RI04

# Computational Molecular Spectroscopy of FeCO in the $\tilde{X}\,^3\Sigma^-$ and $1\,^5\Sigma^-$ Electronic States

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# First-row transition-metal containing molecule is a tough molecule !

## Multi-reference calculation

- Open 3d-shell
- Quasi-degeneracy of 3*d* orbitals (especially in ionic radicals)

  → Many low-lying excited states.

  → Intrinsically Multi-configuration (retained from an isolated metal ion)

## Averaging

- To keep quasi-degeneracy of MO's.
- Constraint from the *ab initio* program ($C_{2v}$, in stead of $C_{\infty v}$)

  eg. For $^6\Delta$ FeNC, five-state averaging in the $C_{2v}$ calculation (2 $A_1$, 1 $B_1$, 1 $B_2$, 1 $A_2$).
  $Fe^+$ ($3d^6 4s^1$ $a\ ^6D$)

# Why FeCO ?

- A possible candidate for astrochemistry
- Structure, molecular properties, and electronic structure

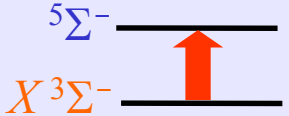
  FeC, FeCO : Covalent bonding

  FeCN/FeNC, FeCl, FeS : Ionic bonding
- Exploitation of different calculation method for different type of bonding

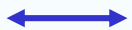
FeCO is regarded as a benchmark molecule

for new basis sets and new calculation method

Exp. (Villalta & Leopold, 1993)




3.24 kcal/mol



Previous *ab Initio*


exception: DFT

So difficult ? Then, let's try !

**Exp.**

Villalta and Leopold (1993)

Negative ion photoelectron spectroscopy

Ground state is $^3\Sigma^-$

$\Delta E = E(^5\Sigma^-) - E(^3\Sigma^-) = 3.24$ kcal/mol

Vibrational frequencies for $^3\Sigma^-$ and $^5\Sigma^-$

Kasai, Obi, Ohshima, Endo, Kawaguchi (1995)

MW $B_0 = 4358.596(39)$ MHz, $D_{J,0} = 0.001221361(80)$ MHz

Kagi, Kasai, Ungerechts, Kawaguchi (1997)

FT-MW $B_0 = 4363.89135(37)$ MHz

Ground state is $^3\Sigma^-$

Tanaka, Shirasaka, Tanaka (1997)

MW $B_0 = 4363.88342(40)$ MHz, $D_{J,0} = 0.00121799(84)$ MHz

Ground state is $^3\Sigma^-$

$r_s$ structure (FeC = 1.7270 Å, CO = 1.1586 Å)

## Theor. Calc. 1

Bauschlicher, Pettersson, and Siegbahn (1987)

CASSCF/ Wachters + 2*p* + diffuse *d*  Geometry for $^3\Sigma^-$ only?

Castro, Salahub, Fournier (1994)

GTO-DFT: *X* $^3\Sigma^-$, $D_e$ to Fe($^5D$, $3d^6 4s^2$) + CO($^1\Sigma^+$) = 17 kcal/mol

$\omega_e$ 658 $cm^{-1}$($\nu_{Fe-C}$) 1982 $cm^{-1}$($\nu_{CO}$)

Adamo and Lelj (1995)

B3LYP/GTO5Z + Ahlrichs Polarization

$\Delta E = E(^5\Sigma^-) - E(^3\Sigma^-)$ = 5.5 kcal/mol

$r_{FeC}$ = 1.900 Å, $r_{CO}$ = 1.146 Å in the $^5\Sigma^-$ state

## Theor. Calc. 2

Honda, Noro, and Miyoshi (2000)

Only $^3\Sigma^-$, MR-SDCI Fe-C = 1.757 and CO = 1.155 Å

MCPF Fe-C = 1.720 and CO = 1.209 Å, $D_e$ = -9.8 kcal/mol

Noro, Sekiya, Koga, Matsuyama (2000)

MR-SDCI/CGTF

$\Delta E = E(^5\Sigma^-) - E(^3\Sigma^-)$ = 0.42 kcal/mol

$^3\Sigma^-$: FeC = 1.797 Å, CO = 1.147 Å

$^5\Sigma^-$: FeC = 1.879 Å, CO = 1.150 Å

Ricca and Bauschlicher (2001)

CCSD(T)/cc-pV5Z

$\Delta E = E(^5\Sigma^-) - E(^3\Sigma^-)$ = -0.42 kcal/mol

$^3\Sigma^-$: FeC = 1.746 Å, CO = 1.158 Å

$^5\Sigma^-$: FeC = 1.860 Å, CO = 1.149 Å

## Calculation level

- State-Averaged CASSCF, then
- MR-SDCI or MR-ACPF (averaged coupled-pair functional).

## Basia sets

Roos *et al.*, ANO (Atomic Natural Orbital)

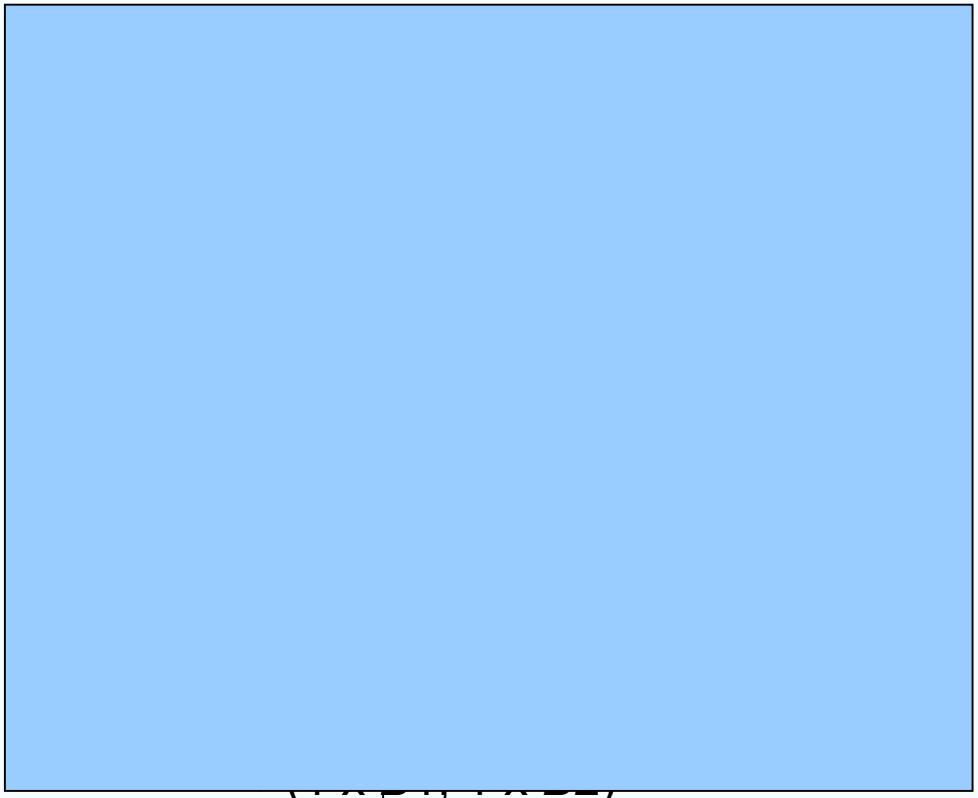
Fe : (21*s*, 15*p*,10*d*, 6*f*, 4*g*)/[8*s*, 7*p*, 5*d*, 3*f*, 2*g*]

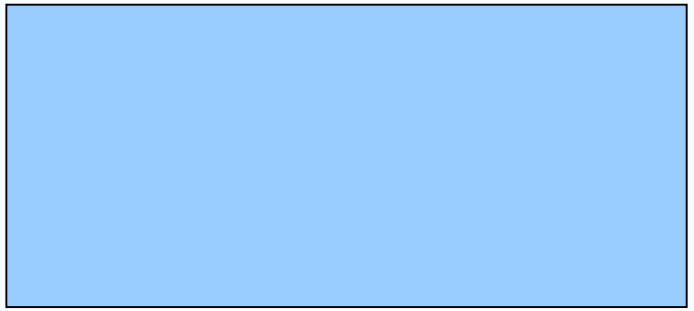
C, O : (14*s*, 15*p*, 4*d*, 3*f*)/[6*s*, 5*p*, 3*d*, 2*f*]

## Program

MOLPRO 2002.6

# Initial Guess MOs for the MCSCF calculations





Merge under $C_{2v}$ Symmetry
at the MCSCF stage.

(a) $^3\Sigma^-$ MCSCF MOs ($A_2$, Full valence, no-core)

(b) $^5\Sigma^-$ MCSCF MOs ($A_2$, Full valence, no-core) from the (a) $^3\Sigma^-$ MCSCF MOs

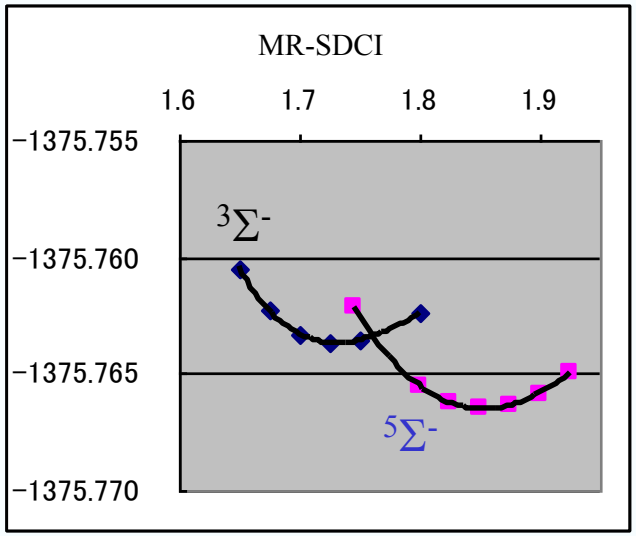
# CI Active space (Preliminary)

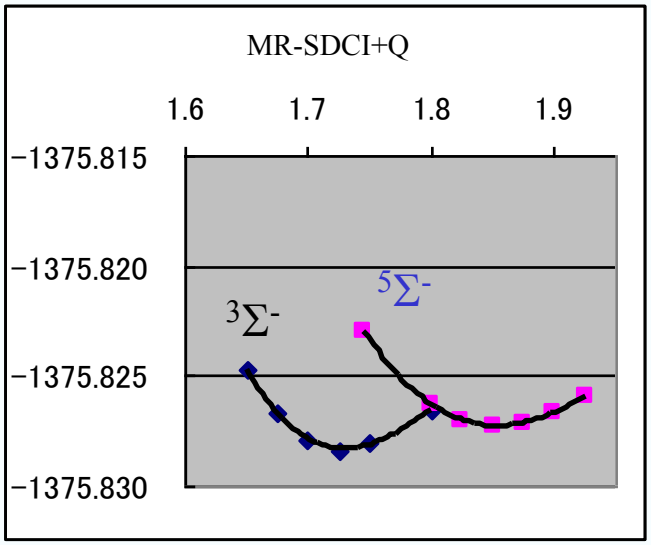
| | | $r_{FeC}$ /Å ($^3\Sigma^-$) | $r_{CO}$ /Å ($^3\Sigma^-$) | $r_{FeC}$ /Å ($^5\Sigma^-$) | $r_{CO}$ /Å ($^5\Sigma^-$) | $\Delta E(^5\Sigma^- - ^3\Sigma^-)$ (kcal/mol) |
|---|---|---|---|---|---|---|
| (a) 12 Elecs. in 10 Orbs. | MR-SDCI | 1.796 | 1.159 | 1.902 | 1.159 | -4.36 |
| | +Q | 1.805 | | 1.914 | | -3.70 |
| | | | | | | 4 |
| | ACPF | 1.809 | | 1.918 | | -3.74 |
| | $+E_{rel}$ | 1.788 | | 1.905 | | -3.72 |
| (b) 12 Elecs. in 10 Orbs. (Closed: 8σ, 9σ, 10σ) | MR-SDCI | 1.734 | 1.150 | 1.855 | 1.146 | -1.85 |
| | +Q | 1.728 | 1.157 | 1.856 | 1.151 | 0.60 |
| | $+E_{rel}$ | 1.720 | 1.159 | 1.843 | 1.153 | 0.87 |
| | ACPF | 1.729 | 1.157 | 1.868 | 1.151 | 0.39 |
| | $+E_{rel}$ | 1.720 | 1.158 | 1.854 | 1.152 | 0.68 |
| (c) 14 Elecs. in 11 Orbs. (Closed: 8σ and 9σ) | MR-SDCI | 1.731 | 1.159 | 1.853 | 1.159 | -1.53 |
| | +Q | 1.730 | | 1.856 | | 0.67 |

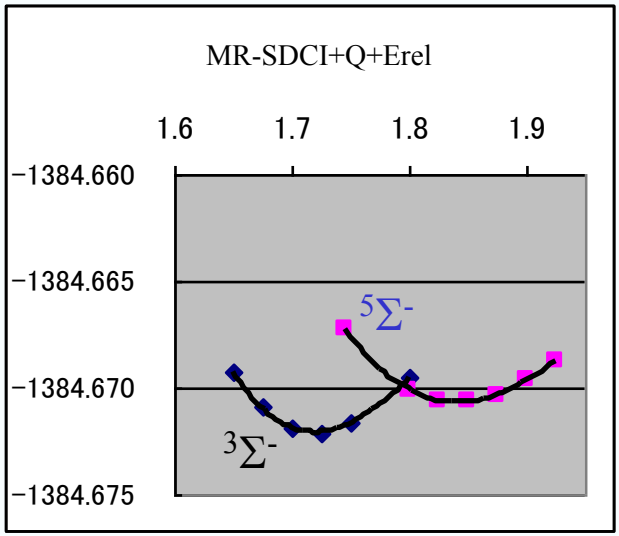
- Active space (b) was adapted.
- 8σ、9σ、10σ dynamic electron correlations and cost.

# $^3\Sigma^-$ , $^5\Sigma^-$ states of FeCO [CI(b) active space]

$r$(CO) = 1.159 Å, fixed at exp. value




| | MR-SDCI | MR-SDCI + Q | MR-SDCI + Q + $E_{rel}$ |
|---|---|---|---|
| $\Delta E$ | -1.76 kcal/mol | 0.68 kcal/mol | 0.87 kcal/mol |

→ Davidson's correction (+Q) and $E_{rel}$ correction

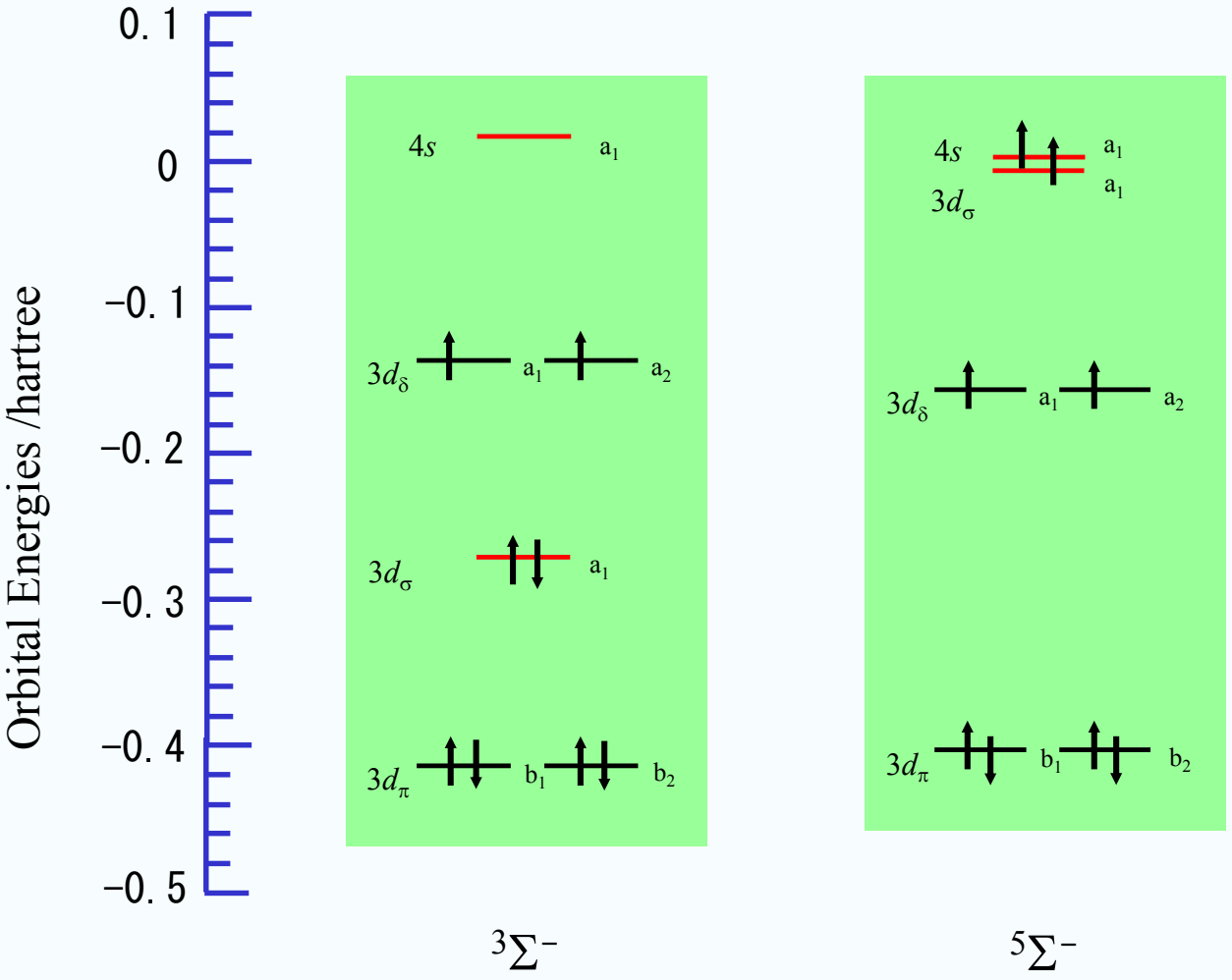
## FeCO Structure and energy (*cf.* Preivous studies)

| | Methods | $r_{FeC}$ / Å | $r_{CO}$ / Å | $\Delta E$ ($^5\Sigma^-$ - $^3\Sigma^-$) /kcal mol$^{-1}$ |
|---|---|---|---|---|
| $^3\Sigma^-$ | | | | |
| Present | MR-ACPF /ANO | 1.742 | 1.157 | 0.59 |
| | **MR-ACPF+$E_{rel}$ /ANO** | **1.729** | **1.159** | **0.97** |
| | MR-SDCI+Q /ANO | 1.735 | 1.158 | 0.93 |
| | **MR-SDCI+Q+$E_{rel}$ /ANO** | **1.722** | **1.160** | **1.21** |
| Noro, *et al*.[1)] | MR-SDCI+Q /CGTF | 1.797 | 1.147 | 0.42 |
| Ricca, *et al*.[2)] | CCSD(T) /cc-pV5Z | 1.746 | 1.158 | -0.42 |
| Adamo and Lelj[3)] | B3LYP /DZ | 1.757 | 1.151 | 5.5 |
| **Exp**. | | | | |
| Vallalta & Leopold[4)] | | **1.727** | **1.159** | **3.25** |
| $^5\Sigma^-$ | | | | |
| Present | MR-ACPF /ANO | 1.868 | 1.151 | |
| | **MR-ACPF+$E_{rel}$ /ANO** | **1.855** | **1.153** | |
| | MR-SDCI+Q /ANO 1.857 | 1.151 | | |
| | **MR-SDCI+Q+$E_{rel}$ /ANO** | **1.844** | **1.153** | |
| Noro, *et al*.[1)] | MR-SDCI+Q /CGTF | 1.879 | 1.150 | |
| Ricca, *et al*.[2)] | CCSD(T) /cc-pV5Z | 1.860 | 1.149 | |
| Adamo and Lelj[3)] | B3LYP /DZ | 1.900 | 1.146 | |

1) T. Noro *et al.*, 2000 2) Ricca & Bauschlicher, 2001 3) Adamo & Lelj, 1995 4) Vallalta & Leopold, 1993

# $^3\Sigma^-$ and $^5\Sigma^-$ Electronic structures

How strong is the coupling between $3d_\sigma$ MO and $4s$ MO ?




$^3\Sigma^-$ $^5\Sigma^-$

Main Configuration CI Coefficient: 0.796 0.882

# FeCO Properties

Roos ANO (Fe, C, O)

σ-donation ($10a_1$), $3d_\pi$-π(CO*) back donation ($4b_1$ and $4b_2$)  Fe — (C ≡O)

| | $^3\Sigma^-$ | $^5\Sigma^-$ |
|---|---|---|
| Dipole moment / D from $\Delta E/\Delta Field$ (Expectation value) | | |
| MR-SDCI + $E_{rel}$ | -3.20 (-2.72) | -0.29 (-0.50) |
| MR-ACPF + $E_{rel}$ | -3.05 (-2.35) | -0.20 (-0.32) |
| Mulliken charge / *e* (MR-SDCI/[Wachters + *f* (Fe), aVTZ (C,O)]) | | |
| Fe | 0.432 | 0.395 |
| C | -0.341 | -0.285 |
| O | -0.092 | -0.110 |
| Ionicity of Fe-C bond (Electro-static) | Larger | Smaller |
| s-doantion, p-back donation (Covalently) | (L, L) | (S, S) |
| Bond lengths ($r_0$ form MORBID) | | |
| $r_0$(Fe-C) /Å | 1.724 | 1.845 |
| $r_0$(C-O) /Å | 1.164 | 1.157 |
| Frequency /cm$^{-1}$ (from MORBID) | | |
| $n_3$ (Fe-C stretch) | 551 | 482 |
| $n_1$ (C-O stretch) | 1954 | 1998 |

# FeCO $^3\Sigma^-$ MR-SDCI+Q+$E_{rel}$/[Roos ANO(Fe, C,O)]

## Perturbational Method with 3-Dimension PES

| | Calc. | Exp. $^3\Sigma^-$ |
|---|---|---|
| $r_e$(Fe-C) /Å | 1.7220 | 1.727($r_0$)[a] |
| $r_e$(C-O) /Å | 1.1599 | 1.159($r_0$)[a] |
| $a_e$(Fe-C-O)/deg | **180.0** | **180.0** |
| $B_e$ /MHz | 4382.5 | |
| $B_{0,}$ /MHz | **4374.2**[b] | **4363.88342(40)**[c] |
| $D_J$ / kHz | **1.11** | **1.21799(84)**[c] |
| $E_e$ /Eh | -1384.67301723 | |
| $\alpha_1$ / cm$^{-1}$ | 0.000750 | |
| $\alpha_2$ / cm$^{-1}$ | -0.000396 | |
| $\alpha_3$ / cm$^{-1}$ | 0.000593 | |
| $\omega_1$(C-O) /cm$^{-1}$ | 1972 | |
| $\omega_2$(Fe-C-O) /cm$^{-1}$ | 374 | |
| $\omega_3$(Fe-C) /cm$^{-1}$ | 566 | |
| $\mu_e$ /D | -3.20 | |
| (Expec. Value | -2.72) | |

| | Calc. | Exp. $^3\Sigma^-$ |
|---|---|---|
| $\omega_e x_e$(11) /cm$^{-1}$ | -9.69 | |
| $\omega_e x_e$ (22) /cm$^{-1}$ | 1.54 | |
| $\omega_e x_e$ (33) /cm$^{-1}$ | -6.56 | |
| $\omega_e x_e$(12) /cm$^{-1}$ | -5.29 | |
| $\omega_e x_e$ (13) /cm$^{-1}$ | 13.92 | |
| $\omega_e x_e$ (23) /cm$^{-1}$ | -6.99 | |
| $g_{22}$ /cm$^{-1}$ | -0.85 | |
| $\nu_1$(C-O) /cm$^{-1}$ | **1954** | **1950±10**[a] |
| $\nu_2$ (Fe-C-O) /cm$^{-1}$ | **372** | **330±50**[a] |
| $\nu_3$(Fe-C) /cm$^{-1}$ | **552** | **530±10**[a] |
| Zero-Point $E$. /cm$^{-1}$ | 1637.2 | |
| $\zeta_{12}$/cm$^{-1}$ | -0.97 | |
| $\zeta_{23}$/cm$^{-1}$ | -0.25 | |
| $\Lambda$-doubling/cm$^{-1}$ | 0.000152 | |

[a] Villalta and Leopold (1993) [b] Difference **0.24 %** [c] Tanaka, *et al.* (1997).

# FeCO $^3\Sigma^-$ and $^5\Sigma^-$ MR-SDCI+Q+$E_{rel}$/[Roos ANO(Fe, C,O)]

## Perturbational Method with 3-Dimension PES

| | $^3\Sigma^-$ | $^5\Sigma^-$ |
|---|---|---|
| $r_e$(Fe-C) /Å | 1.7220 | 1.8435 |
| $r_e$(C-O) /Å | 1.1599 | 1.1532 |
| $a_e$(Fe-C-O)/deg | 180.0 | 180.0 |
| $B_e$ /MHz | 4382.5 | 4012.7 |
| $B_{0,}$ /MHz | 4374.2 | 4012.4 |
| $D_J$ /kHz | 1.11 | 1.11 |
| $E_e$ /Eh | -1384.6730172 | -1384.6711414 |
| $\alpha_1$ / cm$^{-1}$ | 0.000750 | 0.000652 |
| $\alpha_2$ / cm$^{-1}$ | -0.000396 | -0000639 |
| $\alpha_3$ / cm$^{-1}$ | 0.000593 | 0.000643 |
| $\omega_1$(C-O) /cm$^{-1}$ | 1972 | 2027 |
| $\omega_2$(Fe-C-O) /cm$^{-1}$ | 374 | 258 |
| $\omega_3$(Fe-C) /cm$^{-1}$ | 566 | 495 |
| $\mu_e$ /D | -3.20 | -0.29 |
| (Expec. Value | -2.72 | -0.50) |

| | $^3\Sigma^-$ | $^5\Sigma^-$ |
|---|---|---|
| $\omega_e x_e$(11) /cm$^{-1}$ | -9.69 | -13.49 |
| $\omega_e x_e$ (22) /cm$^{-1}$ | 1.54 | 17.88 |
| $\omega_e x_e$ (33) /cm$^{-1}$ | -6.56 | -2.41 |
| $\omega_e x_e$(12) /cm$^{-1}$ | -5.29 | -6.33 |
| $\omega_e x_e$ (13) /cm$^{-1}$ | 13.92 | -4.45 |
| $\omega_e x_e$ (23) /cm$^{-1}$ | -6.99 | -64.20 |
| $g_{22}$ /cm$^{-1}$ | -0.85 | -16.16 |
| $\nu_1$(C-O) /cm$^{-1}$ | 1954 | 1992 |
| $\nu_2$ (Fe-C-O) /cm$^{-1}$ | 372 | 261 |
| $\nu_3$(Fe-C) /cm$^{-1}$ | 552 | 424? |
| Zero-Point *E*. /cm$^{-1}$ | 1637.2 | 1496.9 |
| $\zeta_{12}$/cm$^{-1}$ | -0.97 | -0.97 |
| $\zeta_{23}$/cm$^{-1}$ | -0.25 | -0.23 |
| $\Lambda$-doubling/cm$^{-1}$ | 0.000152 | 0.000159 |

# MORBID Frequency ($cm^{-1}$) $Fe^{12}CO$

MR-SDCI +Q + $E_{rel}$ 3D PES

| | $^3\Sigma^-$ | | | $^5\Sigma^-$ | |
|---|---|---|---|---|---|
| | MORBID | Perturb. | Exp. | MORBID | Perturb. |
| $\nu_1$(C-O str.) | 1954 | 1954 | 1950±10[a] | 1997 | 1992 |
| $\nu_2$(bend) | 370 | 372 | 330±50[a] | 259 | 261 |
| $\nu_3$(Fe-C str.) | 551 | 552 | 530±10[a] | 482 | 424 ? ($x_{23}$ = -64) |
| $B_0$ | 0.1464 | 0.1459 | 0.145563485(13)[b] | 0.1342 | 0.1338 |
| Error (%) | 0.57 | 0.24 | | | |

a) Villalta and Leopold (1993) b) Tanaka et al. (1997)

# MORBID Averaged Bond-length (Expectation value) $Fe^{12}CO$

MR-SDCI +Q + $E_{rel}$ 3D PES

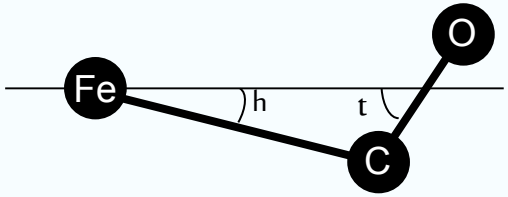
| $^3\Sigma^-$ | $\langle r_{FeC}\rangle$ | $\langle r_{CO}\rangle$ | $\langle r_{FeC}\cos\eta\rangle$ | $\langle r_{CO}\cos\tau\rangle$ |
|---|---|---|---|---|
| (0,0,0) | 1.724 | 1.164 | 1.721 | 1.157 |
| (1,0,0) | 1.725 | 1.172 | 1.722 | 1.165 |
| (0,1,0) | 1.730 | 1.165 | 1.727 | 1.153 |
| (0,2,0) | 1.727 | 1.164 | 1.722 | 1.145 |
| (0,0,1) | 1.732 | 1.163 | 1.729 | 1.156 |

| $^5\Sigma^-$ | $\langle r_{FeC}\rangle$ | $\langle r_{CO}\rangle$ | $\langle r_{FeC}\cos\eta\rangle$ | $\langle r_{CO}\cos\tau\rangle$ |
|---|---|---|---|---|
| (0,0,0) | 1.845 | 1.157 | 1.842 | 1.147 |
| (1,0,0) | 1.848 | 1.165 | 1.845 | 1.155 |
| (0,1,0) | 1.849 | 1.158 | 1.845 | 1.141 |
| (0,2,0) | 1.854 | 1.156 | 1.839 | 1.133 |
| (0,0,1) | 1.854 | 1.157 | 1.850 | 1.145 |

*cf.* Exp. (Villalta, et al. Photoelectron)

$r_{FeC}$ = 1.727 Å

$r_{CO}$ = 1.159 Å



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# まとめ

1. CASSCF軌道のaverageの仕方とMR-SDCIにおけるCI空間の取り方を工夫することで、$X\,^3\Sigma^-$、$^5\Sigma^-$のエネルギー差は 1.21 kcal/mol となって、過去の研究より精度よく見積もることが出来た。

2. **8σ, 9σ, 10σ の動的電子相関と相対論補正が大切。**

3. 構造は$r_{FeC}$が 1.722 Å、$r_{CO}$が1.160 Åとなって、実験値 ($r_{FeC}$ = 1.727 Å、$r_{CO}$ = 1.159 Å) をよく再現するようになった。

4. $^3\Sigma^-$の$B_0$ は、**0.2%**の誤差で実験値を再現できた。