

## Potential Energy Curves for Pt–CO Interactions

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Potential energy surfaces for the low-lying electronic states of the linear Pt–CO complex are studied using the complete active space multiconfiguration self-consistent-field method followed by second-order configuration interaction calculations which included up to 1.9 million configurations. The nature of the chemical bond was discussed in terms of the wave function composition and electronic population analysis. In addition, spin–orbit effects were included through the relativistic configuration interaction method, and the spin–orbit contribution to the dissociation energy is discussed.

### 1. Introduction

The interaction of CO with the Pt(111) surface is one of the most extensively studied systems in surface science, motivated in part by the commercial importance of reactions involving CO and Pt-based catalysts. Generally, the CO–metal bond is expected to be a local property, so that it has been studied using clusters and molecular methods. In other words, the chemical bond and the chemisorptive bond are akin to each other. The CO adsorption has been studied extensively on well-defined single-crystal surfaces of Pt,<sup>1–3</sup> in complexes isolated in argon matrices,<sup>4</sup> and in clusters.<sup>5</sup> The experimental vibrational frequencies of CO on a single crystal are also available.<sup>6</sup> The binding energy has been measured via a low-energy molecular beam scattering (LEMS) experiment.<sup>1</sup> Often the properties have been measured as a function of the adsorbate coverage. Only atop sites on Pt are occupied for low coverages.<sup>2</sup> Bridging CO appears above the coverage of  $\theta_{\text{CO}} = 0.17$  monolayer. Both atop and bridging COs on the Pt surface are bound by 30–35 kcal/mol.<sup>1,2,7</sup> Several theoretical studies have also been carried out to predict the electronic structure and the nature of bonding between Pt and CO. There are Hartree–Fock calculations of Gavezzotti et al.<sup>8</sup> and Bash,<sup>9</sup> Moller–Plesset second-order perturbation theory (MP2) of Rohlfing and Hay,<sup>10</sup> generalized valence bond (GVB) computations of Smith and Carter,<sup>11</sup> and small multiconfiguration self-consistent-field (MCSCF) calculations followed by small valence level CI of Bash and Cohen.<sup>12</sup> The results from the above studies show little agreement between various calculations, demonstrating the sensitivity of the studied system to the techniques employed. The reported dissociation energy varies between 15 and 43 kcal/mol. Surprisingly, the most correlated methods used, namely MCSCF/CI<sup>12</sup> and GVB,<sup>11</sup> differ by 24.5 kcal/mol. Since the experimental results are obtained from the chemisorption experiments carried out for surfaces, they cannot serve as rigorous checks for theoretical studies on an isolated Pt atom + CO interaction. To resolve the existing discrepancies and to shed light on the excited states, we perform large-scale complete active space multiconfiguration self-consistent-field (CASSCF) calculations followed by multireference singles + doubles configuration interaction (MRSDCI) computations. We consider relativistic effects including spin–orbit coupling since the relativistic effects are quite important for the Pt–CO system due to the heavy nature of the platinum atom.

### 2. Method of Calculations

The discrepancies in the results of previous studies alert that special care has to be taken in selecting both basis sets and active spaces for multireference configuration interaction studies. The proper description of the Pt atom may be critical for the reliability

of the results. The present choice of the atomic basis set has been based on the previous experience gained on Pt<sub>2</sub><sup>13</sup> and clusters of Pt and hydrogen atoms.<sup>14,15</sup> The relativistic effective potentials (RECP) which retained the outer 5d<sup>9</sup>6s<sup>1</sup> shells in the valence space replacing the rest of core electrons by relativistic effective potentials (RECP) were employed, and the exponents of valence Gaussian basis set for Pt were taken from Ross et al.<sup>16</sup> The s and p orbitals of the Pt basis sets were prepared by decontracting the original s and p contractions. In the case of the 5d orbitals of Pt, basis functions with the two most diffuse exponents have been left uncontracted. This choice leads to a valence (3s3p3d) basis set. The basis sets for carbon and oxygen retain the 2s2p valence shells and replace core by the RECPs. The basis sets are those of Pacios and Christiansen,<sup>17</sup> but the two most diffuse functions were not contracted. These basis sets were supplemented with one set of d functions adopted from Dunning and Hay,<sup>18</sup> which results in a 3s3p1d set. This choice of basis sets leads to the largest calculation used for Pt–CO up until now. More importantly, this basis set has been shown to be reliable in other calculations on Pt<sub>2</sub>, etc.

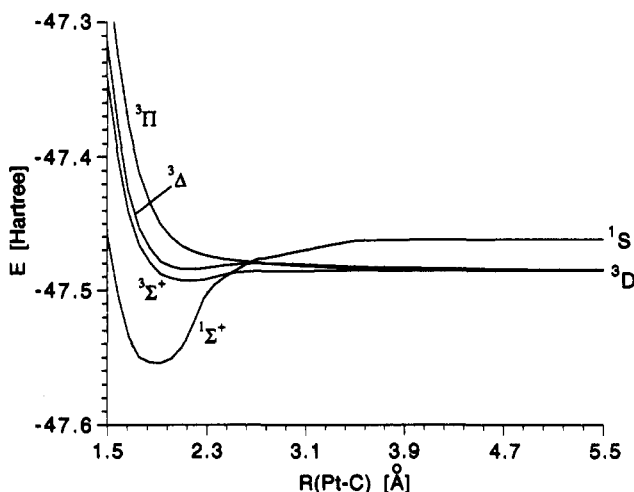
The complete active space self-consistent-field (CASSCF) calculations were performed for the orbital space consisting of 13 molecular orbitals. All calculations described here were carried out in the C<sub>2v</sub> symmetry group. The active space spanned six a<sub>1</sub>, three b<sub>2</sub>, three b<sub>1</sub>, and one a<sub>2</sub> orbital. Those orbitals which correlate into the outer 5d and 6s orbitals of the platinum atom and occupied  $\sigma$ , occupied  $\pi$ , and the corresponding virtual  $\pi^*$  of CO at the infinite separation were included in the active space. The choice of active space is consistent with the standard description of bonding in metal carbonyls as  $\sigma$  donation from the CO HOMO to the  $\sigma$  orbital of the metal atom, followed by  $\pi$  back-donation from the metal atom to carbon monoxide  $\pi^*$  orbital. Twenty electrons were distributed in all possible ways among the orbitals in the active space. Our trial computations with the freezing of molecular orbitals corresponding to C<sub>2v</sub> and O<sub>2v</sub> lead to the conclusion that these orbitals are active and should be left in the active space. The assumed active space leads to almost 1.9 million configuration spin functions (CSF) in the largest MRSDCI calculations. Following the CASSCF, we performed the MRSDCI calculations with the intent of including higher-order electron correlation effects.

Following the MRSDCI calculations, the relativistic configuration interaction (RCI) calculations which included low-lying electronic configurations of different spatial and spin symmetries in the presence of the spin–orbit operator were carried out to estimate the spin–orbit contribution to the dissociation energy and equilibrium geometries. The configurations corresponding to the low-lying states were used as reference configurations along with singly- and doubly-excited configurations from the reference configurations. All the calculations were performed in the C<sub>2v</sub>

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**TABLE I: Energy Separation between the Molecular Ground State and the Lowest Excited State of Pt-CO at the Dissociation Limit and the Experimental  $^1S$ - $^3D$  Splitting of the Pt Atom (in eV)**

theory						
mol states	atomic state of Pt	SCF	CASSCF	SOCI	SOCI+Q	exp <sup>a</sup>
$^3\Sigma^+$ , $^3\Pi$ , $^3\Delta$	$^3D$	0	0	0	0	0
$^1\Sigma^+$	$^1S$	1.110	0.642	0.717	0.615	0.478

<sup>a</sup> Reference 19, experimental values are averaged over  $J$  state.**Figure 1.** Potential energy curves for Pt-CO interactions.

symmetry. The 20 outer electrons were distributed among 12  $a_1$ , 6  $b_2$ , 6  $b_1$  and 3  $a_2$  orbitals. The virtual orbitals lying beyond this space were excluded from these calculations. Twenty-one reference configurations, 3 from  $^1\Sigma^+$  with  $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 2\pi^4 1\delta^4$  and  $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^1 1\pi^4 2\pi^4 1\delta^4$  configurations, 12 from  $^3\Pi$  with the  $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^1 1\pi^4 2\pi^3 1\delta^4$  configuration, and 6 from  $^3\Delta$  with the  $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^1 1\pi^4 2\pi^3 1\delta^3$  configuration, were included in the RCI calculations. All CASSCF/MRSDCI computations were made using the modified version of ALCHEMY II<sup>23</sup> to include the RECPs.<sup>24</sup> The RCI computations were based on the general RCI method for polyatomics.<sup>25</sup>

### 3. Results and Discussion

Table I compares our computed energy separations of Pt-CO at 8.0 Å (dissociation limit) with the  $J$ -averaged experimental energy separations of the  $^1S$ - $^3D$  splitting of the Pt atom. The best calculated value of the energy separation (0.615 eV) differs by 0.137 eV from the experimental result,<sup>19</sup> indicating a proper reproduction of potential curves in the asymptotic region. The optimization of the C-O bond length at the Pt-C dissociation limit gives 1.127 Å (CASSCF) and 1.131 Å (MRSDCI), in excellent agreement with the experimental C-O bond length of 1.128 Å.<sup>20</sup>

Figure 1 shows the potential energy curves of several electronic states, namely the  $^1\Sigma^+$  ground state dissociating into the  $^1S$  platinum atom, and low-lying excited triplet states, namely  $^3\Sigma^+$ ,  $^3\Pi$ , and  $^3\Delta$  dissociating into the  $^3D$  state of the platinum atom. The adiabatic dissociation energy is 64.1 kcal/mol, while the dissociation to the  $^3D$  state is computed as 49.9 kcal/mol. It should be noted that the improved correlation methods (Table II) give a higher dissociation energy. This observation agrees with the dissociation energy calculations for other bonds<sup>21</sup> and may indicate a more general rule. Because of the heavy nature of the Pt atom, the zero-point vibrational correction lowers the dissociation energies by 1.57 kcal/mol (ZPV energies computed at the SCF level).

As seen from Table II, the Pt-C distance predicted by different theoretical studies varies in a wide range from 1.707 to 1.99 Å.

**TABLE II: Ground-State Bond Lengths, Dissociation Energies, and Dipole Moments of the Pt-CO System (Distances in Å, Energies in kcal/mol, and Dipole Moments in D)**

	this work		ref 12		ref 11
	CASSCF	MRSDCI <sup>a</sup>	MCSCF	CI	
$R(\text{Pt-C})$	1.904	1.900 (1.900)	1.732	1.707	1.977
$R(\text{C-O})$	1.151	1.147 (1.154)	1.164 <sup>b</sup>	1.164 <sup>b</sup>	1.184
$D_e$ (to $^1S$ Pt)	58.49	59.49 (64.09)	45.89	70.34	44.51
$D_e$ (to $^3D$ Pt)	43.69	42.93 (49.90)	21.21	42.66	37.35
$\mu^c$		2.04		1.75	1.12

<sup>a</sup> MRSDCI + Q in parentheses. <sup>b</sup> Assumed. <sup>c</sup> A positive sign indicates that the negative end of the dipole points toward the O atom.**TABLE III: Bond Lengths (in Å), Dissociation Energies (in kcal/mol), Energy Separations (in eV), and Dipole Moments (in D) for the Lowest  $^3\Sigma^+$  State of the Pt-CO System**

	this work		ref 12		ref 11
	CASSCF	MRSDCI <sup>a</sup>	CASSCF	CI	
$R(\text{Pt-C})$	2.024		1.943	1.824	2.99
$R(\text{C-O})$	1.126		1.164 <sup>b</sup>	1.164 <sup>b</sup>	1.13
$D_e$	4.18	14.11 (16.97)	8.76	19.37	1.0
$T_e$ , vertical	1.88	1.33 (1.46)			
$T_e$ , adiabatic	1.71	1.24 (1.43)	0.52	0.79	0.32
$\mu^c$		-2.51			-1.68

<sup>a</sup> MRSDCI + Q (in parentheses). <sup>b</sup> Assumed. <sup>c</sup> A positive sign indicates that the negative end of the dipole points toward the O atom.**TABLE IV: Bond Lengths (in Å), Dissociation Energies (in kcal/mol), Energy Separations (in eV), and Dipole Moments (in D) of the Lowest  $^3\Delta$  State of Pt-CO**

	this work		ref 12	
	CASSCF	MRSDCI <sup>a</sup>	CASSCF	CI
$R(\text{Pt-C})$	2.178		1.942	1.895
$R(\text{C-O})$	1.126		1.164 <sup>b</sup>	1.164 <sup>b</sup>
$D_e$	0.27	10.16 (13.56)	6.91	18.21
$T_e$ , vertical	2.15	1.47 (1.57)		
$T_e$ , adiabatic	1.90	1.42 (1.58)	0.65	1.06
$\mu^c$		-3.01		

<sup>a</sup> MRSDCI + Q (in parentheses). <sup>b</sup> Assumed. <sup>c</sup> A positive sign indicates the negative end of dipole points toward the O atom.

The chemisorption simulation using an atom superposition and electron delocalization (ASED) technique<sup>22</sup> predicted CO adsorption at the height of 2.05 Å from the surface. Our best calculated value is 1.90 Å and is almost the same as the CASSCF and MRSDCI levels. The CO bonding is predicted reasonably well by all methods applied. The formation of a strong chemical bond weakens the C=O bond, which is elongated by about 0.02 Å. The corresponding C=O vibrational frequencies are 2098.5  $\text{cm}^{-1}$  in PtCO and 2143.0  $\text{cm}^{-1}$  in dissociated PtCO, in agreement with experimental results<sup>6</sup> for atop site of 2000–2100  $\text{cm}^{-1}$  and free CO vibration of 2143  $\text{cm}^{-1}$ .

The predicted lowest  $^3\Sigma^+$  excited state has a significant stabilization energy of 17 kcal/mol. Again, former studies gave very different results. The Pt-C bond predicted before differs by 1 Å (Table III). Our result of 2.024 Å confirms the results of Basch and Cohen.<sup>12</sup> Due to the weak interactions, the C-O bond distance of 1.126 Å is almost the same as the one in a free molecule. The predicted bond energy of 1.0 kcal/mol by the GVB method is far from our best result of 17 kcal/mol as well as from another CI calculation<sup>12</sup> which gave 19.4 kcal/mol. Even bigger differences are noted in the calculations of the adiabatic energy separations. This property is especially sensitive to the extensiveness of the method applied. Our predicted energy separation of 1.43 eV indicates that the expected spin-orbit mixing of the excited states would not be significant.

The lowest  $^3\Delta$  state is also bonding, similar to the  $^3\Sigma^+$  state, and has a stabilization energy of 13.56 kcal/mol and the

TABLE V: Leading Configurations of the Low-Lying Electronic States of Pt-CO in the MRSDCI Wave Function

state	coeff	1σ s	2σ z	3σ x <sup>2</sup> + y <sup>2</sup> - z <sup>2</sup>	4σ s	5σ x <sup>2</sup> + y <sup>2</sup> - z <sup>2</sup>	1π yz	2π y	3π y	1π' xz	2π' x	3π' x	1δ x <sup>2</sup> - y <sup>2</sup>	2δ xy <sup>a</sup>
<sup>1</sup> Σ <sup>+</sup>	-0.924	2	2	2	2	0	2	2	0	2	2	0	2	2
	-0.112	2	2	2	2	0	1	2	1	1	2	1	2	2
	-0.095	2	2	2	2	0	2	2	0	2	0	2	2	2
	-0.095	2	2	2	2	0	2	0	2	2	2	0	2	2
<sup>3</sup> Σ <sup>+</sup>	-0.928	2	2	2	1	1	2	2	0	2	2	0	2	2
	-0.113	2	2	2	1	1	1	2	1	1	2	1	2	2
	0.096	2	2	2	1	1	0	2	2	2	2	0	2	2
	0.096	2	2	2	1	1	2	2	0	0	2	2	2	2
<sup>3</sup> Δ	-0.926	2	2	2	2	1	2	2	0	2	2	0	2	1
	-0.114	2	2	2	2	1	1	2	1	1	2	1	2	1
	-0.098	2	2	2	2	1	2	2	0	0	2	2	2	1
	-0.098	2	2	2	2	1	0	2	2	2	2	0	2	1
<sup>3</sup> Π	-0.925	2	2	2	2	1	2	2	0	2	1	0	2	2
	-0.101	2	2	2	2	1	2	2	0	0	1	2	2	2
	0.098	2	2	2	2	1	1	2	1	1	1	1	2	2
	-0.098	2	2	2	2	1	0	2	2	2	1	0	2	2

<sup>a</sup> Nature of atomic orbitals involved.

TABLE VI: Gross Atomic and Gross Orbital Mulliken Population of the Low-Lying Electronic States of Pt-CO

state	gross atomic population			gross orbital population								
				Pt			C			O		
	Pt	C	O	s	p	d	s	p	d	s	p	d
<sup>1</sup> Σ <sup>+</sup>	9.74	3.92	6.34	0.80	0.03	8.90	1.60	2.20	0.11	1.93	4.35	0.06
<sup>3</sup> Σ <sup>+</sup>	9.95	3.70	6.34	1.44	0.17	8.33	1.46	2.13	0.11	1.96	4.33	0.06
<sup>3</sup> Δ	10.04	3.66	6.30	1.82	0.24	7.96	1.51	2.04	0.10	1.93	4.30	0.06
<sup>3</sup> Π	9.92	3.77	6.30	2.03	0.16	7.73	1.51	2.14	0.12	1.95	4.29	0.06

equilibrium Pt-C bond of 2.18 Å. The bond is slightly longer and weaker (Table IV) than the one of the <sup>3</sup>Σ<sup>+</sup> state. The third potential curve originating from the <sup>3</sup>D state of Pt corresponding to the <sup>3</sup>Π state is repulsive for all Pt-C distances with a large adiabatic energy separation from the ground state of 2.35 eV (CASSCF) and 2.36 eV (MRSDCI).

The standard description of bonding in metal carbonyls is one of donation from the highest occupied σ orbital (which is essentially a carbon lone pair) to the metal atom, followed by a π back-donation from the metal atom to the carbonyl 2π orbital (which is a π\* antibonding orbital with a large carbon component). The above picture can be easily adapted to the description of molecular interactions via the multireference wave function. The dominant configuration spin function (CSF) corresponds to the 1σ<sup>2</sup>2σ<sup>2</sup>3σ<sup>2</sup>4σ<sup>2</sup>δ<sup>4</sup>1π<sup>4</sup>2π<sup>4</sup> closed-shell configuration in the case of the ground state or to a CSF having an electron in the 5σ antibonding orbital in the case of the lowest excited states. These configurations are responsible for an electron donation to the Pt-C bond and are responsible for bond formation. The presence of an electron on the antibonding orbital reduces the strength of the bond in the case of the excited states. As seen from Table V, other significant CSFs correspond to electronic transitions from the platinum d orbital to the CO π\* orbital, interpreted here as a π back-donation. The balance between these two effects leads to the formation of a bond or to a repulsive curve.

The Mulliken population analysis (Table VI) indicates that the Pt and C atoms are involved in the metal-CO bond. The electronic population on oxygen is almost unchanged for different electronic states. Since the net atomic charge on oxygen is 0.30 e, this is balanced by a corresponding deficiency in the electronic charge density on carbon. The propensity of the platinum atom to donate electrons toward the carbon site determines the strength of the Pt-C bond. In the case of the <sup>1</sup>Σ<sup>+</sup> state, the carbon atom has a gross Mulliken population of 3.92, which is higher than the ones in any studied triplet states, indicating the increase of the electron density in the Pt-C bond. The better description of the situation in the Pt-C region is "electron sharing" instead of "electron donation". In the case of the excited states there is a significant shift of electronic density from the 5d to 6s orbitals

of Pt, which we attribute as the most probable cause for the weakening of the Pt-CO bond.

Due to the importance of spin-orbit effects of the platinum atom, the contribution of this effect to the dissociation energy has also been studied. The large separation between the ground electronic state and the low-lying excited states prevents significant mixing of ground and excited states. Consequently, the <sup>1</sup>Σ<sup>+</sup> wave function is contaminated with excited triplets by less than 1%. The corresponding energy lowering for the equilibrium geometry is only 0.05 eV. The lowering of the energy at the adiabatic dissociation point (<sup>1</sup>S of Pt) is also small (0.04 eV). The spin-orbit effects have almost no impact on the <sup>1</sup>Σ<sup>+</sup> dissociation energy. The situation is somewhat different for the excited states. The RCI wave function is a combination of <sup>3</sup>Π (66%) and <sup>3</sup>Δ (33%) states. The energy is lowered by 0.44 eV compared to the case without spin-orbit coupling. The dissociation energy due to the spin-orbit correction drops to 38 kcal/mol, close to the experimental heat of chemisorption. These results give one more indication of the local character of the adsorption of CO on the Pt surfaces.

#### 4. Conclusions

The large differences in the results of different theoretical studies for the Pt-CO complex indicate that special care has to be taken to assure results on the quantitative level. Active d electrons of platinum require large and well-balanced basis sets. The correlation effects require a rigorous multireference treatment. To fulfill these conditions, large-scale configuration interaction calculations including up to 1.9 million configurations were performed within the CASSCF/MRSDCI formalism. The effect of unlinked quadruple clusters to the MRSDCI through the multireference Davidson correction has been taken into account. The Davidson correction is shown to be very important here for the case of Pt-CO.

The calculated dissociation energy to the <sup>3</sup>D state of Pt and the ground state of CO (38 kcal/mol) is close to experimental energy of CO binding on the platinum surface, indicating the local character of the chemisorption bond.

The structure of the wave function indicates that the Pt-C bond is controlled by two processes: σ bond formation due to the

donation of the electronic density to the bond from Pt and C and back-donation of d electrons from Pt to the antibonding  $\pi^*$  orbital of CO. This model applies to all the electronic states studied here. The importance of spin-orbit effects for the energetics of Pt and CO reaction is due to the large spin-orbit splitting on the  $^3D$  state of platinum. However, for the  $^1\Sigma^+$  ground state of the PtCO complex spin-orbit effects were found to be small since the triplet excited states of PtCO were found to be considerably higher in energy.

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