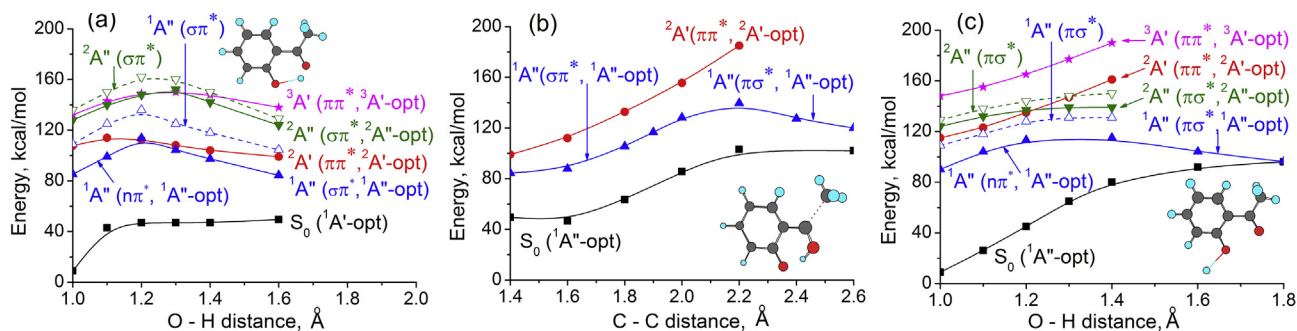


Fig. 4. Electronic state structure of 2-HAP and PES corresponding to the hydrogen atom migration: (a) H atom migration from the OH group to the oxygen atom of the COCH₃ group; (b) CH₃ elimination from the HCOCH₃ group after the H atom migration; (c) H atom elimination from the OH group after rotation by 180° around the C–O axis. Ground S₀ and excited ¹A' state energies (solid line, filled squares and triangles) correspond to the ¹A' state optimization; dashed line and open triangles denote positions of ¹A'' and ²A'' levels during ground state optimization; finally, energies of higher excited states ²A'', ²A' and ³A' (solid line, filled inverted triangles, circles and stars) are obtained by separate optimization of each corresponding state.

elimination of the hydrogen atom, as observed in the other two isomers of HAP, becomes impossible.

Fig. 4a shows a diagram of the electronic levels of 2-HAP when the O–H distance increases with respect to the equilibrium position. The mutual location of the electronic states ³A' and ²A'' is similar to the location of analogous states of 3-HAP and 4-HAP. As the distance O–H increases, these levels intersect, and nonadiabatic transition ³A' → ²A'' becomes possible.

Further motion of the H atom along the reaction coordinate in the ²A'' state does not stimulate detachment of hydrogen. On the contrary, it occupies energetically more favorable position near the oxygen atom of COCH₃ group resulting in the HCOOH tautomer formation of 2-HAP.

The electronic states ²A'' and ¹A'' of the 2-HAP tautomer are the excitations of σπ* type, which are positioned higher than states of ππ* type. Calculations show that the barrier of the H atom separation in the ²A'' state exceeds the energy of the photon of the actinic light (148.1 kcal/mol). The H atom separation in the opposite direction, after the rotation of the OH group by 180° around the C–O axis, is also not energetically favorable. In addition, the time needed for the rotation of the OH group by 180° is much higher than the ²A'' state lifetime. The transition to the lower ¹A'' level is most likely. After this transition, either CH₃ elimination from HCOCH₃ group (Fig. 4b) or the return of the hydrogen atom back to the oxygen of the OH group and the equilibrium decay through the channels (1)–(3) becomes possible.

CH₃ elimination channel of 2-HAP tautomer in the ¹A'' state has a barrier of 140 kcal/mol (Fig. 4b) and is energetically unfavorable. H atom detachment from this tautomer is possible only after the 180° rotation of the HCOCH₃ group around the C–O axis and overcoming the barrier of 115 kcal/mol (Fig. 4c). Elimination channels of CH₃ and COCH₃ groups (Fig. 5) have barriers of 106 and 123.7 kcal/mol, respectively. Thus, the only significant dissociation channel from the minimum of the tautomer in electronic state ¹A'' is due to the CH₃ elimination.

After ³A' → ²A'' transition, the direct dissociation of 2-HAP from the

²A'' electronic state is possible through (2) and (3) channels. Reaction mechanisms of these reactions are similar to the mechanisms of appropriate reactions in 3-HAP and 4-HAP isomers (Fig. 5). An exception is the H atom separation channel (1), which is closed for 2-HAP in electronic state ²A'', as was already mentioned above.

Due to the presence of intramolecular hydrogen bond in the 2-HAP isomer, electronic levels ²A' and ¹A'' are almost degenerate. ³A' → ²A' transition followed by relaxation of the molecule toward the energy minimum of the ²A' electronic state leads to intersection of ²A' and ¹A'' states that occurs without increasing the O–H and C–C bond lengths. Presence of CI near the equilibrium geometry of the ²A' state allows the molecule to relax easily to the ¹A'' electronic level followed by the CH₃ elimination described above.

Due to the similarity of the structures, it could be interesting to compare the photodissociation mechanisms of 2-HAP and salicylic acid, which contains the carboxylic COOH group instead of the acetyl CH₃CO group. In the salicylic acid the excitation to the lowest optically bright S₁ state is also followed by the H atom transfer from OH to COOH group resulting in the tautomer formation that finally leads to S₁ → S₀ radiationless relaxation through a conical intersection [27].

This comparison shows that 2-HAP and the salicylic acid have similar organization of electronic levels (Fig. 6). After migration of the hydrogen atom from OH to COCH₃ group, and rotation of the HCOCH₃ group around the C–C axis by an angle of about 90° with simultaneous distortion of the C–O–CH₃ angle, S₁ and S₀ states intersect. The limiting stage for this process is the tautomerization reaction through TS₁ barrier with 113.9 kcal/mol height. This process competes with H, CH₃, and COCH₃ fragments through TS₃, TS₂, and TS₄ barriers, as shown in Fig. 6.

In order to estimate the probability of the S₁ → S₀ transition, we performed RRKM calculations of the reaction rate constants through barriers TS₁, TS₂, TS₃, and TS₄ according to Fig. 6. Calculations revealed that only approximately 1% of the 2-HAP molecules can reach the conical intersection point corresponding to the S₁–S₀ transition,

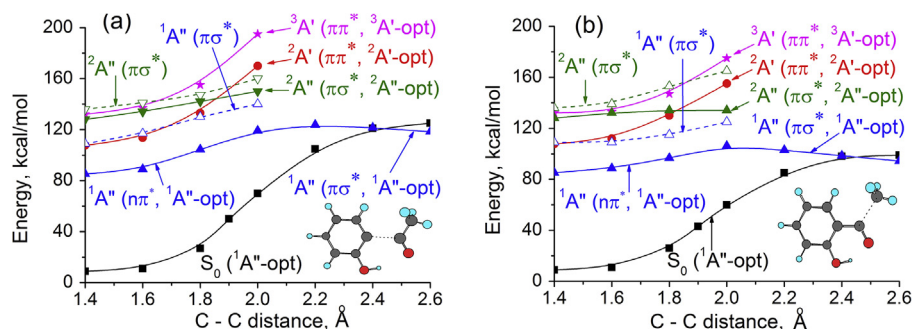


Fig. 5. Electronic state structure of 2-HAP and PES corresponding to the elimination of COCH₃ fragment (a) and of CH₃ fragment (b). Ground S₀ and excited ¹A' state energies (solid line, filled squares and triangles) correspond to the ¹A' state optimization; dashed line and open triangles denote positions of ¹A'' and ²A'' levels during ground state optimization; finally, energies of higher excited states ²A'', ²A' and ³A' (solid line, filled inverted triangles, circles and stars) are obtained by separate optimization of each corresponding state.

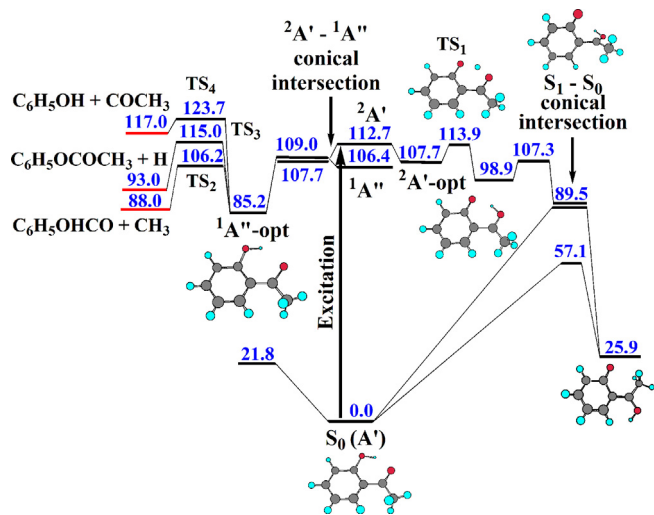


Fig. 6. Energy level diagram of the relaxation pathways of 2-HAP after the initial electronic excitation to the $2A'$ state.

whereas 98.5% and 0.5% will decompose in the excited state through CH_3 and H elimination channels, respectively. So, the $S_1 \rightarrow S_0$ relaxation through the conical intersection does not play any significant role in the excited state photodissociation dynamics of 2-HAP due to the presence of the faster CH_3 elimination channel. In molecular beam experiments [30] the dissociation products of 2-HAP, which can be produced by reactions in the ground state, have not been actually observed.

5. Discussion

Earlier investigation of photochemical properties of phenol and its derivatives concentrated mainly on the hydrogen atom separation from hydroxyl groups. This process is really important, since it provides one possible efficient mechanism of nonradiative conversion of excited electronic energy of biomolecules and molecular clusters into the heat energy. It may also play a key role in the generation of protonated ions in MALDI (Matrix Assisted Laser Desorption/Ionization) experiments. However, deprotonation reactions often have rather high barriers, and are therefore not energetically favorable.

Experimental and theoretical study of salicylic acid [27] revealed that molecules with intramolecular hydrogen bonds have the possibility to relax from an excited to the ground electronic state non-radiatively, through a low-lying conical intersection. Moreover, the process of reaching the CI point sometimes is energetically more favorable than the H separation reaction. Experimental study of photodissociation of 2-, 3-, and 4-HAP isomers [30] revealed that the presence of intramolecular hydrogen bond, similar to the case of salicylic acid, quenches the hydrogen elimination channel. However, the reaction products observed in the experiment differed from what should have been observed upon decay from the ground electronic state S_0 .

In this study we performed detailed analysis of electronic state structure of 2-, 3-, and 4-HAP isomers. We investigated not only H atom elimination channel and $S_1 \rightarrow S_0$ transition through intramolecular tautomerization process, but also took into account CH_3 and COCH_3 elimination channels in the excited electronic states and considered the structural organization of higher electronic states. Our analysis established that in all three studied HAP isomers the most favorable pathway is the CH_3 separation reaction in the excited S_1 state. Also in the 2-HAP isomer, the CH_3 separation channel remains dominant, and does not allow the molecule to relax into the ground electronic state through $S_1 \rightarrow S_0$ conical intersection. This explains the absence of the ground state dissociation products in the mass spectrum of 2-HAP isomer [30].

However, concurrently with the CH_3 detachment reaction, COCH_3

elimination reaction was also observed. In addition, mass spectra of 3- and 4-HAP isomers also have H atom elimination lines, which cannot be explained only by reactions in the first excited state. For the explanation, the higher electronic energy levels have also been taken into consideration.

It turned out that the structure of levels $3A'$ and $2A''$ is analogous to the structure of levels $2A'$ and $1A''$. $3A'$ electronic state near the equilibrium configuration is positioned close to the energy of the actinic photon (148.1 kcal/mol). The absorption of photons with this energy will likely initiate the excitation to the $3A'$ level.

The $3A'$ electronic state does not have low-lying dissociation channels; however, it intersects with $2A''$ term through a small increase in O–H, C– CH_3 , and C– COCH_3 bond lengths. Since the energy of the electronic level $2A''$ is lower than the energy of the $3A'$ level, excitation of one of the vibrational modes of O–H, C– CH_3 , or C– COCH_3 bonds can initiate $3A' \rightarrow 2A''$ transition followed by the decay along this vibrational mode. In view of the short lifetime of highly excited electronic states, the relaxation process $2A'' \rightarrow 1A''$ can compete with the dissociation process in the $2A''$ electronic state. After the relaxation into the $1A''$ state, the motion along the appropriate reaction coordinate likely will be continued, but the reaction products probably will have higher translational energy.

In molecular beam experiments with HAP [30], a very wide distribution of reaction products by velocities was observed. Apparently, H atoms and COCH_3 fragments are the result of dissociation in $2A''$ electronic state. In 2-HAP isomer the H atom separation in the $2A''$ state is impossible, which explains why this channel was not observed in the experiment.

6. Conclusions

Investigation of photodissociation processes occurring in hydroxyacetophenone (HAP) after the absorption of UV photon revealed the dependence of the further reactions on the presence of intramolecular hydrogen bond. The 2-HAP isomer containing this bond decays from the excited states through CH_3 and COCH_3 fragment elimination channels. 3- and 4-HAP isomers dissociate through H, CH_3 , and COCH_3 detachment channels. It is shown that the formation of these fragments happens due to the rapid decay of optically “dark” $2A''$ electronic state. Excited state deprotonation reaction in 2-HAP isomer is impossible, which explains the absence of the corresponding fragment in the mass spectrum of 2-HAP.

Some molecules relax to the first excited level $1A''$, which results in a wide distribution of reaction fragments by velocities. The most probable decay channel for all HAP isomers in the $1A''$ state is the CH_3 group elimination. The relaxation of 2-HAP isomer to the ground electronic state through the conical intersection between S_1 and S_0 states is energetically unfavorable, which is confirmed by the absence of 2-HAP dissociation products that can be produced by reactions in the S_0 state [30].

Approaches applied in this work for the study of electronically excited substituted phenols form a basis for the future study of other analogous compounds containing functional groups COH, COOH, COCH_3 , NH_2 , and others.

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