Supplementary Material for:

Assignment of the Vibrational Spectra of Diiron Nonacarbonyl, $Fe_2(CO)_9$

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TABLE 1.—SELECTION RULES FOR $Fe_2(CO)_9$

C_{6h}^2	factor-group analysis[a]							
	A_g	B_g	E_{1g}	E_{2g}	A_u	B_u	E_{1u}	E_{2u}
T_A					1	0	1	0
T	0	1	0	1				
R	1	0	1	0	0	1	0	1
$\Gamma_{vib.}$	10	8	8	10	8	10	10	8
$\nu(CO)_t$	1	1	1	1	1	1	1	1
$\nu(CO)_b$	1	0	0	1	0	1	1	0
activities	Raman		Raman	Raman	i.r.		i.r.	

T_A = acoustic modes, T = optic branch translatory modes, R = libratory modes, $\Gamma_{vib.}$ = internal vibrational modes of two coupled molecules. t = terminal, b = bridging.

correlations

molecule, D_{3h} ⟶ site, C_{3h} $\xrightarrow{x2}$ crystal, C_{6h}^2

$7A_1'$ (Raman)
$3A_2'$ ⟶ $10A'$ (Raman) $10(A_g + B_u)$

$10E'$ (Raman, i.r.) $\quad$ $10E'$ (Raman, i.r.) $\quad$ $10(E_{2g} + E_{1u})$

$2A_1''$
$6A_2''$ (i.r.) ⟶ $8A''$ (i.r.) $\qquad$ $8(B_g + A_u)$

$8E''$ (Raman) $\qquad$ $8E''$ (Raman) $\quad$ $8(E_{1g} + E_{2u})$

[a] Based upon $P6_3/m \equiv C_{6h}^2$, $z = 2$,

TABLE 2.—MODE NUMBERING FOR $Fe_2(CO)_9$

D_{3h}	A_1'	A_2'	E'	A_1''	A_2''	E''
$\nu(CO)_t$	ν_1		ν_{11}		ν_{23}	ν_{29}
$\nu(CO)_b$	ν_2		ν_{12}			
$\delta(FeCO)_t$	ν_3	ν_8	$\nu_{13,14}$	ν_{21}	ν_{24}	$\nu_{30,31}$
$\delta(FeCO)_b$		ν_9	ν_{15}		ν_{25}	ν_{32}
$\nu(Fe-C)_t$	ν_4		ν_{16}		ν_{26}	ν_{33}
$\nu(Fe-C)_b$ [a]	ν_5		ν_{17}			
$\delta(CFeC)_t$	ν_6	ν_{10}	$\nu_{18,19}$	ν_{22}	ν_{27}	$\nu_{34,35}$
$\Delta(Fe_2C_3)$ [a]	ν_7		ν_{20}		ν_{28}	ν_{36}
total	7	3	10	2	6	8

[a] These two rows together describe the modes of the Fe_2C_3 cluster. The distinction between $\nu(Fe-C)_b$ and $\Delta(Fe_2C_3)$ modes is for accounting purposes only and is unlikely to be an accurate reflection of the truth.

Figure S1. The selection rules and mode numbering for $Fe_2(CO)_9$. Note that the correlations (middle part) are for the internal modes only, the lattice modes are not included. Reproduced from [1] with permission of the Royal Society of Chemistry.

Table S1. Comparison of the observed and calculated geometries for the isolated molecule (Gaussian) and periodic calculations (CASTEP) of $Fe_2(CO)_9$.

	Expt. [2]	Jang et al. [3] [a] BP86/DZP	Jang et al. [3] [a] B3LYP/DZP	This work [b] B3LYP/aug-ccVTZ	This work CASTEP
Distances / Å[d]					
Fe–Fe′	2.523	2.5188	2.5253	2.5227	2.5071
Fe–C(1)	1.835	1.8186	1.8288	1.8286	1.8026
Fe–C(2)	2.013	2.066	2.0076	1.9998	1.9897
C(1)–O(1)	1.127	1.1664	1.1516	1.1382	1.1540
C(2)–O(2)	1.160	1.1862	1.1756	1.1634	1.1772
Angles / °					
Fe–Fe′–C(1)	120.9			120.5	121.3
Fe′–C(2)–Fe	77.6			78.2	78.1
C(1)–Fe–C(1′)	96.1	95.9	96.4	96.5	95.5
C(2)–Fe–C(2′)	84.9			84.4	84.5
Fe–C(1)–O(1)	177.1	176.9	177.5	177.6	176.7
Fe–C(2)–O(2)	141.2			140.9	140.9

[a] D_{3h} symmetry imposed on the molecule (isolated molecule calculation). [b] C_{3h} symmetry imposed on the molecule (isolated molecule calculation). [c] Periodic calculation of the complete unit cell. [d] Primes indicate symmetry related atoms. C(1) and C(2) are terminal and bridging carbons respectively. O(1) and O(2) are the oxygen atoms attached to C(1) and C(2) respectively.

Table S2. Transition energies, infrared intensities and assignments for $Fe_2(CO)_9$ from a periodic-DFT (CASTEP) calculation.

Transition energy/cm⁻¹	Average [a]/cm⁻¹	Range [b]/cm⁻¹	Infrared intensity/km mol⁻¹	IR active?	Raman active?	C_{3h}	D_{3h}	Assignment
0			0.00	N	N	E1u	E'	Acoustic translation
0			0.00	N	N	E1u	E'	Acoustic translation
0			0.00	N	N	Au	A2"	Acoustic translation
30			0.00	N	Y	E2g	E'	Optic translation
30			0.00	N	Y	E2g	E'	Optic translation
51			0.00	N	N	Bg	A2"	Optic translation
65			0.00	N	N	E2u	E"	Libration
65			0.00	N	N	E2u	E"	Libration
70			0.00	N	Y	E1g	E"	Libration
70			0.00	N	Y	E1g	E"	Libration
77			0.00	N	N	Bu	A2'	Libration
86	86	1	0.00	N	Y	E2g	E'	ν20
86			0.00	N	Y	E2g	E'	ν20
86			0.29	Y	N	E1u	E'	ν20
86			0.29	Y	N	E1u	E'	ν20
87			0.00	N	Y	Ag	A2'	Libration
87	93	11	0.54	Y	N	Au	A1"	ν22
88	90	4	0.00	N	Y	E1g	E"	ν36
88			0.00	N	Y	E1g	E"	ν36
92			0.00	N	N	E2u	E"	ν36
92			0.00	N	N	E2u	E"	ν36
99			0.00	N	N	Bg	A1"	ν22
105	106	2	0.92	Y	N	E1u	E'	ν19
105			0.92	Y	N	E1u	E'	ν19
107			0.00	N	Y	E2g	E'	ν19
107			0.00	N	Y	E2g	E'	ν19
117	123	11	0.00	N	N	Bu	A1'	ν7
118	119		0.00	N	N	E2u	E"	ν35
118			0.00	N	N	E2u	E"	ν35
119			0.00	N	Y	E1g	E"	ν35
119			0.00	N	Y	E1g	E"	ν35
128			0.00	N	Y	Ag	A1'	ν7
129	135	12	0.00	N	N	Bu	A2'	ν10
131	133	5	0.00	N	Y	E2g	E'	ν18
131			0.00	N	Y	E2g	E'	ν18
135			3.82	Y	N	E1u	E'	ν18
135			3.82	Y	N	E1u	E'	ν18
138	141	7	5.84	Y	N	Au	A2"	ν28
141			0.00	N	Y	Ag	A2'	ν10
145			0.00	N	N	Bg	A2"	ν28
172	172	0	0.00	N	Y	E1g	E"	ν34
172			0.00	N	Y	E1g	E"	ν34
172			0.00	N	N	E2u	E"	ν34
172			0.00	N	N	E2u	E"	ν34
250	251	2	15.94	Y	N	Au	A2"	ν27
252			0.00	N	N	Bg	A2"	ν27
269	269	1	0.00	N	N	Bu	A1'	ν6
270			0.00	N	Y	Ag	A1'	ν6
325	325	0	0.00	N	Y	E1g	E"	ν33
325			0.00	N	Y	E1g	E"	ν33
326			0.00	N	N	E2u	E"	ν33
326			0.00	N	N	E2u	E"	ν33
383	383	1	0.00	N	N	Bu	A2'	ν9
383			0.00	N	Y	Ag	A2'	ν9
396	396	0	10.41	Y	N	E1u	E'	ν17
396			10.41	Y	N	E1u	E'	ν17
396			0.00	N	Y	E2g	E'	ν17
396			0.00	N	Y	E2g	E'	ν17
420	420	0	0.00	N	N	Bu	A1'	ν5

420			0.00	N	Y	Ag	A1'	ν5
431	432	1	0.05	Y	N	Au	A1"	ν21
432			0.00	N	N	Bg	A1"	ν21
444	444	1	31.93	Y	N	E1u	E'	ν16
444			31.93	Y	N	E1u	E'	ν16
445			0.00	N	Y	E2g	E'	ν16
445			0.00	N	Y	E2g	E'	ν16
466	467	1	0.00	N	N	E2u	E"	ν32
466			0.00	N	N	E2u	E"	ν32
468			0.00	N	Y	E1g	E"	ν32
468			0.00	N	Y	E1g	E"	ν32
473	475	2	45.50	Y	N	Au	A2"	ν26
475			0.00	N	N	Bg	A2"	ν26
475	475	0	0.00	N	Y	E2g	E'	ν15
475			0.00	N	Y	E2g	E'	ν15
475			91.11	Y	N	E1u	E'	ν15
475			91.11	Y	N	E1u	E'	ν15
495	495	0	0.00	N	N	Bu	A1'	ν4
495			0.00	N	Y	Ag	A1'	ν4
501	502	1	0.00	N	Y	E1g	E"	ν31
501			0.00	N	Y	E1g	E"	ν31
502			0.00	N	N	E2u	E"	ν31
502			0.00	N	N	E2u	E"	ν31
519	519	0	0.00	N	N	Bu	A2'	ν8
519			0.00	N	Y	Ag	A2'	ν8
541	541	0	0.00	N	Y	E2g	E'	ν14
541			0.00	N	Y	E2g	E'	ν14
541			8.74	Y	N	E1u	E'	ν14
541			8.74	Y	N	E1u	E'	ν14
579	598	9	810.94	Y	N	Au	A2"	ν25
588			0.00	N	N	Bg	A2"	ν25
611	612	1	0.00	N	N	E2u	E"	ν30
611			0.00	N	N	E2u	E"	ν30
612			0.00	N	Y	E1g	E"	ν30
612			0.00	N	Y	E1g	E"	ν30
625	626	1	1011.37	Y	N	E1u	E'	ν13
625			1011.37	Y	N	E1u	E'	ν13
626			0.00	N	Y	E2g	E'	ν13
626			0.00	N	Y	E2g	E'	ν13
643	643	1	0.00	N	Y	Ag	A1'	ν3
644			0.00	N	N	Bu	A1'	ν3
661	692	62	2749.55	Y	N	Au	A2"	ν24
723			0.00	N	N	Bg	A2"	ν24
1809	1809	0	5494.12	Y	N	E1u	E'	ν12
1809			5494.12	Y	N	E1u	E'	ν12
1809			0.00	N	Y	E2g	E'	ν12
1809			0.00	N	Y	E2g	E'	ν12
1875	1875	0	0.00	N	Y	Ag	A1'	ν2
1875			0.00	N	N	Bu	A1'	ν2
1976	1976	0	0.00	N	N	E2u	E"	ν29
1976			0.00	N	N	E2u	E"	ν29
1976			0.00	N	Y	E1g	E"	ν29
1976			0.00	N	Y	E1g	E"	ν29
1978	1978	0	4704.47	Y	N	E1u	E'	ν11
1978			4704.47	Y	N	E1u	E'	ν11
1979			0.00	N	Y	E2g	E'	ν11
1979			0.00	N	Y	E2g	E'	ν11
2017	2038	42	5808.27	Y	N	Au	A2"	ν23
2058			0.00	N	N	Bg	A2"	ν23
2074	2074	1	0.00	N	Y	Ag	A1'	ν1

[a] Average of the factor group components. [b] Difference between highest and lowest factor group components.

References

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