

Theoretical Study on the Potential Energy Surface of the CH₄-CO complex

Nobuaki Tanaka,* Hiromasa Nishikiori, and Tsuneo Fujii

Department of Environmental Science and Technology, Faculty of Engineering, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan

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Abstract

Motivation. Methane and carbon monoxide play important roles in atmospheric and combustion chemistry. In the atmosphere weakly bound complex will be a candidate for the green house effect due to the ability to accumulate the additional vibration energy. It is important to elucidate the intermolecular interaction between CH₄ and CO.

Method. The MP2 calculation are carried out for the geometry optimization and following frequency analysis of CH₄ complexes with CO. Single point energies were calculated at the CCSD(T)/6-311++G(2d,2p) and MP2/aug-cc-pVXZ (X = D, T, and Q) levels to evaluate the basis set and electron correlation effects.

Results. Interaction energies were calculated as a function of the intermolecular distance between CH₄ and CO where the CO molecule approaches CH₄ in the face, edge, or vertex direction. The HF potentials are calculated to be repulsive while after including the electron correlation the potentials become bound indicative of the importance of the dispersion energy for the attraction. The largest interaction energy was predicted for the face direction with oxygen-end approach of the CO molecule. On the basis of the equilibrium geometries, the structures were further optimized. Four weakly bound complexes have been found on the potential energy surface.

Conclusions. The potential energy surface of the CH₄-CO complex has been investigated. The C_s complex is calculated to be the most stable compared with the C_{3v} complexes at the MP2/6-311++G(2d,2p) level. The structure of the C_s complex is in good agreement with that obtained by the microwave spectroscopy.

Keywords. CH₄; CO; complex; MP2.

Abbreviations and notations

BSSE, basis set superposition error	MP2, second order Møller-Plesset perturbation theory
CP, counterpoise	NBO, natural bond orbital
CT, charge transfer	PES, potential energy surface

1 INTRODUCTION

From the interest and importance in atmospheric and theoretical chemistry, weakly bound CO complexes, CO-Ar [1,2], CO-CO [3], CO-HF [4], CO-H₂O [5], CO-N₂ [6], and CO-CO₂ [7] have been investigated. For complexation there are two possible orientations of CO, that is, oxygen-end and carbon-end attaches. For the complex where the electrostatic interaction plays an important role, such as hydrogen bond complexes, carbon-end attached complex is energetically more stable than oxygen-end attached complex. Carbon monoxide is a famous molecule for its polarity $\text{C}=\text{O}^+$. To predict a correct direction of the dipole moment of CO, the electron correlation must be included [7]. Much more studies have been reported on the CH₄ complexes, CH₄-He [8], CH₄-Ar [9], CH₄-H₂O [10], CH₄-HF [11], CH₄-NO [12], and CH₄-NO⁺ [13]. Previously the CH₄-CO complex was studied experimentally [14-16] and theoretically [16]. Millimeter wave spectra of the CH₄-CO complex

* Correspondence author; phone: +81-26-269-5527; fax: +81-26-269-5550; E-mail: ntanaka@shinshu-u.ac.jp

showed similarity to those of the Ar-CO and Ne-CO complexes [14]. Most recently rotational spectra were measured in the frequency range from 4 to 19 GHz to obtain the van der Waals bond distance, intermolecular stretching frequency, and force constants [15]. Red-shifted CO vibration band was observed in solid films [16]. However, only vertex complexes were considered for the ab initio calculation. The interaction energy of 14 kJ mol^{-1} calculated at the MP2/6-311++G(3df,2pd) level seems to be too large for the CH₄-CO complex. Even the OC-HF and CH₄-NO⁺ complexes have the interaction energies of -3.35 [4] and -4.93 [13] kcal mol⁻¹ at the MP3/6-311++G**(2d)//HF/6-31G* and MP2/6-311++G(2df,2p) levels, respectively. In this paper the potential energy surface of the CH₄-CO complex has been investigated where the face, edge, and vertex approaches of CO to CH₄ are considered.

2 METHODS

Geometry optimization and frequency analysis are performed at the second-order Møller-Plesset theory, MP2, with the 6-311++G(2d,2p) basis set. Single point energies were calculated at the MP2/aug-cc-pVXZ (X = D, T, Q) and CCSD(T)/6-311++G(2d,2p) levels. Analysis of the charge distribution and charge-transfer processes was performed using the natural bond orbital (NBO) partitioning scheme [17]. The basis set superposition error (BSSE) was calculated according to the counterpoise (CP) method proposed by Boys and Bernardi [18]. All calculations were performed using Gaussian 03W [19].

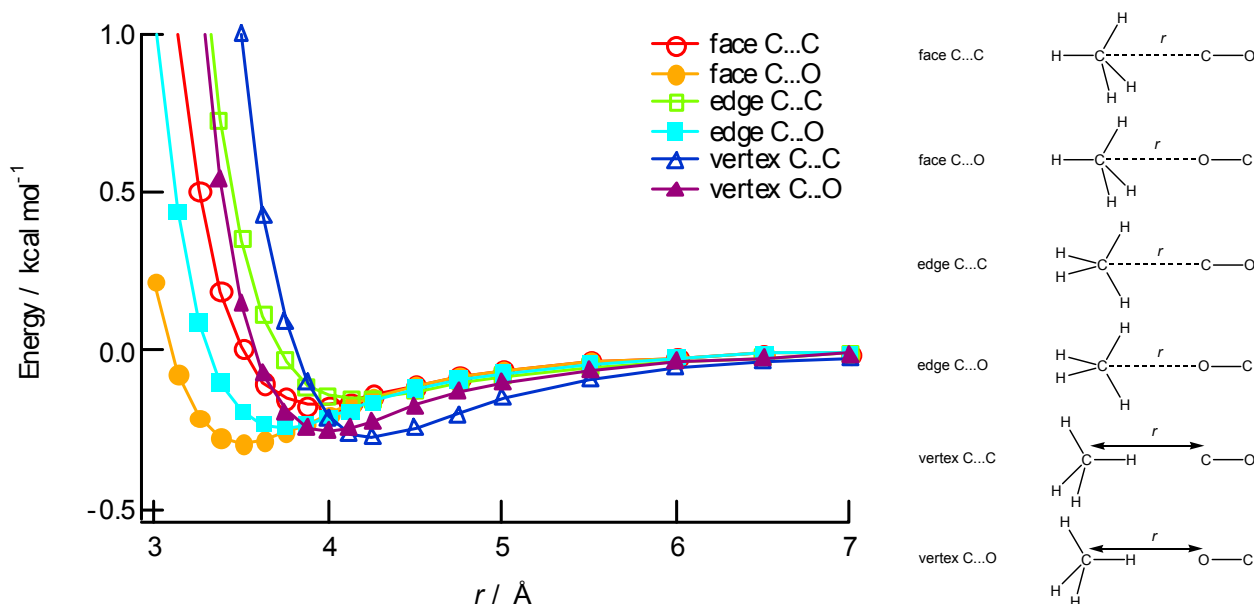


Figure 1. Left: Intermolecular potential energies for the face (C...C, C...O), edge (C...C, C...O), and vertex (C...C, C...O) approaches calculated at the MP2/aug-cc-pVTZ level. Right: Configurations of the CH₄...CO approach.

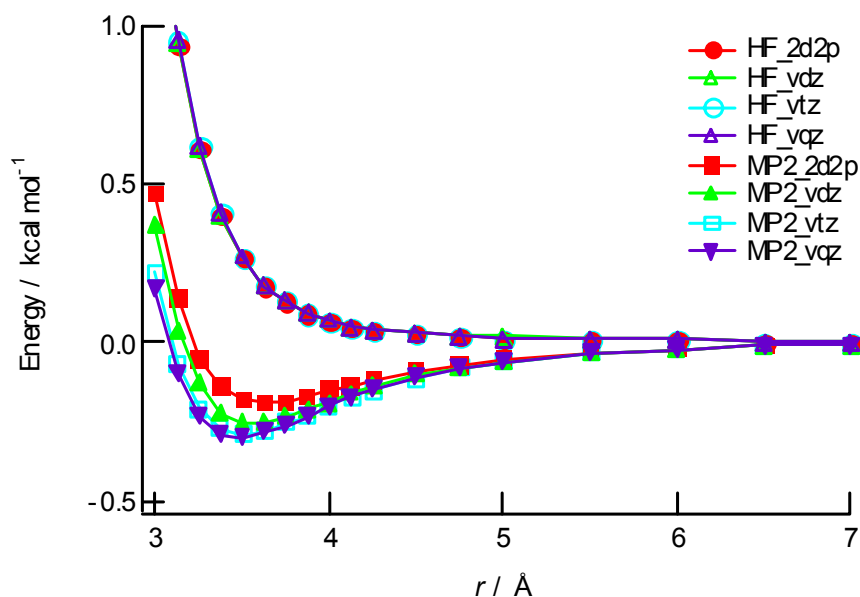


Figure 2. Basis set dependence of intermolecular potential energy for the face C...O approach.

3 RESULTS AND DISCUSSION

3.1 Geometries and Energetics

The CH₄...CO interaction energies were calculated as a function of the intermolecular distance r at the MP2/aug-cc-pVTZ level where the CO molecule approaches CH₄ with the face, edge, or vertex direction as depicted in Figure 1. The face C...O approach was calculated to possess the largest interaction energy. For the face C...O approach the interaction energies were calculated using 6-311++G(2d,2p) and aug-cc-pVXZ (X = D and Q) basis sets to evaluate the basis set effect. As shown in Figure 2 the basis set effect on the HF interaction energies is small. Intermolecular potentials calculated at the HF level are repulsive. On the other hand, the MP2 correlation interaction energies arising mainly from the dispersion energies are greatly dependent on the basis sets. Smaller 6-311++G(2d,2p) and aug-cc-pVDZ basis sets underestimate the interaction energy compared with the aug-cc-pVQZ basis set. Further optimization of the six stationary points at the MP2/6-311++G(2d,2p) level gave one C_s and three C_{3v} complexes. Two edge conformations are not stable. The face C...O conformation was calculated to be a transition state. The optimized structures of the CH₄-CO complex are shown in Figure 3. Geometry parameters and changes in values from the corresponding monomers are listed in Table 1. The optimized bond lengths were close to those of the corresponding monomers. In C_{3v} complexes, the C-H bond(s) participating in the interaction with the CO molecule is/are less elongated compared with the other C-H bond(s). On the contrary the C1-H3 bond of the complex I is less elongated. The C6-O7 bond of the complex III is slightly contracted while that of the other complexes is elongated. Rotational constants of A, B, and C for the complex I are calculated to be 42.2187, 3.7421, and 3.5128 GHz, respectively, at the MP2/6-

311++G(2d,2p) level. On the basis of the microwave spectrum of the CH₄-CO complex, Liu and Jäger obtained the rotational constant (B) of 3108.3218 MHz [15]. The angle between the CO molecular axis and the *a*-principal inertial axis of the complex is derived to be 72.4° where the oxygen atom end of the CO molecule is closer to the CH₄ molecule. Experimentally observed CH₄-CO complex corresponds to the calculated complex I. The intermolecular distance of 3.996 Å is longer than calculated value. Pedersen et al. investigated the T-shape Ar-CO van der Waals complex where the optimized equilibrium distance between Ar and the center of mass of CO is calculated to be 3.72 Å at the CCSD(T)/aug-cc-pVQZ-33211 level [1] which is 0.09 Å shorter than that obtained by the microwave spectrum [2]. It is interesting to note that the CH₄-NO⁺ complex possessing the isoelectronic structure with CH₄-CO has the similar conformation [13].

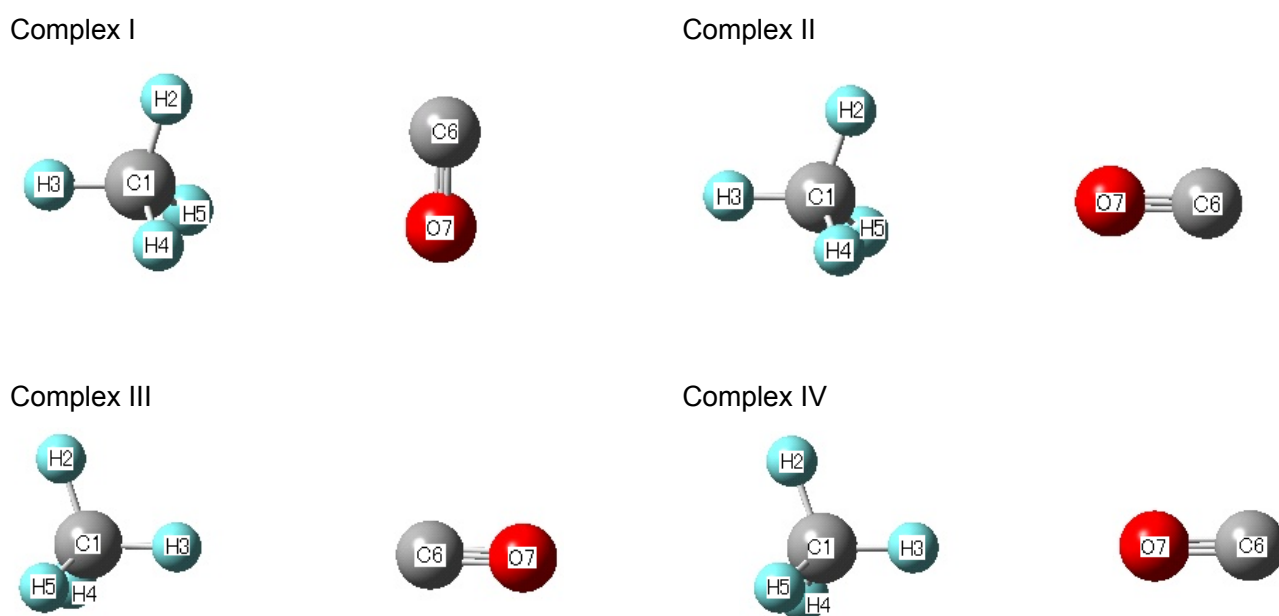


Figure 3. Optimized structures of the CH₄-CO complex calculated at the MP2/6-311++G(2d,2p) level.

Table 1. Bond lengths (Å) of the CH₄-CO complexes calculated at the MP2/6-311++G(2d,2p) level of theory. Changes in value from the corresponding monomer are given in parentheses.

	I		II		III		IV	
r_{C1-H2}	1.0841	(+0.00078)	1.0839	(+0.00056)	1.0842	(+0.00081)	1.0840	(+0.00065)
r_{C1-H3}	1.0839	(+0.00055)	1.0840	(+0.00061)	1.0837	(+0.00031)	1.0838	(+0.00041)
r_{C1-H4}	1.0841	(+0.00074)	1.0839	(+0.00056)	1.0842	(+0.00081)	1.0840	(+0.00065)
r_{C1-H5}	1.0841	(+0.00073)	1.0839	(+0.00056)	1.0842	(+0.00081)	1.0840	(+0.00065)
r_{C6-O7}	1.1380	(+0.00008)	1.1381	(+0.00012)	1.1379	(-0.00008)	1.1381	(+0.00015)
$r_{C1...O7}$	3.5882		3.4389		5.3398		3.9566	
$r_{C1...C6}$	3.7079		4.5769		4.2019		5.0947	

BSSE corrected interaction energies are listed in Tables 2. In the absence of the electron

correlation energy the complexes are not in the bound state indicative of the role of the dispersion interaction for the attraction. At the MP2/aug-cc-pVQZ level, the interaction energies are calculated to be -0.47 , -0.30 , -0.28 , and -0.26 kcal mol⁻¹ for complexes I, II, III, and IV, respectively. Table 2 also compares the electron correlation effect on the interaction energies of the CH₄-CO complexes at the MP3, MP4SDTQ, CCSD and CCSD(T) levels with the 6-311++G(2d,2p) basis set. The MP3 interaction energies are smaller than the other energies. However, the electron correlation method dependence of the interaction energies is not significant.

Table 2. BSSE corrected interaction energies (kcal mol⁻¹) of the CH₄-CO complexes.

	I	II	III	IV
HF/6-311++G(2d,2p)	0.33	0.33	0.17	0.11
HF/aug-cc-pVDZ	0.33	0.33	0.17	0.11
HF/aug-cc-pVTZ	0.33	0.33	0.17	0.11
HF/aug-cc-pVQZ	0.33	0.33	0.17	0.11
MP2/6-311++G(2d,2p)	-0.29	-0.17	-0.20	-0.17
MP3/6-311++G(2d,2p)	-0.22	-0.06	-0.17	-0.14
MP4SDTQ/6-311++G(2d,2p)	-0.29	-0.16	-0.23	-0.19
CCSD(T)/6-311++G(2d,2p)	-0.27	-0.13	-0.21	-0.17
MP2/aug-cc-pVDZ	-0.36	-0.24	-0.23	-0.21
MP2/aug-cc-pVTZ	-0.45	-0.28	-0.27	-0.25
MP2/aug-cc-pVQZ	-0.47	-0.30	-0.28	-0.26

3.2 Vibrational Spectra

At the MP2/6-311++G(2d,2p) level the vibrational modes of the CH₄ monomer consist of a triply degenerate antisymmetric t₂ C-H stretching (3215.9 cm⁻¹), a symmetric a₁ C-H stretching (3087.4 cm⁻¹), a doubly degenerate e C-H bending (1594.8 cm⁻¹), and a triply degenerate t₂ C-H bending (1369.7 cm⁻¹). The t₂ C-H stretching and t₂ C-H bending are infrared active. The stretching vibrational frequency of the CO monomer was calculated to be 2113.5 cm⁻¹. Table 3 shows the vibrational frequencies and infrared intensities of the complexes calculated at the MP2/6-311++G(2d,2p) level. There are five intermolecular modes and ten intramolecular modes. Frequency shifts are small indicative of the small interaction. The antisymmetric and symmetric C-H stretching vibrational frequencies decrease. Frequency shift in the CO moiety of the complex III from the monomer shows the plus sign opposite to that of the other complexes, corresponding to the C6-O7 bond contraction. Xia et al. observed the C-O stretching vibration shift of -0.632 cm⁻¹ due to the complexation [113] which is in good agreement with that of the complex I. Complexation gives the intensity in the C-H bending modes of the complexes I and II and in the C-H stretching modes of the complexes III and IV.

Table 3. Harmonic vibrational frequencies (cm^{-1}) and intensities (km mol^{-1}) calculated at the MP2/6-311++G(2d,2p) level of theory.

mode ^a	I		II		III		IV	
	ν	<i>I</i>	ν	<i>I</i>	ν	<i>I</i>	ν	<i>I</i>
C-H stretch	3210.6	20.5	3210.9	17.3	3215.1	9.9	3214.1	13.0
C-H stretch	3209.4	15.0	3210.9	17.3	3207.3	18.8	3209.8	17.8
C-H stretch	3209.1	16.3	3210.7	22.1	3207.3	18.8	3209.8	17.8
C-H stretch	3081.0	0.0	3082.3	0.0	3081.2	1.0	3082.6	0.4
C-O stretch	2113.0	32.4	2112.3	37.6	2113.6	39.1	2112.4	39.0
C-H bend	1594.5	0.3	1593.7	0.1	1597.0	0.0	1596.3	0.0
C-H bend	1594.3	0.2	1593.7	0.1	1597.0	0.0	1596.3	0.0
C-H bend	1371.4	12.7	1371.0	12.0	1373.4	9.8	1373.4	10.5
C-H bend	1371.2	12.0	1371.0	12.0	1373.4	9.8	1373.4	10.5
C-H bend	1370.3	14.5	1369.1	15.5	1369.0	10.5	1370.1	10.4
I	78.1	0.0	64.7	0.0	62.6	0.0	83.3	0.1
I	63.0	0.0	64.5	0.0	62.6	0.0	83.3	0.1
I	51.9	0.0	49.2	0.0	41.5	0.0	43.3	0.0
I	27.8	0.2	28.5	0.4	17.2	0.2	30.4	0.3
I	20.5	0.1	28.5	0.4	17.2	0.2	30.4	0.3

^a I: Intermolecular vibration.**Table 4.** Changes in natural atomic charges (me) of complexes.

	I	II	III	IV
C1	-1.0	+2.7	-3.2	-2.2
H2	-2.6	-0.2	-0.9	-1.3
H3	+0.7	-3.1	+5.0	+5.4
H4	+1.0	-0.2	-0.9	-1.3
H5	+1.0	-0.2	-0.9	-1.3
C6	+0.8	+1.5	-0.6	+3.3
O7	+0.2	-0.7	+1.4	-2.7

3.3 Charge Distribution

Contribution of the CT effect to the complexation was examined using the NBO analysis. Table 4 shows the changes in natural atomic charges (Δq) for the CH_4 -CO complexes calculated with the 6-311++G(2d,2p) basis set. In complex I, both C6 and O7 atoms lose charges while the in-contact C1 and H2 atoms gain charges. In the C_{3v} complexes, the in-contact atom of the CO moiety gains charge while that of the CH_4 moiety loses charge. The net CT was evaluated to be from CO to CH_4 by 1.0, 0.9, 0.8, and 0.6 me for the complexes I, II, III, and IV, respectively. Complexation resulted in the charge rearrangement in the components. Although the changes in value are small, each component of the CH_4 -CO complex becomes more polarized to gain dipole-induced dipole interaction.

4 CONCLUSIONS

The PES of the CH_4 -CO complex has been investigated. Four stable complexes have been found at the MP2/6-311++G(2d,2p) level. The C_s complex is calculated to be the most stable compared

with three C_{3v} complexes. The structure of the C_s complex is in good agreement with that obtained by the microwave spectroscopy. The interaction energies of the complexes have been calculated at the MP2/aug-cc-pVXZ ($X = D, T, \text{ and } Q$) level. The dispersion energy largely contributes to the complexation compared with the electrostatic and charge transfer energies.

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