

## Computational Study of 3-Aminophenol·(CO<sub>2</sub>)<sub>1</sub> Cluster: CO<sub>2</sub> Capture Ability of 3-Aminophenol

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The structure of 3-aminophenol·(CO<sub>2</sub>)<sub>1</sub> cluster was computationally studied both in the ground and the lowest singlet excited electronic states. The ground state structure and binding energy of the cluster was investigated using the second-order Møller-Plesset perturbation theory (MP2) at the complete basis set (CBS) limit. The excited state geometry of the cluster was obtained at the second-order approximate coupled cluster (CC2) level with cc-pVDZ basis set, and the S<sub>0</sub>-S<sub>1</sub> absorption spectrum was simulated by calculating Franck-Condon overlap integral. The ground state geometry of the global minimum with a very high binding energy of 4.3 kcal/mol was found for the cluster, due to the interaction between amino group and CO<sub>2</sub> in addition to the strong π-π interaction between the aromatic ring and CO<sub>2</sub>. The excited state geometry shows a very big shift in the position of CO<sub>2</sub> compared to the ground state geometry, which results in low intensity and broad envelope in the Franck-Condon simulation.

**Key Words:** Aminophenol, CO<sub>2</sub> Capture, Complete basis set limit

### Introduction

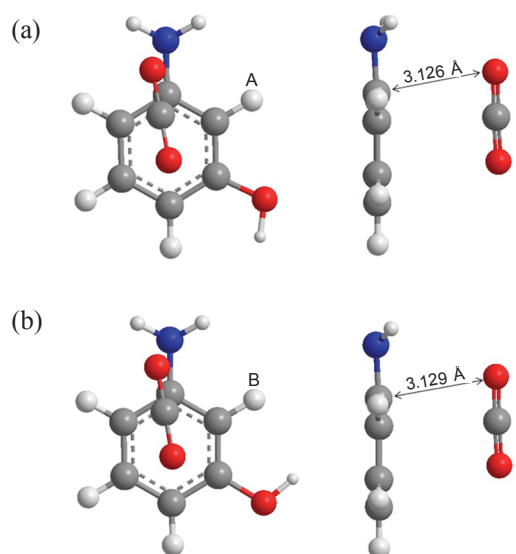
Removing or capturing CO<sub>2</sub> is becoming more and more important as CO<sub>2</sub> is considered to be the major green-house gas responsible for the global warming. As an efficient CO<sub>2</sub>-capturing material, monoethanolamine (MEA) has been studied by many groups. The solubility of CO<sub>2</sub> in a 30 mass % MEA solution is very high when measured at temperatures between 0 and 150 °C and at partial pressures of CO<sub>2</sub> ranging from 0.001 to 20,000 kPa.<sup>1</sup> The reaction between MEA and CO<sub>2</sub> in aqueous solution and gas phase was investigated.<sup>2</sup> The CO<sub>2</sub> capture ability of benzene is also expected to be good based on *ab initio*<sup>3,4</sup> and DFT<sup>4</sup> calculations. In this paper, the CO<sub>2</sub> capture ability of 3-aminophenol (3AP) was investigated by calculating the binding energy of 3AP and CO<sub>2</sub> using MP2 method at CBS limit. 3AP was chosen because it is an inexpensive and stable aromatic molecule with both hydroxyl and amino groups, whose relative positions are the same as in MEA. As it resembles both of the above mentioned CO<sub>2</sub>-capturing molecules, it might show an enhanced CO<sub>2</sub>-capturing ability than either of them. The structure, molecular vibration, and isomerization barrier of 3-aminophenol have been investigated using infrared and Raman spectra, *ab initio* calculations, and force field.<sup>8</sup> However, to the best of our knowledge, the binding energy of 3AP and CO<sub>2</sub> has never been studied before. The CO<sub>2</sub> capture ability of methane was also investigated for comparison of the accuracy of the current computation with previous ones at high level. As the binding energy of a molecular complex can be computed quite reliably by extrapolating to the complete basis set (CBS) limit,<sup>9,10</sup> the binding energies of the clusters were calculated at the CBS limit. The first excited state geometry of 3AP·(CO<sub>2</sub>)<sub>1</sub> cluster was determined using second-order approximate coupled cluster (CC2) method with cc-pVDZ basis set. The S<sub>0</sub>-S<sub>1</sub> absorption spectrum was simulated by calculating Franck-Condon overlap.

### Computational Method

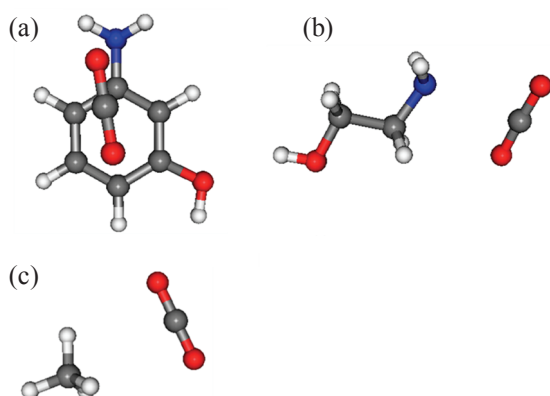
The optimized geometries of 3AP·(CO<sub>2</sub>)<sub>1</sub>, methane·(CO<sub>2</sub>)<sub>1</sub>, and MEA·(CO<sub>2</sub>)<sub>1</sub> clusters were determined using MP2 method in combination with aug-cc-pVTZ basis set. In order to extrapolate to the CBS limit, additional single point calculations were performed using MP2/aug-cc-pVDZ at these optimized geometries. Relative energies of two conformers of 3AP·(CO<sub>2</sub>)<sub>1</sub> cluster were determined at CBS limit using the extrapolation method described in the reference 10. The binding energies using the counterpoise correction<sup>12</sup> of these clusters were also obtained at CBS limit. The excited state geometry of 3AP·(CO<sub>2</sub>)<sub>1</sub> cluster was obtained at CC2<sup>13-15</sup> level with cc-pVDZ basis set, and the S<sub>0</sub>-S<sub>1</sub> absorption spectrum was simulated by calculating Franck-Condon overlap integral using Molpro.<sup>19,20</sup> The binding energy calculations were performed with the Gaussian 03 program package<sup>11</sup> at Korea Institute of Science and Technology Information (KISTI) and the excited state calculation was performed with the Turbomole 6.1 program package<sup>18</sup> on a PC.

### Results and Discussion

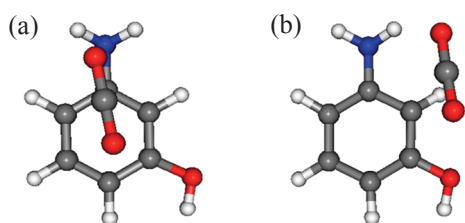
Two conformers of 3AP·(CO<sub>2</sub>)<sub>1</sub> cluster, *cis* and *trans*, are represented in Figure 1, of which the *trans* conformer is the most stable one. The energy of the *cis* conformer relative to *trans* is represented in Table 1, where we find that the *trans* structure is more stable than the *cis* structure at all basis sets. A qualitative explanation for the stability of the *trans* conformer is as follows. The electron density on the hydrogen labeled as A between NH<sub>2</sub> and OH is attracted by OH group in the *trans* structure, thus the repulsion induced by NH<sub>2</sub> is reduced. On the other hand, the electron density on the hydrogen labeled as B is less attracted by OH group in the *cis* structure thus the repulsion induced by NH<sub>2</sub> is strong. Because of this instability, the *cis* structure becomes less stable than the *trans* structure. We can



**Figure 1.** The optimized geometries of (a) *trans* and (b) *cis* 3AP·( $\text{CO}_2$ )<sub>1</sub> using MP2 with aug-cc-pVTZ basis set.



**Figure 2.** Optimized structures of (a) 3AP·( $\text{CO}_2$ )<sub>1</sub>, (b) MEA·( $\text{CO}_2$ )<sub>1</sub>, and (c) methane·( $\text{CO}_2$ )<sub>1</sub> clusters using MP2 with aug-cc-pVTZ basis set.



**Figure 3.** Optimized (a) ground and (b) first excited state geometries at CC2/cc-pVDZ level.

confirm this fact using Mulliken atomic charges analysis, which shows that the charge on hydrogen A is 0.409 in *trans* structure and that on B is 0.328 in *cis* structure. The small relative energy difference between *trans* and *cis* structures suggests that both conformers are present at ambient conditions; *cis/trans* ratio being 0.382 at 300 K. However, as the OH group does not significantly participate in the binding between 3AP and  $\text{CO}_2$ , the binding energy is assumed to be nearly the same in the two conformers. Thus only the *trans* structure, which is the global

**Table 1.** Relative energies of the *cis* structure with respect to the *trans* structure of 3AP·( $\text{CO}_2$ )<sub>1</sub> using MP2 method in combination with each basis sets

	aug-cc-pVDZ	aug-cc-pVTZ	CBS
Relative energies (kcal/mol)	0.588	0.577	0.571

**Table 2.** Binding energies of the clusters using MP2 method in combination with each basis set

	Binding energies (kcal/mol)		
	aug-cc-pVDZ	aug-cc-pVTZ	CBS
$\text{CH}_4\text{-CO}_2$	0.636	0.870	1.030
3AP- $\text{CO}_2$	3.402	3.932	4.332
MEA- $\text{CO}_2$	2.881	3.259	3.538

**Table 3.** Binding energy of 3AP·( $\text{CO}_2$ )<sub>1</sub> cluster compared with benzene·( $\text{CO}_2$ )<sub>1</sub> cluster.

	Binding energies (kcal/mol)		
benzene- $\text{CO}_2$	1.3 <sup>a</sup>	0.4 <sup>b</sup>	1.1 <sup>c</sup>
3AP- $\text{CO}_2$		4.332	

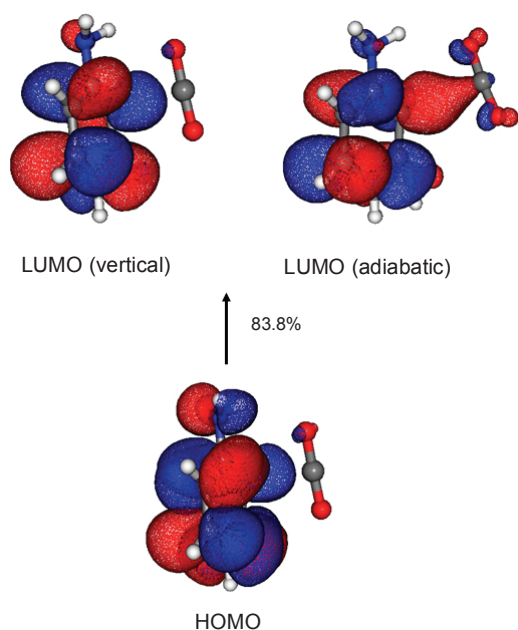
<sup>a</sup>Ref. 4; <sup>b</sup>Ref. 4; <sup>c</sup>Ref. 3.

minimum, is considered in the calculation of binding energy and  $S_0$ - $S_1$  absorption spectrum.

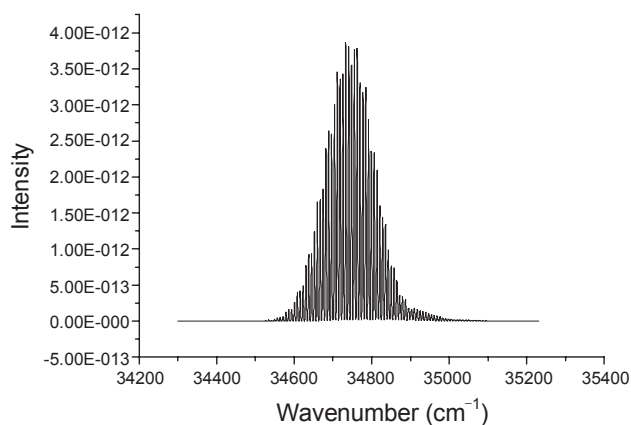
The global minimum structures of 3AP·( $\text{CO}_2$ )<sub>1</sub>, methane·( $\text{CO}_2$ )<sub>1</sub>, and MEA·( $\text{CO}_2$ )<sub>1</sub> clusters are represented in Figure 2. In Table 2, the binding energies of the clusters without geometry correction are presented. Because of the weak binding energies of these clusters, the geometries are not changed significantly between the cluster and the monomers. Since the binding energy of methane·( $\text{CO}_2$ )<sub>1</sub> cluster is 0.88 kcal/mol using MP2 with aug-cc-pVTZ basis set with geometry correction included, it is not a bad approximation to ignore the geometry correction. Because the binding energy of methane·( $\text{CO}_2$ )<sub>1</sub> cluster at the CBS limit has good agreement with 0.93 kcal/mol at MCCM-UT-CCSD level and 1.12 kcal/mol at MCCM-CO-CCSD(T) level in ref. 16, we can confirm the accuracy at this level.

The binding energy of 3AP·( $\text{CO}_2$ )<sub>1</sub> cluster is consistently higher than that of MEA·( $\text{CO}_2$ )<sub>1</sub> cluster in Table 2 at every basis set used. Thus we can expect that 3AP catches  $\text{CO}_2$  more strongly than MEA, which can be ascribed to the strong  $\pi$ - $\pi$  interaction of 3AP·( $\text{CO}_2$ )<sub>1</sub> cluster between the aromatic ring and  $\text{CO}_2$ . In Table 3, the binding energy of 3AP·( $\text{CO}_2$ )<sub>1</sub> cluster is compared with that of benzene·( $\text{CO}_2$ )<sub>1</sub> cluster at several levels of theory. 3AP has higher affinity to  $\text{CO}_2$  than benzene. We can deduce the existence of another interaction than the  $\pi$ - $\pi$  interaction between the aromatic ring and  $\text{CO}_2$ . Because of asymmetric binding between the aromatic ring and  $\text{CO}_2$  to amino group, we can assume the interaction between the amino group of 3AP and  $\text{CO}_2$ .

The first excited state geometry of 3AP·( $\text{CO}_2$ )<sub>1</sub> cluster was determined using CC2 method with cc-pVDZ basis set and shown in Figure 3. In Figure 3, the excited state shows an excessive shift in the position of  $\text{CO}_2$  compared to the ground



**Figure 4.** Orbitals involved in the  $S_0$ - $S_1$  transition of  $3AP \cdot (CO_2)_1$  cluster.



**Figure 5.** Simulated  $S_0$ - $S_1$  spectrum of  $3AP \cdot (CO_2)_1$  cluster.

state. As shown in Figure 4, HOMO-LUMO transition takes up 83.8% of the transition probability, and the transition type is  $\pi\pi^*$ . At the optimized geometry of the first excited state, an electronic cloud of LUMO is driven to the carbon atom that lies between -OH and -NH<sub>2</sub> in 3AP. When an electron is promoted from HOMO to LUMO, a stronger bond is formed between 3AP and CO<sub>2</sub>. Therefore CO<sub>2</sub> is excessively shifted to this electron rich position. Because of this excessive shift in the position of CO<sub>2</sub>, together with the low-frequency intermolecular vibrational mode between the aromatic ring and CO<sub>2</sub>, we can predict a weak and broad absorption envelope in the transition between the two states. They are shown in the Franck-

Condon simulated spectrum of Figure 5 clearly. The 0-0 band of  $3AP \cdot (CO_2)_1$  cluster was calculated to be 33684 cm<sup>-1</sup> although it is not found in Figure 5 because of very weak intensity. The preliminary experimental  $S_0$ - $S_1$  spectrum in our group didn't show any resolvable REMPI peaks of  $3AP \cdot (CO_2)_1$  cluster, which agrees quite well with the current computational study.

## Conclusion

The binding energy of  $3AP \cdot (CO_2)_1$  cluster computed using MP2 method at CBS limit was found to be very high, because of the strong  $\pi$ - $\pi$  interaction between the aromatic ring and CO<sub>2</sub> and another interaction between the amino group and CO<sub>2</sub>. The first excited state geometry shifted from ground state was also determined using CC2 method with cc-pVDZ basis set. Because of the huge geometry change upon electronic excitation, the calculated  $S_0$ - $S_1$  spectrum shows very weak broad absorption that has a good agreement with preliminary experimental  $S_0$ - $S_1$  spectrum in our group.

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