# Ab Initio Calculations on $CO_2$ Binding to Carbonyl Groups

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Ab initio molecular orbital calculations were performed at the SCF and MP2 levels, using a 6-31G basis set, for complexes of $CO_2$ with carbonyl compounds. The specific interaction between $CO_2$ and the carbonyl oxygen can be described as a Lewis acid−base reaction. Two different geometries, one having $C_{2v}$ symmetry and the other having $C_s$ symmetry, were studied. The $C_s$ symmetry was found to yield stronger binding of the $CO_2$ complexes. The degeneracy of the $\nu_2$ bending mode in free $CO_2$ was lifted when the $CO_2$ was bound. The calculated $\nu_2$ splittings at the SCF level, using a 6-31G basis set, were comparable to literature values determined by IR spectroscopy of $CO_2$-impregnated polymers. When steric hindrance was present, the binding energy of $CO_2$ to carbonyls was reduced, resulting in lower $\nu_2$ splittings. The interaction energy between benzene and $CO_2$ was determined to be much lower than that associated with a carbonyl oxygen and $CO_2$. The preference of $CO_2$ for the carbonyl group over the benzene ring, along with the role that steric hindrance plays, allows an understanding of the specific interactions of $CO_2$ with polymers.

## Introduction

Gas permeability of polymers is not well understood at the molecular level but may partly depend on the propensity of gas molecules to weakly bind to certain sites along the polymer chain and occupy void spaces in amorphous regions. This would determine the solubility of the gas in the polymer.[1] It has been shown through the use of IR spectroscopy[2] that polymers possessing electron-donating functional groups display specific interactions with carbon dioxide. These interactions are most probably of Lewis acid−base nature.[2] There exists other spectroscopic evidence[2−9] and ab initio calculations[10−12] that show carbon dioxide acts as a Lewis acid in the presence of Bronsted and Lewis bases such as water, amines, amides, and basic polymers. Eckert et al.[13] have reported equilibrium constants for the interactions of $CO_2$ with three Lewis bases: triethylamine, pyridine, and tributyl phosphate.

Poly(methyl methacrylate) (PMMA) is an example of a basic polymer containing a carbonyl oxygen. The $CO_2$ interacts with the carbonyl oxygen, possibly explaining the unusual swelling of PMMA[14,15] by high-pressure $CO_2$. It has been shown[16−18] that the antisymmetric stretching mode of the $CO_2$ does not provide evidence for specific interactions between $CO_2$ and PMMA. Eckert, Liotta, et al.[2] have shown experimentally that the $\nu_2$ degenerate bending mode of $CO_2$ provides evidence of specific interactions between $CO_2$ and PMMA; they concluded that a Lewis acid−base interaction of $CO_2$ with the carbonyl groups of various polymers would lift the degeneracy of the $\nu_2$ bending mode of free $CO_2$. The $D_{\infty h}$ symmetry in free $CO_2$ no longer exists for bound $CO_2$ and a $C_{2v}$ or $C_s$ symmetry $CO_2$−carbonyl complex may result as shown in Figures 1 and 2. The out-of-plane mode (Figure 3) occurs at a higher frequency than the in-plane mode (Figure 4). Eckert, Liotta, et al.[2] were unable to deduce the exact geometry of the complex from the spectroscopic evidence.

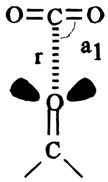

**Figure 1.** $CO_2$ complex having $C_{2v}$ symmetry. The geometrical parameters r and $a_1$ are indicated where $a_1$ is the $O_{carbonyl}$-C−O angle.

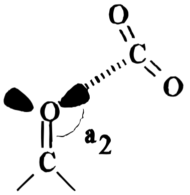

**Figure 2.** $CO_2$ complex having $C_s$ symmetry. The geometrical parameter $a_2$ is indicated. The angle $a_2$ is the $C_{carbonyl}$−$O_{carbonyl}$−C angle.

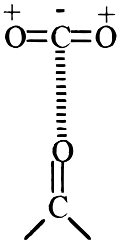

**Figure 3.** Out-of-plane bending for bound $CO_2$ is the higher frequency mode.

The current ab initio calculations investigate the $\nu_2$ splitting of the $CO_2$ bending mode and the possible configurations shown in Figures 1 and 2. Five simple carbonyl-containing compounds were used as models in the current work: formaldehyde, acetic acid, acetaldehyde, acetone, and methyl acetate. In addition, ethyl benzoate and benzoic acid have been used as model compounds to mimic the possible interactions of $CO_2$ with poly(ethylene terephthalate) (PET).

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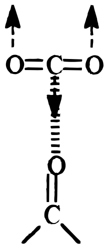

**Figure 4.** In-plane bending mode of bound $CO_2$ is the lower frequency mode.

**TABLE 1: Frequency Values for the Degenerate Bending Mode of $CO_2$ at Different Levels of Theory Using Several Basis Sets**

| level | $\nu_2$(cm$^{-1}$) | % difference |
|---|---|---|
| literature[2] | 667.0 | |
| SCF/6-31G | 656.6 | −1.6 |
| SCF/6-31G* | 745.9 | 11.8 |
| SCF/6-31+G | 596.4 | −10.6 |
| SCF/6-31+G* | 749.6 | 12.4 |
| SCF/6-311G | 648.6 | −2.8 |
| SCF/D95 | 716.5 | 7.4 |
| SCF/D95+ | 675.1 | 1.2 |
| MP2/6-31G | 520.6 | −21.9 |
| MP2/6-31G* | 636.1 | −4.6 |
| MP2/D95* | 653.4 | −2.0 |
| MP2/D95+* | 651.6 | −2.3 |

## Computational Methods

Complete geometry optimizations for $CO_2$−carbonyl complexes were performed using ab initio molecular orbital theory. Calculations were performed at the SCF and MP2 levels of theory. We have employed STO-3G and 6-31G basis sets on all $CO_2$ complexes assuming $C_{2v}$ and $C_s$ symmetry according to Figures 1 and 2. The $CO_2$ axis was kept coplanar with the carbonyl group as indicated in the figures. Frequency calculations were performed on all complexes using the 6-31G basis set at the SCF and MP2 levels. All binding energies were determined by taking the difference between the optimized energies of separate $CO_2$ plus model carbonyl and the optimized energies of the corresponding complex. Complete geometry optimizations and frequency calculations were performed on free $CO_2$ at the SCF and MP2 levels of theory using several different basis sets listed in Table 1. The GAUSSIAN 92 system of programs was used for all calculations.[19]

## Results and Discussion

Table 1 shows the $\nu_2$ bending mode of free $CO_2$ calculated at different levels of theory with several basis sets. It can be seen that the SCF/6-31G calculations provided good results for the $\nu_2$ mode of free $CO_2$ in comparison to the literature value. Block et al.[20] performed ab initio calculations on free $CO_2$ at the MP2/D95** level and obtained a value of 655.7 cm$^{-1}$ for the $\nu_2$ bending mode, slightly lower than the SCF/6-31G value obtained in this work. As a consequence of the results obtained in Table 1, the 6-31G basis set was used in subsequent calculations on the model compounds and their respective complexes with carbon dioxide.

Geometrical parameters defined in Figures 1 and 2 were determined at the SCF/6-31G level as given in Table 2. In all cases it can be seen that the $CO_2$ molecule is slightly bent when bound. This indicates a transfer of electron density to the carbon of the $CO_2$, acting as a Lewis acid. Mullikan population analyses confirm this transfer of charge (0.0041−0.0049) between the model compound and $CO_2$. Binding energies, $\nu_2$ frequencies, and splittings at the MP2 level are given in Table 3. Both the SCF and MP2 levels of theory indicate that the $C_s$ geometry is the lower energy configuration. The stronger binding in $C_s$ symmetry resulted in a greater splitting of the $\nu_2$ bending mode. One might think that because of steric hindrance the $CO_2$ axis would be 90° out of the plane giving the $CO_2$ complex $C_1$ symmetry. Jamroz et al.[21] investigated this possible mode of binding to some carbonyl compounds and found that the $C_1$ and $C_s$ symmetries resulted in similar binding energies at the SCF/3-21G* level of theory. Based on these results and $C_1$ calculations performed on formaldehyde, the $C_1$ configuration was not investigated further. At the SCF/3-21G* level, the $\nu_2$ bending mode splittings were found[12] to be between 8.2 and 13.6 cm$^{-1}$, too high in comparison to experiment. The splittings calculated at the SCF/6-31G level (Table 2) were comparable to the experimental splittings[2] obtained on carbonyl-containing polymers such as PMMA impregnated with $CO_2$ (Table 4). The MP2 results obtained in Table 3 also show comparable splittings of the $\nu_2$ mode; however, the absolute values of the frequencies are too low. The splittings calculated for $C_s$ symmetry are closer to experiment than the splittings calculated for $C_{2v}$ symmetry. This provides evidence for the $C_s$ symmetry shown in Figure 2 as the favored geometry.

Previous ab initio calculations[21] on $CO_2$ binding to model compounds indicate that steric repulsion can lead to weaker complexes. This can also be seen in our work with methyl acetate. Assuming $C_s$ symmetry, attack from the ester side (Figure 5) resulted in a lower energy than attack from the methyl side (Figure 5), as seen in Tables 2 and 3. The angle, $a_2$, as shown in Figure 2 is affected to a greater extent (Table 2) for an ester-side attack at the lone pairs on the carbonyl oxygen due to the larger steric hindrance associated with this group. The lower binding due to the steric repulsion of the larger substituent resulted in a lower splitting of the $\nu_2$ bending mode as seen in Table 2.

The experimental results[2] shown in Table 4 include only one interactive site for the $CO_2$: namely, the carbonyl oxygen. Poly(ethylene terephthalate) (PET) has two possible binding sites along the polymer backbone: the phenyl ring and the carbonyl oxygen. To test the possible role of binding at the phenyl ring, calculations were performed on complexes of benzene and carbon dioxide. Previous CNDO/2 calculations[13] on a benzene−$CO_2$ complex indicated a minimum energy geometry (Figure 6) where the primary axis of the $CO_2$ molecule was lined up directly above a long $C_2$ axis of the benzene ring. SCF/6-31G calculations in our own work confirmed this geometry as being the minimum energy configuration of the benzene−$CO_2$ complex.

According to Nandel and Jain[21] (and verified by the current work) the electron density values on individual atoms at the optimum geometry of the benzene−$CO_2$ complex are changed very little. There is almost no charge transfer from the benzene to the $CO_2$. There is a small reorganization of electronic charges on the atoms, indicating that dipoles are induced in benzene by the field of the quadrupole moment of the $CO_2$ molecule.[2,21] The resulting binding energy at the SCF/6-31G level was very small, 1.1 kcal/mol. This also resulted in a low $\nu_2$ splitting of 1.3 cm$^{-1}$.

Experimentally,[2] the presence of several basic sites in PET made assignment of the observed splitting in the bending mode of $CO_2$ complicated. To better understand possible PET interactions with $CO_2$, benzoic acid and ethyl benzoate were used as model compounds. Interaction with the phenyl ring showed minimal binding at the SCF/6-31G level. Bending

**TABLE 2: Geometrical Parameters (r, $a_1$, $a_2$), Binding Energies (BE), Bending Frequencies ($\nu_2$), and Splittings ($\Delta\nu_2$) for $CO_2$ Complexes with Model Carbonyl Compounds Using a 6-31G Basis Set at the SCF Level**[a]

| compound | symmetry | r | $a_1$ | $a_2$ | BE | $\nu_2$ splitting | | $\Delta\nu_2$ |
|---|---|---|---|---|---|---|---|---|
| acetone | $C_{2v}$ | 2.774 | 91.46 | 180.00 | 3.819 | 664.3 | 658.6 | 5.7 |
| | $C_s$ | 2.745 | 91.47 | 132.82 | 4.376 | 664.0 | 656.2 | 7.8 |
| acetaldehyde | $C_{2v}$ | 2.806 | 91.40 | 180.00 | 3.445 | 663.8 | 658.8 | 5.0 |
| | $C_s$ | 2.760 | 91.34 | 130.77 | 4.996 | 663.4 | 657.2 | 6.2 |
| formaldehyde | $C_{2v}$ | 2.841 | 91.36 | 180.00 | 3.062 | 663.2 | 658.8 | 4.4 |
| | $C_s$ | 2.763 | 91.38 | 120.38 | 3.879 | 663.1 | 655.6 | 7.5 |
| acetic acid | $C_{2v}$ | 2.771 | 91.41 | 180.00 | 3.773 | 663.9 | 659.1 | 4.8 |
| | $C_s$ | 2.733 | 91.40 | 130.40 | 5.248 | 665.7 | 657.4 | 8.3 |
| methyl acetate | $C_{2v}$ | 2.729 | 91.37 | 180.00 | 4.366 | 664.1 | 659.3 | 4.8 |
| (ester side attack) | $C_s$ | 2.755 | 91.20 | 159.21 | 4.98 | 662.4 | 658.7 | 3.7 |
| (methyl side attack) | $C_s$ | 2.733 | 91.41 | 130.42 | 5.204 | 665.9 | 656.7 | 9.2 |

[a] The bond distance, r, is given in Å. Angles $a_1$ and $a_2$ are given in degrees and defined in Figures 1 and 2. All $\nu_2$ values are given in $cm^{-1}$. Binding energies are given in kcal/mol.

**TABLE 3: Binding Energies (BE), $\nu_2$ Frequencies, and $\Delta\nu_2$ Values of $CO_2$ Complexes with Carbonyl Compounds Using a 6-31G Basis Set at the MP2 Level**

| compound | symmetry | BE (kcal/mol) | $\nu_2$ splitting ($cm^{-1}$) | | $\Delta\nu_2$ |
|---|---|---|---|---|---|
| acetone | $C_{2v}$ | 2.512 | 525.5 | 519.4 | 6.1 |
| | $C_s$ | 3.999 | 525.1 | 516.3 | 8.8 |
| acetaldehyde | $C_{2v}$ | 2.302 | 525.2 | 519.8 | 5.4 |
| | $C_s$ | 4.053 | 525.1 | 517.5 | 7.6 |
| formaldehyde | $C_{2v}$ | 2.114 | 525.0 | 520.2 | 4.8 |
| | $C_s$ | 3.406 | 523.6 | 516.6 | 7.0 |
| acetic acid | $C_{2v}$ | 2.570 | 525.4 | 520.3 | 5.1 |
| | $C_s$ | 4.245 | 525.0 | 517.5 | 7.5 |
| methyl acetate | $C_{2v}$ | 3.148 | 525.3 | 521.1 | 4.2 |
| (ester side attack) | $C_s$ | 3.976 | | | |
| (methyl side attack) | $C_s$ | 4.148 | 524.8 | 517.3 | 7.5 |

**TABLE 4: Experimental Results**[2] **from IR Spectroscopy on Bending Vibrations of $CO_2$ Bound to Polymers**

| | $\nu_2$ ($cm^{-1}$) | | $\Delta\nu$ ($cm^{-1}$) |
|---|---|---|---|
| polymer | | | |
| PMMA | 662.6 | 656.6 | 6.0 |
| PEMA | 663.0 | 654.7 | 8.3 |
| PBMA | 662.1 | 654.7 | 7.4 |
| PVMK | 661.7 | 652.6 | 9.1 |
| $CO_2$ | 667 | | |

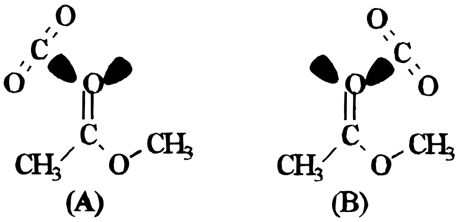

**Figure 5.** Possible directions of attack of $CO_2$ on methyl acetate. The diagram on the left (A) represents attack on the methyl side, while the diagram on the right (B) indicates attack from the ester side.

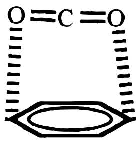

**Figure 6.** Minimum energy geometry of the benzene−$CO_2$ complex determined using a 6-31G basis set at the SCF level.

mode splittings were calculated to be 4.2 $cm^{-1}$ for a $C_s$ symmetry complex between $CO_2$ and ethyl benzoate as shown in Figure 7.

According to the present ab initio calculations, $CO_2$ binding in PET could be a result of binding at the phenyl ring or the carbonyl position. The carbonyl position is preferred over the phenyl ring. The calculated splittings of the $\nu_2$ bending mode suggest that binding of $CO_2$ to PET occurs primarily at the carbonyl position of the PET backbone (Figure 7). Due to steric hindrance, the experimental splitting is only about 4 $cm^{-1}$.[2] Similar results were obtained when ab initio calculations were performed on methyl acetate, where it was found that (due to steric hindrance) the splitting of the $\nu_2$ mode was lower for attack from the ester side than for the methyl side. It is possible the steric hindrance of the PET backbone resulted in a lower splitting of the bending mode of bound $CO_2$ relative to other carbonyl containing polymers.

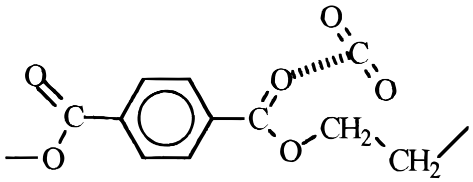

**Figure 7.** Possible binding geometry of $CO_2$ to PET polymer backbone.

## Conclusions

Complexes between carbonyl-containing model compounds and $CO_2$ indicate that $C_s$ symmetry (Figure 2) was preferred over $C_{2v}$ symmetry (Figure 1), resulting in a higher binding energy (Tables 2 and 3). The higher binding energy resulted in a greater splitting of the $\nu_2$ degenerate bending mode of free $CO_2$. These greater splittings of the bending mode were comparable to experimental results of carbonyl-containing polymers. Mulliken populations indicated a Lewis acid−base interaction occurred.

The splitting observed in $CO_2$-impregnated PET is difficult to assign experimentally.[2] Ab initio calculations indicate that the carbonyl oxygen is the preferred binding site for $CO_2$ along the polymer backbone. Due to the steric hindrance associated with the polymer backbone, splittings of the $\nu_2$ bending mode are lower than other carbonyl-containing polymers where steric hindrance is not as strong because the carbonyl group is not located in the polymer backbone as it is in the PET case. The relatively weak interactions between $CO_2$ and basic sites indicate that sorption of $CO_2$ in basic polymers may be enhanced.

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