

Density Functional and Ab Initio Studies on Structures and Energies of the Ground State of CrCO

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ABSTRACT: CrCO was studied using density functional theory (DFT) and ab initio methods. We obtained the two-dimensional potential energy surface (PES), geometry, and vibrational frequencies for CrCO in a septet state. Two minimum structures were found in the CCSD(T) calculation, including a local minimum that is a weak van der Waals (vdW) complex. All DFT methods yield only one minimum structure. We demonstrate that the bond dissociation energy (0.50 kcal/mol) and vibrational frequency (1981.1 cm⁻¹) of CrCO calculated using CCSD(T) are in better agreement with experimental values (<1.5 kcal/mol and 1977 cm⁻¹) than any of the reported theoretical studies. © 2006 Wiley Periodicals, Inc. *Int J Quantum Chem* 107: 458–463, 2007

Key words: density functional theory; ab initio; chromium carbonyl; potential energy surface; bond dissociation energy

Introduction

The transition metal carbonyl compounds, M(CO)_n, serve as building blocks in organometallic chemistry, and play important roles in heterogeneous catalysis. To understand the mechanism of such catalytic activity and to improve the

design of better catalysts, the nature of the intermediates involved in the reaction should be known. Toward this goal, there have been numerous experimental [1–3] and theoretical investigations [4, 5].

One of the simplest cases of M(CO)_n is CrCO. There have been many investigations of CrCO, using density functional theory (DFT) [6–10] and ab initio [11, 12] methods. Although CrCO is a simple system, accurate information is not available about the ground state of CrCO. For the lowest-energy state of CrCO, DFT and ab initio methods have provided results contrary to each other. The former gave a bent structure with septet [6–10] and the latter a linear structure with septet [11, 12]. In ad-

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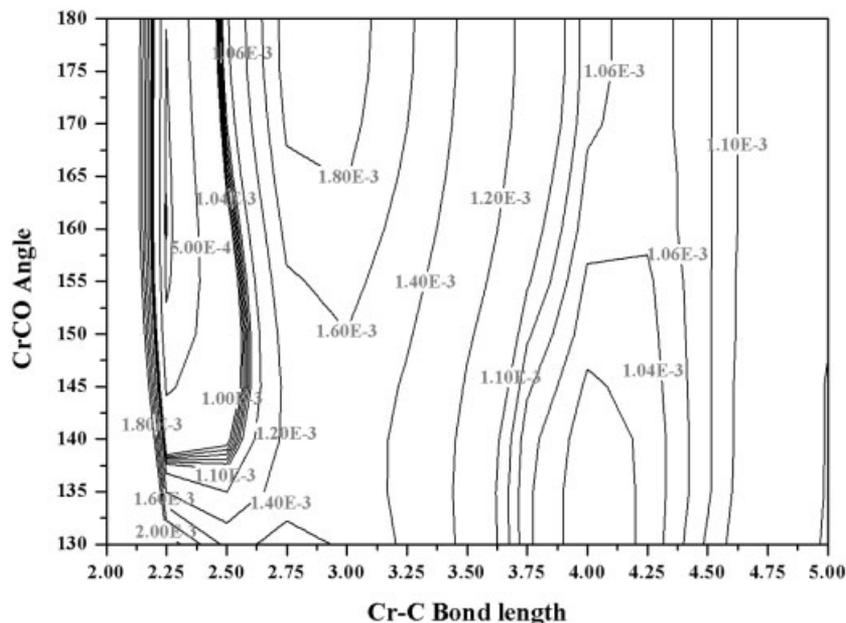


FIGURE 1. PES (hartree) using CCSD(T)/6-311+G(3df) and fixing C—O distance (1.133 Å). The minimum is located at near 2.25 Å of Cr—C distance and 160° of \angle CrCO angle; the other is located at near 4.00 Å of Cr—C distance and 135° of \angle CrCO angle.

dition, most studies did not provide vibrational frequencies and the bond dissociation energy (BDE) including proper basis set superposition error (BSSE) correction. For a few studies providing such information, calculated values did not reproduce the experimental value well. It is difficult to reproduce the BDE of CrCO theoretically because the experimental BDE of CrCO is very small value (<1.5 kcal/mol) [13]. Recently CrCO was investigated by the CCSD(T) method [14]. This result shows that CrCO is bent and a septet, which is the same as the result of DFT calculation. Since the study did not provide any frequency information, one cannot confirm that the structure was at a stationary point. To resolve this issue, the potential energy surface (PES) and vibrational frequencies using higher-level calculations are of high demand. We systematically investigated these issues using the CCSD(T) method with a basis set of appropriate size.

Computational Details

We performed DFT calculations using hybrid functional (B3PW91 [15], B3P86 [15, 16], mPW1PW91 [17, 18], O3LYP [19]), GGA (BLYP [20, 21], BPW91

[18, 20], BP86 [16, 20], PBE [22], OLYP [23]) and LDA [24, 25]. In addition, we performed ab initio calculations, such as MP2 [26, 27], CCSD [28, 29], and CCSD(T) [30]. All ab initio calculations were performed with frozen-core approximation. All calculations have been carried out with the Gaussian 03W and Gaussian 03 program [31]. We used 6-311+G(3df) (Cr: (15s11p6d3f1g)/[10s7p4d3f1g], C and O: (12s6p3d1f)/[5s4p3d1f]) basis sets for most calculations. To locate the ground state of CrCO, we scanned the ground-state PES of CrCO (fixing the distance of C—O as 1.133 Å) using B3LYP/6-311+G(3df), CCSD(T)/6-311+G(d), and CCSD(T)/6-311+G(3df). The results of CCSD(T)/6-311+G(3df) and B3LYP/6-311+G(3df) are presented in Figures 1 and 2. In the PES of CrCO at the CCSD(T) level, we used both 6-311+G(3df) and 6-311+G(d) (Cr: (15s11p6d1f)/[10s7p4d1f], C and O: (12s6p1d)/[5s4p1d]) basis sets. The molecular structures were fully optimized; harmonic vibrational frequencies have been calculated at the optimized geometries. The calculated BDE includes the corrections of zero-point energies (ZPE) and thermal enthalpy (298 K), and the BSSE corrected by the counterpoise method [32]. In the case of ab initio methods, we used 50% of the BSSE correction, following the suggestion that the magnitude of BSSE might be

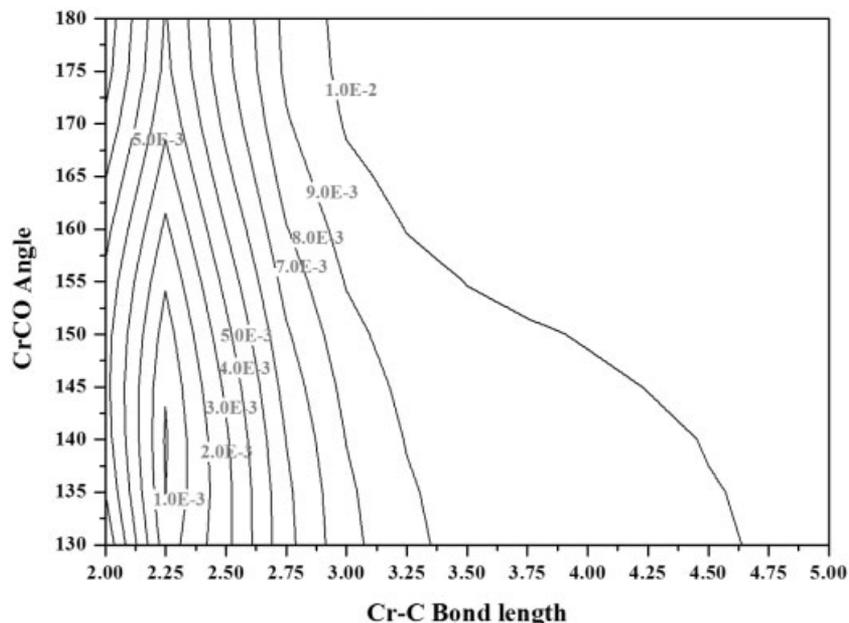


FIGURE 2. PES (hartree) using B3LYP/6-311+G(3*df*) and fixing C—O distance (1.133 Å). The minimum is located at near 2.25 Å of Cr—C distance and 140° of \angle CrCO angle.

overestimated in the counterpoise method [33]. The calculated relative energies and enthalpies, BDE, fully optimized geometrical parameters are shown in Table I and vibrational frequencies in CrCO are shown in Table II.

Results and Discussion

MOLECULAR STRUCTURES

Experimentally, CrCO was detected in the Ar matrix at 4 K and the observed stretching frequency is 1977cm^{-1} [34]. However, there is no other experimental structural information. Experimental evidence shows that the lowest-energy state of CrCO is septet and its dissociation energy is <1.5 kcal/mol [13].

We scanned the PES of CrCO to clarify the accurate global minimum of CrCO. We used B3LYP/6-311+G(3*df*), CCSD(T)/6-311+G(*d*), and CCSD(T)/6-311+G(3*df*). The results of each method using the 6-311+G(3*df*) basis set are presented in Figures 1 and 2. The PES of CrCO using CCSD(T)/6-311+G(3*df*) is different from that using CCSD(T)/6-311+G(*d*). The CCSD(T)/6-311+G(*d*) result indicates that CrCO does not have a bound state near 2 Å. Instead, near 4.25 Å, CrCO has a slightly bound state that is an extremely weak van der Waals (vdW) complex. In contrast the CCSD(T)/6-

311+G(3*df*) result is that CrCO has both the global minimum state near 2.25 Å and the local minimum state near 4 Å. The 6-311+G(*d*) basis set does not properly describe the PES of CrCO. As shown in Figure 2, the PES of B3LYP/6-311+G(3*df*) is completely different from the PES of CCSD(T)/6-311+G(3*df*). Both methods show that the lowest-energy has the Cr—C bond length of near 2.25 Å (see Figs. 1 and 2). However, the \angle CrCO angles are different (CCSD(T): near 160°, B3LYP: near 140°). In addition, B3LYP does not find the local minimum structure around a longer Cr—C distance (~ 4 Å).

Based on the scanned PES, we have carried out geometry optimization, and the results with the 6-311+G(3*df*) basis set are presented in Tables I and II. All methods show that all bent structures have no imaginary frequency. In contrast, all linear structures have 2 imaginary frequencies. All calculations suggest that the bent structure is the ground state of CrCO. All DFT methods seem to overestimate the interaction between the Cr atom and the C atom as indicated from the large dissociation energy (see Table 1), and predict the shorter bond length of Cr—C. Although the molecular shape is correctly found to be bent in all DFT methods, the description of PES is not accurate. CCSD(T) shows that CrCO has a local minimum structure that is an extremely weak vdW complex. Its dissociation en-

TABLE I
Geometry parameters dipole moment (Debye), and relative energies and enthalpies^a (kcal/mol) between C_s ($^7A'$) and $C_{\infty v}$ ($^7\Sigma_g$) structures of CrCO calculated with the 6-311+G(3df) basis set.*

	C_s ($^7A'$)												$C_{\infty v}$ ($^7\Sigma_g$)		
	B3LYP	O3LYP	B3PW91	B3P86	mPW1PW91	LDA	BLYP	OLYP	BPW91	BP86	PBE	MP2	CCSD	CCSD(T) Local	CCSD(T)
$r(\text{Cr}-\text{C})$	2.205	2.198	2.189	2.171	2.197	2.060	2.166	2.174	2.148	2.136	2.134	2.313	2.480	3.959	2.246
$r(\text{C}-\text{O})$	1.142	1.148	1.141	1.141	1.137	1.148	1.159	1.158	1.157	1.158	1.158	1.137	1.126	1.133	1.135
$\angle \text{Cr}-\text{C}-\text{O}$	139.48	137.71	140.48	140.54	140.32	143.18	140.33	138.17	141.52	141.70	141.51	157.06	153.31	135.05	160.52
μ	0.77	0.88	0.75	0.77	0.76	0.81	0.90	0.97	0.80	0.80	0.82	3.0	2.8	0.41	3.2
$r(\text{Cr}-\text{C})$	2.192	2.183	2.172	2.157	2.178	2.059	2.163	2.165	2.140	2.131	2.128	2.285	2.394	4.197	2.235
$r(\text{C}-\text{O})$	1.132	1.137	1.131	1.131	1.128	1.139	1.149	1.147	1.148	1.149	1.148	1.135	1.124	1.133	1.134
μ	1.7	1.7	1.8	1.7	1.9	1.3	1.1	1.4	1.3	1.3	1.3	3.4	3.1	0.21	3.4
ΔE_{rel}^b	-2.5	-3.2	-2.2	-2.3	-2.1	-2.6	-2.9	-3.5	-2.6	-2.5	-2.6	-0.081	-0.092	-0.027	-0.064
ΔH_{rel}^c	-1.7	-2.4	-1.4	-1.5	-1.3	-1.8	-2.0	-2.7	-1.7	-1.7	-1.7	0.78	0.77	2.00	0.80
ΔE_{dis}^d	6.4	6.3	6.1	8.2	5.8	21.9	11.2	8.8	10.8	13.2	13.5	-0.11	-0.77	0.33	0.97
ΔE_{dis}^e -BSSE ^e	6.0	5.9	5.6	7.8	5.3	21.4	10.8	8.4	10.3	12.7	13.1	-0.56	-1.1	0.24	0.46
ΔH_{dis}^f	6.5	6.5	6.2	8.4	5.9	21.9	11.3	8.9	10.9	13.3	13.6	-0.071	-0.75	-0.42	1.00
ΔH_{dis}^f -BSSE ^e	6.2	6.1	5.8	7.9	5.5	21.5	10.9	8.5	10.5	12.8	13.2	-0.51	-1.1	-0.51	0.50

* Lengths in Ångstroms (Å) and angles in degrees (°).

^a The experimental value of the dissociation energy of CrCO is <1.5 kcal/mol [13].

^b $\Delta E_{\text{rel}} = E(^7A') - E(^7\Sigma_g)$.

^c $\Delta H_{\text{rel}} = H(^7A') - H(^7\Sigma_g)$.

^d $\Delta E_{\text{dis}} = E(\text{Cr: } ^7S) + E(\text{CO: } ^1\Sigma_g) - E(\text{CrCO: } ^7A')$.

^e Values with "BSSE" mean the BSSE-corrected results.

^f $\Delta H_{\text{dis}} = H(\text{Cr: } ^7S) + H(\text{CO: } ^1\Sigma_g) - H(\text{CrCO: } ^7A')$.

TABLE II
Vibrational frequencies^a (cm⁻¹) of C_s ($\tilde{\Sigma}_g^+$) and C_{2v} ($\tilde{\Sigma}_g^+$) structures of CrCO calculated with the 6-311+G(3df) basis set.

	B3LYP	O3LYP	B3PW91	B3P86	mPW1PW91	LDA	BLYP	OLYP	BPW91	BP86	PBE	MP2	CCSD	CCSD(T) Local	CCSD(T)
	C _s ($\tilde{\Sigma}_g^+$)														
A'	178.4	182.8	179.3	181.9	176.9	198.5	186.7	188.0	187.8	188.0	189.4	88.0	34.3	275.5	90.3
A'	273.6	277.9	274.5	292.6	265.7	379.7	319.1	303.5	320.5	331.7	332.7	116.7	85.7	770.5	170.3
A ^b	2025.8	2001.1	2044.5	2045.2	2065.2	2002.5	1920.0	1943.6	1946.9	1939.4	1945.2	2084.6	2210.6	2231.6	2100.9
	C _{2v} ($\tilde{\Sigma}_g^+$)														
II	-284.7	-334.6	-274.6	-282.9	-262.9	-365.9	-337.3	-375.6	-324.6	-324.6	-336.4	-71.2	-68.4	-1633.4	-75.6
II	-284.7	-334.6	-274.6	-282.9	-262.9	-365.9	-337.3	-375.6	-324.6	-324.6	-336.4	-71.2	-68.4	78.3	-75.2
Σ_g^+	237.6	237.2	247.7	261.3	240.9	334.3	270.5	255.2	280.3	289.0	289.9	128.7	82.0	-880.7	174.6
Σ_g^b	2128.4	2102.4	2142.8	2145.3	2169.3	2088.4	2006.0	2035.7	2029.6	2022.4	2029.7	2108.7	2233.0	1886.9	2124.8

^a Unscaled values.

^b C—O stretching frequencies.

ergy is only 0.24 kcal/mol (see Table I). As shown in Figure 2, B3LYP does not provide a local minimum structure. All DFT methods are expected to follow the same trend, since the DFT methods are generally known to describe the vdW interaction poorly.

VIBRATIONAL FREQUENCY

The vibrational frequencies of CrCO using several ab initio methods and DFT with 6-311+G(3df) basis set are presented in Table II. We use the scale factors of 0.954 and 0.943 for CCSD/6-311+G(*d*) and CCSD(T)/6-311+G(3df), respectively. These values are provided on the U. S. National Institute of Standard and Technology (NIST) web page (<http://srdata.nist.gov/cccbdb/>). CCSD(T) method gives a value of $2100.9 \times 0.943 = 1981.1$, which is in excellent agreement with the experiment one (see Table II).

BOND DISSOCIATION ENERGY (BDE)

The BDE of the CrCO case using various ab initio methods and DFT, as well as the results, are also presented in Table I. All DFT methods overestimate the BDE of CrCO. GGA methods in particular largely overestimate BDEs, with magnitudes approximately twice that of hybrid methods. The exact exchange term plays an important role in the thermochemical value. However, mixing exact exchange terms is not sufficient for a complete description of a vdW complex. CCSD and MP2 methods provide negative BDE values, implying the unbound state of CrCO. Only a high-level ab initio method, such as CCSD(T) and a basis set of large size, can accurately describe the transition metal complex formed by weak interactions.

A previous CCSD(T) calculation gave a BDE value (D_0) of 2 kcal/mol [14]. However, this value is not the result of vibrational analysis, but is rather a "best" estimated value (see Ref. [14]). In addition, it is not corrected by BSSE, which is important for an accurate description of the BDE. We also emphasize that the experimental value of BDE of CrCO is not exactly 1.5 kcal/mol, but rather <1.5 kcal/mol [13]. In other words, the experiment gave only the upper limit of 1.5 kcal/mol. The previous result of CCSD(T) (2 kcal/mol) is out of this range (<1.5 kcal/mol). Up to now, there has been no report of a calculated value that falls within the experimental range.

We performed a vibrational frequency calculation and added the BSSE correction using CCSD(T)/6-311+G(3df). The results are presented in Table I. The BDE of CrCO is 0.50 kcal/mol (ΔH ,

BSSE corrected value) at the CCSD(T)/6-311+G(3df) level (see Table I). This value is within the experimental range of <1.5 kcal/mol. We also propose a local minimum energy state of CrCO, which has a long Cr—C distance (3.959 Å). Its BDE (0.24 kcal/mol) is less than that, at 0.46 kcal/mol of the lowest-energy state (see Table I).

Conclusions

We calculated optimized geometries, C—O stretching frequencies, and BDE of CrCO using various DFT and ab initio methods with the 6-311+G(3df) basis set. According to the CCSD(T)/6-311+G(3df) calculation, the lowest-energy state of CrCO is “bent” with septet; a local minimum structure that is a weak vdW complex was also identified. CCSD(T)/6-311+G(3df), BDE, and vibrational frequencies of CrCO are in excellent agreement with the experimental values. Although DFT methods give a ground structure similar to that found with the CCSD(T) method, they produce a significantly different PES at weak interaction region because of the deficiency in the description of vdW interactions due to the inadequacy of all DFT methods, including hybrid methods, in describing vdW interactions.

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