

Structure and Dynamics of Iron Pentacarbonyl

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1. The Energy-Factored Force Field for Metal Carbonyls

The Energy-Factored Force Field for Metal Carbonyls is well known, but it is useful to summarise it here in order to appreciate the application to the Fe(CO)₅ dynamics. In general, vibrational eigenvalues λ are obtained by solving the secular equation¹

$$| \mathbf{F} \cdot \mathbf{G} - \lambda \cdot \mathbf{E} | = 0 \quad \text{or} \quad | \mathbf{F} - \lambda \cdot \mathbf{G}^{-1} | = 0$$

In the energy-factored CO force field approximation,^{2,3,4,5} introduced by Cotton and Kraihanzel² for the treatment of the CO stretching vibrations of carbonyl metal complexes, it is assumed that the coupling between the CO oscillators is entirely non-mechanical. This assumption is valid because the CO groups do not have atoms in common. Hence, the $\mathbf{G}^{-1}$ matrix takes the diagonal form $\mathbf{G}_{\text{CO}}^{-1} = \mu_{\text{CO}} \cdot \mathbf{E}$, where μ_{CO} is the reduced mass of ¹²C¹⁶O, $[m(^{12}\text{C}) \cdot m(^{16}\text{O})] / [m(^{12}\text{C}) + m(^{16}\text{O})]$. In the following, the matrix $\mathbf{F}$ is termed $\mathbf{K}_{\text{CO}}$. It contains the so-called “energy-factored CO force field parameters”, k_{CO} (“CO stretching force constants”) and $k_{\text{CO,CO}}$ (“CO interaction constants”) being the diagonal and off-diagonal elements, respectively.

$$| \mathbf{K}_{\text{CO}} - \lambda \cdot \mu_{\text{CO}} \cdot \mathbf{E} | = 0$$

With the substitution $y = \lambda \cdot \mu_{\text{CO}}$,^{4,6} the secular equation reads

$$| \mathbf{K}_{\text{CO}} - y \cdot \mathbf{E} | = 0$$

where $y = (4 \cdot \pi^2 \cdot c_0^2 \cdot \mu_{\text{CO}} / N_A) \cdot (\tilde{\nu}_{\text{CO}})^2 = 4.0396 \cdot 10^{-4} \cdot (\tilde{\nu}_{\text{CO}})^2$,⁷ the units being cm⁻¹ for $\tilde{\nu}_{\text{CO}}$ and N·m⁻¹⁸ for y as well as for the elements of $\mathbf{K}_{\text{CO}}$. In most cases, the number of $\tilde{\nu}_{\text{CO}}$ data is not sufficient to evaluate the complete set of CO force field parameters. Cotton and Kraihanzel made assumptions about the relationships among the force constants in order to reduce their number. However, a full analysis is possible if additional data from isotopically substituted molecules (preferentially with ¹³C¹⁶O)¹ are obtained, which, in the following, are denoted as $^* \tilde{\nu}_{\text{CO}}$ and $^* y = 4.0396 \cdot 10^{-4} \cdot (^* \tilde{\nu}_{\text{CO}})^2$.

The $\mathbf{G}_{\text{CO}}^{-1}$ matrix for a ¹³C¹⁶O-labelled complex is denoted as $^* \mathbf{G}_{\text{CO}}^{-1}$. It contains the reduced mass of ¹³C¹⁶O ($^* \mu_{\text{CO}}$) in the labelled positions and the reduced mass of ¹²C¹⁶O (μ_{CO}) in the unlabelled positions. With Bor's notation⁶ for the ratio of the reduced masses of ¹²C¹⁶O and ¹³C¹⁶O, $a = \mu_{\text{CO}} /$

$^*\mu_{\text{CO}} = \{m(^{12}\text{C}) \cdot [m(^{13}\text{C}) + m(^{16}\text{O})]\} / \{m(^{13}\text{C}) \cdot [m(^{12}\text{C}) + m(^{16}\text{O})]\}$ ($a = 0.95591$),² it takes the form $^*\mathbf{G}_{\text{CO}}^{-1} = \mu_{\text{CO}} \cdot \mathbf{A}^{-1}$, where $\mathbf{A}$ is a diagonal matrix containing the factor a in the labelled position(s), the other elements being unity. Bearing in mind that the isotopic substitution leaves $\mathbf{K}_{\text{CO}}$ essentially unchanged, one obtains the secular equation

$$\left| \mathbf{K}_{\text{CO}} - ^*\lambda \cdot \mu_{\text{CO}} \cdot \mathbf{A}^{-1} \right| = 0 \quad \text{or} \quad \left| \mathbf{K}_{\text{CO}} - ^*y \cdot \mathbf{A}^{-1} \right| = 0$$

which, for convenience, is rearranged to

$$\left| \mathbf{A} \cdot \mathbf{K}_{\text{CO}} - ^*y \cdot \mathbf{E} \right| = 0 \quad \text{or} \quad \left| \mathbf{A}^{1/2} \cdot \mathbf{K}_{\text{CO}} \cdot \mathbf{A}^{1/2} - ^*y \cdot \mathbf{E} \right| = 0$$

2. Computer program for the evaluation of the energy-factored CO force field parameters

A computer program written in Fortran 77 (by B. Weimann, MPI für Kohlenforschung) is used to evaluate the energy-factored CO force field parameters k_{CO} and $k_{\text{CO,CO}}$ from the experimentally available frequency data $\tilde{\nu}_{\text{CO}}$ and $^*\tilde{\nu}_{\text{CO}}$ in an iterative fashion.

The input file includes:

- (i) The observed frequencies $\tilde{\nu}_{\text{CO}}$ and $^*\tilde{\nu}_{\text{CO}}$ along with individual weighting factors (≤ 1) which account for differing reliabilities of the experimental data. Bands with uncertain assignments or unobserved bands are introduced with estimated frequencies and very low weighting factors (routinely 10^{-8}).
- (ii) Information on the symmetry of the carbonyl metal unit, if applicable, which is given in the form of the indices of those $\mathbf{K}_{\text{CO}}$ matrix elements which have to be taken as identical.
- (iii) The factor $a^{1/2}$. Instead of the exact value $a^{1/2} = 0.97771$ a so-called "practical" or "effective" value may be introduced.^{9,3,12}

The program considers pre-set upper and lower limits for both the diagonal and off-diagonal elements of $\mathbf{K}_{\text{CO}}$. For each element, a finite number of equidistant values are taken, and all combinations of these values are forming a grid. For each node of this grid the eigenvalues of $\mathbf{K}_{\text{CO}}$ and of the various $\mathbf{A}^{1/2} \cdot \mathbf{K}_{\text{CO}} \cdot \mathbf{A}^{1/2}$ matrices are calculated. These calculated eigenvalues are compared with the experimental y and *y values, and the variance is determined. The node with the lowest variance is taken as the centre of a new, smaller grid, and the procedure is repeated until a given lower limit for the size of the grid is reached. Starting with the centre of this grid, the method of steepest descent is used to find the minimum of variance, *i.e.*, those values of the $\mathbf{K}_{\text{CO}}$ matrix elements which give the best fit to the observed $\tilde{\nu}_{\text{CO}}$ and $^*\tilde{\nu}_{\text{CO}}$ data.

The output file reports:

- (i) The final $\mathbf{K}_{\text{CO}}$ matrix elements k_{CO} and $k_{\text{CO,CO}}$.
- (ii) The eigenvalues of the final $\mathbf{K}_{\text{CO}}$ and $\mathbf{A}^{1/2} \cdot \mathbf{K}_{\text{CO}} \cdot \mathbf{A}^{1/2}$ matrices in the form of the calculated $\tilde{\nu}_{\text{CO}}$ and $^*\tilde{\nu}_{\text{CO}}$ data.

(iii) The eigenvector matrices $\mathbf{N}$ and $^*\mathbf{N}$ which, apart from diagonalizing $\mathbf{K}_{\text{CO}}$ ($\mathbf{y} \cdot \mathbf{E} = \mathbf{N}^T \cdot \mathbf{K}_{\text{CO}} \cdot \mathbf{N}$) and $\mathbf{A}^{1/2} \cdot \mathbf{K}_{\text{CO}} \cdot \mathbf{A}^{1/2}$ ($^*\mathbf{y} \cdot \mathbf{E} = ^*\mathbf{N}^T \cdot \mathbf{A}^{1/2} \cdot \mathbf{K}_{\text{CO}} \cdot \mathbf{A}^{1/2} \cdot ^*\mathbf{N}$), respectively, connect the internal CO stretching coordinates (r_i and *r_i , respectively) with the normal coordinates (Q_k and *Q_k , respectively): $\mathbf{r} = \mathbf{N} \cdot \mathbf{Q}$ and $^*\mathbf{r} = ^*\mathbf{N} \cdot ^*\mathbf{Q}$, respectively ($\mathbf{Q} = \mathbf{N}^T \cdot \mathbf{r}$ and $^*\mathbf{Q} = ^*\mathbf{N}^T \cdot ^*\mathbf{r}$, respectively).

It is worth pointing out that Jones¹³ raised objections to the use of the EFFF, but Turner and colleagues^{9,14} made a spirited defence, depending of course precisely on the circumstances in which it is used.

3. Eigenvector Matrix

The Eigenvector matrix $\mathbf{N}$ was obtained using band positions from FTIR spectra of $\text{Fe}(\text{CO})_5$ with natural isotope abundance. Spectra of both dilute and concentrated solutions were recorded in xenon as the solvent at low temperature (162 K), where the exchange mechanisms are very slow or not operational. The exact positions of six ν_{CO} and ν^*_{CO} stretches of the naturally, in sufficient abundance occurring isotopologs $\text{Fe}(^{12}\text{CO})_5$ $\{\text{Fe}(^{12}\text{CO})_5$ (2023.9 cm^{-1} , a_2'' and 1999.6 cm^{-1} , e') and $\text{Fe}(^{13}\text{CO})(^{12}\text{CO})_4$ $\{\text{axial isotopomer}$ 1988.5 cm^{-1} , low-freq. a_1 and 2106.1 cm^{-1} , high-freq. a_1 , and $\text{equatorial isotopomer}$ 1963.2 cm^{-1} , low-freq. a_1 and 2109.4 cm^{-1} , high-freq. $a_1\}$ could be gleaned from those spectra. Within the energy-factored CO force field approximation, this set of parameters is sufficient to determine, by a programmed iteration,¹⁵ the five k_{CO} and $k_{\text{CO},\text{CO}}$ force field parameters (k_{ax} , k_{eq} , $k_{\text{ax},\text{ax}}$, $k_{\text{eq},\text{eq}}$, $k_{\text{ax},\text{eq}}$) of the $\mathbf{K}_{\text{CO}}$ matrix (eq. 1) and the Eigenvector matrix $\mathbf{N}$ (eq. 2). The Eigenvalues $\mathbf{Y}$, $y_i = \lambda \cdot \mu_{\text{CO}}$, were obtained after diagonalization of $\mathbf{K}_{\text{CO}}$ (eq. 3) according to eq. 4.

$$\mathbf{K}_{\text{CO}} = \begin{pmatrix} k_{\text{eq}} & k_{\text{eq},\text{eq}} & k_{\text{eq},\text{eq}} & k_{\text{ax},\text{eq}} & k_{\text{ax},\text{eq}} \\ k_{\text{eq},\text{eq}} & k_{\text{eq}} & k_{\text{eq},\text{eq}} & k_{\text{ax},\text{eq}} & k_{\text{ax},\text{eq}} \\ k_{\text{eq},\text{eq}} & k_{\text{eq},\text{eq}} & k_{\text{eq}} & k_{\text{ax},\text{eq}} & k_{\text{ax},\text{eq}} \\ k_{\text{ax},\text{eq}} & k_{\text{ax},\text{eq}} & k_{\text{ax},\text{eq}} & k_{\text{ax}} & k_{\text{ax},\text{ax}} \\ k_{\text{ax},\text{eq}} & k_{\text{ax},\text{eq}} & k_{\text{ax},\text{eq}} & k_{\text{ax},\text{ax}} & k_{\text{ax}} \end{pmatrix} \quad (\text{eq. 1})$$

$$k_{\text{ax}} = 1698.1, k_{\text{eq}} = 1655.2, k_{\text{ax},\text{ax}} = 43.4, k_{\text{eq},\text{eq}} = 39.9, k_{\text{ax},\text{eq}} = 28.0$$

$$\mathbf{N} = \begin{pmatrix} 0.3984 & 0.3984 & 0.3984 & 0.5117 & 0.5117 \\ -0.4178 & -0.4178 & -0.4178 & 0.4880 & 0.4880 \\ 0 & 0 & 0 & 0.7071 & -0.7071 \\ 0.8165 & -0.4082 & -0.4082 & 0 & 0 \\ 0 & -0.7071 & 0.7071 & 0 & 0 \end{pmatrix} \quad (\text{eq. 2})$$

$$\begin{aligned} |\mathbf{K}_{\text{CO}} - \mathbf{y}_i \cdot \mathbf{E}| &= 0 \\ |\mathbf{A} \times \mathbf{K}_{\text{CO}} - \mathbf{y}_i^* \cdot \mathbf{E}| &= 0 \end{aligned} \quad (\text{eq. 3})$$

$$\mathbf{Y} = \mathbf{N} \times \mathbf{K}_{\text{CO}} \times \mathbf{N}^T = \begin{pmatrix} 1806.6 & -0.1 & 0.0 & 0.1 & 0.0 \\ -0.1 & 1669.5 & 0.0 & 0.1 & 0.0 \\ 0.0 & 0.0 & 1654.7 & 0.0 & 0.0 \\ 0.1 & 0.1 & 0.0 & 1615.2 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 1615.3 \end{pmatrix} \quad (\text{eq. 4})$$

4. Wavenumbers of individual CO stretching vibrations

The wavenumbers of the individual CO stretches can be calculated using eq. 5. Instead of the ideal ratio of the reduced masses $\mu_{\text{CO}} / \mu^*_{\text{CO}}$, $a = 0.95591$, the practical value of 0.95492 was used.¹⁶

$$\bar{\nu}_{\text{CO}} = \sqrt{\frac{\mathbf{y}_i \cdot \mathbf{N}_A}{4 \cdot \pi^2 \cdot c_0^2 \cdot \mu_{\text{CO}}}} = \begin{pmatrix} 2114.8 \\ 2032.9 \\ 2023.9 \\ 1999.6 \\ 1999.7 \end{pmatrix} \quad (\text{eq. 5})$$

5. Exchange Matrices

For the Berry pseudorotation, six equiprobable permutations have to be considered (Figs. S1 and S2).

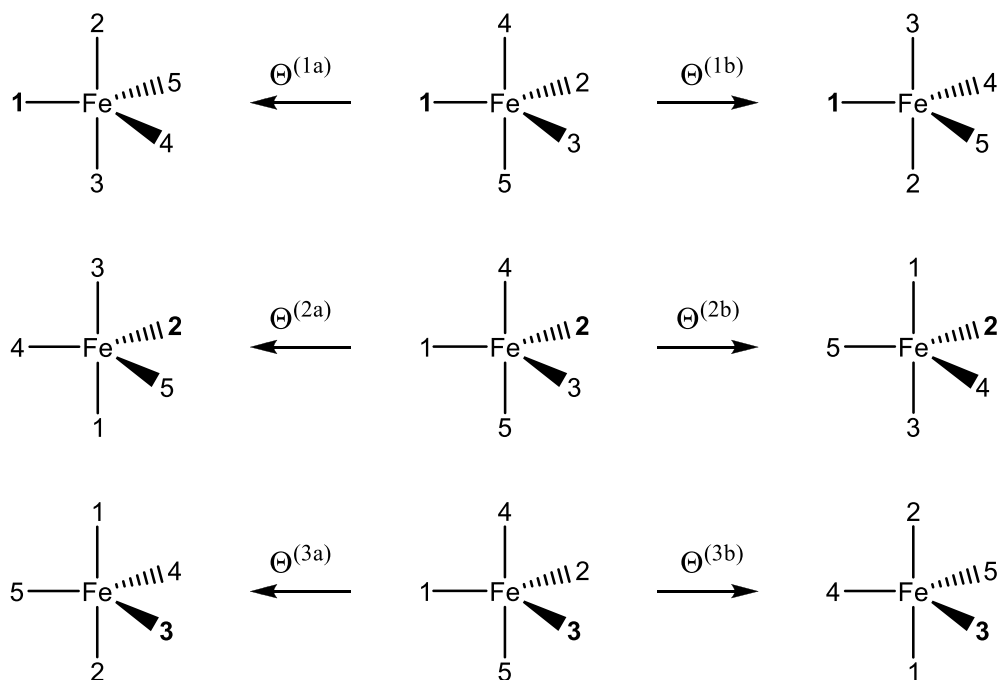


Fig. S1. Set of the equiprobable permutations of the carbonyl ligands (denoted 1 to 5) in $\text{Fe}(\text{CO})_5$ according to the Berry mechanism; pivot elements are set in bold face.

The transformations of the dipole moments during the CO site exchange are characterized by a set of permutation matrices laid out below for the Berry pseudorotation ($\Theta^{(1a)}$ to $\Theta^{(3b)}$, Fig. S1) with the pivot elements of **1**, **2**, and **3**, and either clockwise (*a*) or anti-clockwise (*b*) rotation as indicated.

$$\begin{aligned}
\Theta^{(1a)} &= \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \end{pmatrix} & \Theta^{(1b)} &= \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \end{pmatrix} \\
\Theta^{(2a)} &= \begin{pmatrix} 0 & 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \end{pmatrix} & \Theta^{(2b)} &= \begin{pmatrix} 0 & 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \end{pmatrix} \\
\Theta^{(3a)} &= \begin{pmatrix} 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \end{pmatrix} & \Theta^{(3b)} &= \begin{pmatrix} 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \end{pmatrix}
\end{aligned}$$

Fig. S2. Permutation matrices for the Berry pseudorotation in $\text{Fe}(\text{CO})_5$.

6. Z-matrices

Following the approach laid out previously,¹⁷ the dynamic effects arising from the exchange can be accounted for by the exchange term, in brief given here in matrix form,

$$\left(\frac{d\mathbf{D}}{dt} \right)_{\text{chemical-exchange}} = \mathbf{K} \cdot \mathbf{D} \quad (\text{eq. 6})$$

$$\mathbf{K} = \frac{k_{\text{react}}}{n} (\mathbf{Z} - \mathbf{1}) \quad (\text{eq. 7})$$

where $\mathbf{K}$ represents the exchange matrix that describes the rates at which the vibrational dipole moments of the different modes are interchanged. The $\mathbf{Z}$ matrices are calculated on the basis of the $\mathbf{N}$ and Θ matrices according to eq. 8. The evaluation of the individual permutations in the Berry and twist mechanisms, $\mathbf{Z}_i = (\mathbf{N} \times \Theta_i \times \mathbf{N}^T)^2$, yielded three pairs of identical $\mathbf{Z}_i$ matrices resulting from six equiprobable permutations in a given mechanism.

$$\bar{\mathbf{Z}} = \frac{1}{n} \sum_{i=1}^n (\mathbf{N} \times \Theta_i \times \mathbf{N}^T)^2 \quad (\text{eq. 8})$$

The matrices were averaged resulting in $\mathbf{Z}_{\text{Berry}}$ below.

$$\mathbf{Z}_{\text{Berry}, \dots} = \begin{pmatrix} 0.9490 & 0.0421 & 0.0000 & 0.0043 & 0.0043 \\ 0.0421 & 0.4109 & 0.0000 & 0.2735 & 0.2735 \\ 0.0000 & 0.0000 & 0.0000 & 0.5000 & 0.5000 \\ 0.0043 & 0.2735 & 0.5000 & 0.1667 & 0.0555 \\ 0.0043 & 0.2735 & 0.5000 & 0.0555 & 0.1667 \end{pmatrix}$$

The degenerate e'_x and e'_y components of the e' mode can be combined resulting in a reduced $\mathbf{Z}^{\text{red}}$ matrices, which reveals the major pathways of dipole moment exchange in the off-diagonal elements:

$$\mathbf{Z}_{\text{Berry}, \dots}^{\text{red}} = \begin{pmatrix} 0.9490 & 0.0421 & 0.0000 & 0.0086 \\ 0.0421 & 0.4109 & 0.0000 & 0.5470 \\ 0.0000 & 0.0000 & 0.0000 & 1.0000 \\ 0.0086 & 0.5470 & 1.0000 & 0.4444 \end{pmatrix}$$

The variable temperature spectra of $\text{Fe}(\text{CO})_5$ were simulated on the basis of eq. 9 with trial values of the rate constant k_{react} for the CO site exchange process, using the $\mathbf{K}$ matrix determined from eq. 1.

$$I(\omega) = \text{Re} \{ \sum_j V(-I\mu\{\Lambda_j\}, \text{Re}\{\Lambda_j\}, [G'_j]^{-1/2}) \sum_{\alpha, \alpha'} p_{\alpha} S_{\alpha j} S_{j \alpha'}^{-1} \} \quad (\text{eq. 9})$$

The required spectral parameters in the absence of exchange were adapted from the spectrum recorded at 162 K. In order to obtain the best possible fits, minor temperature-dependent modifications to the widths and spectral positions of the absorption bands had to be introduced.

7. Computational Details

Geometries for 'pristine' $\text{Fe}(\text{CO})_5$ were fully optimized at the BP86/AE1 level, *i.e.* employing the exchange and correlation functionals of Becke¹⁸ and Perdew,¹⁹ respectively, together with an ultrafine integration grid (a pruned grid with 99 radial shells with 590 angular points per shell) and the augmented Wachters basis²⁰ on Fe (8s7p4d) and 6-31G(d) basis elsewhere. Tight optimization convergence criteria were applied throughout. Starting from the transition states, the intrinsic reaction coordinate (IRC)²¹ was followed in internal (Z-Matrix) coordinates until (or close to) the respective minima (due to symmetry, only one such path needs to be followed), again using tight convergence criteria. Harmonic frequencies were computed analytically for the stationary points (minimum and transition state) as well as for selected points on the IRC, and are reported without scaling (see Table 4 in the main paper). These computations employed the Gaussian 03 program package.²²

In addition, the optimizations and frequency calculations for the stationary points for $\text{Fe}(\text{CO})_5$ and $\text{Fe}(\text{CO})_5 \cdots \text{Xe}$ were repeated at the BP86-D3/AE2 level, *i.e.* using the Grimme dispersion correction²³ with Becke-Johnson damping,²⁴ the same Wachters basis on Fe, 6-311+G(d,p) basis on C and O, and the aug-cc-pVTZ-PP basis together with the Stuttgart-Köln RSC-28-MDF relativistic effective core potential on Xe,²⁵ again using the ultrafine grid and tight convergence

criteria. Energies and frequencies for $\text{Fe}(\text{CO})_5 \cdots \text{Xe}$ were corrected for basis-set superposition error (BSSE) using the Counterpoise method for $\text{Fe}(\text{CO})_5$ and Xe fragments.²⁶ These frequencies were also used to calculate zero-point energies and thermodynamic corrections to enthalpies and free energies at 298 K. The scan in Figure 6 was obtained by fixing the $\text{Fe} \cdots \text{Xe}$ distance to selected values and relaxing all other parameters at the BP86-D3/AE2 level (including BSSE correction); the BP86/AE2 data were obtained by subtracting the -D3 correction from the BP86-D3/AE2 energies at each of the optimized points. These computations employed the Gaussian 09 program package.²⁷

To probe the reliability of DFT for the activation barrier under scrutiny, single-point calculations were performed at the coupled cluster singles-doubles-with-perturbatively-included-triples level, CCSD(T), the 'gold standard' in *ab initio* quantum chemistry. A slightly different basis was used for this purpose, namely a relativistic small-core effective core potential on Fe along with its (6s5p3d1f) valence basis, denoted SDD,²⁸ and Dunning's correlation-consistent cc-pVTZ basis elsewhere²⁹ (designated SDD/cc-pVTZ). At the BP86/SDD/cc-pVTZ level, the energy difference between the D_{3h} and C_{4v} stationary points is $2.0 \text{ kcal mol}^{-1}$ (involving full geometry optimisations at that level), very similar to the BP86-D3/AE2 result ($2.2 \text{ kcal mol}^{-1}$ in Table 2 in the main paper). At the CCSD(T)/SDD/cc-pVTZ level (employing BP86/SDD/cc-pVTZ structures), this energy difference is $2.0 \text{ kcal mol}^{-1}$, incidentally identical to the DFT result. There is, thus, no reason to doubt the applicability of DFT in this case.

Cartesian coordinates for the following computed geometries *etc.* $\text{Fe}(\text{CO})_5$ D_{3h} //BP86/AE1, $\text{Fe}(\text{CO})_5$ C_{4v} //BP86/AE1, 1 $\text{Fe}(\text{CO})_5$, IRC #1 (IRC 0.05), $\text{Fe}(\text{CO})_5$, IRC #1 (IRC 0.10), $\text{Fe}(\text{CO})_5$, IRC #1 (IRC 0.15), $\text{Fe}(\text{CO})_5$, IRC #1 (IRC 0.20), $\text{Fe}(\text{CO})_5$, IRC #1 (IRC 0.25), $\text{Fe}(\text{CO})_5$, IRC #1 (IRC 0.30), $\text{Fe}(\text{CO})_5$, IRC #1 (IRC 0.35), $\text{Fe}(\text{CO})_5$ D_{3h} //BP86-D3/AE2, $\text{Fe}(\text{CO})_5$ C_{4v} //BP86-D3/AE2, $\text{Fe}(\text{CO})_5 \cdots \text{Xe}$ C_s //BP86-D3/AE2 and $\text{Fe}(\text{CO})_5 \cdots \text{Xe}$ C_{4v} //BP86-D3/AE2 are provided in a separate file.

8. Details of spectral measurements and samples preparation

$\text{Fe}(\text{CO})_5$ was obtained from Aldrich and purified by trap-to-trap condensation prior to use. Argon (BOC pureshield grade) and Xenon (BOC, 99.9995%) were used as supplied. Infrared spectra (3500 cm^{-1} to 1200 cm^{-1}) were recorded at a resolution of 0.5 cm^{-1} with 64 scans of the interferogram on Thermo Nicolet Magna 2000 (at temperatures at and above r.t.) and Avatar FTIR spectrometers (*low temperatures*), using custom made miniature high-pressure stainless steel ($28 \text{ }^\circ\text{C}$ to 113°C)³⁰ and annealed copper IR cells (162 K to 316 K),³¹ which were adapted from published designs. In brief, for measurements at a constant density of 14.7 mol dm^{-3} , and *temperatures above r.t.*, the spectroscopic cell consisted of a threaded window holder and cell body, sealed by a teflon o-ring. The cell was equipped with an external heating jacket and indium-sealed CaF_2 windows of 10 mm thickness each. The optical path length was approximately 2 mm. The sample temperature was measured by a thermocouple housed within the cell in direct contact with the solution. A constant temperature in the solution was achieved (with fluctuations of no more than $\pm 0.05 \text{ K}$ above r.t., $\pm 0.2 \text{ K}$ below r.t.) by a proportional feedback temperature controller connected to the heating jacket. A connection to the filling and mixing station was made by small-diameter ($1/16^{\text{th}}$ inch) stainless steel tubing and high-pressure valves. The cell was directly

connected *via* stainless steel tubing to a pressure transducer (RDP electronics), and *via* a high pressure valve to a liquid nitrogen-cooled stainless steel cold finger and a gas filling station (see Fig. S3 for an outline). Prior to preparing a solution, the entire high pressure system was cleaned with pentane, followed by liquid CO₂ and then sealed and evacuated in HV overnight, then purged by repeated filling and venting cycles using compressed argon and, finally, pressure-tested up to 6000 psi argon. In order to load sample into the spectroscopic cell, the cell was charged with Fe(CO)₅ (by injecting neat Fe(CO)₅ through an opening behind valve V5) under argon and then sealed, briefly evacuated to remove all argon, after which xenon was admitted into the system. In order to reach a pressure of *ca.* 2000 psi, further xenon was compressed into the cell by carefully warming the cold finger containing liquid xenon.

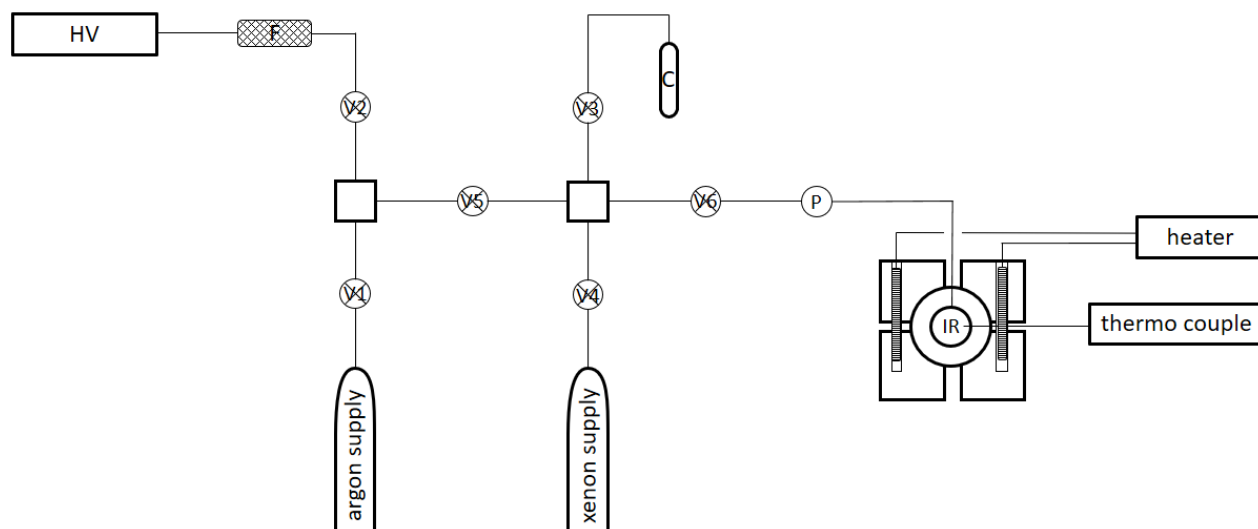


Fig. S3. Outline of the high-pressure manifold used to make solutions of Fe(CO)₅ in liquid and supercritical xenon, charge the optical high-pressure cell, and control the pressure; V1-V6, high-pressure valves; F, Al₂O₃ filter; C, cold finger; IR, optical high-pressure cell; P, pressure transducer; □ mixing chamber.

After each temperature increase, the pressure inside the closed system was adjusted (by expanding more xenon from the warmed-up cold finger into the cell) in order to maintain a constant density. This adjustment was needed since the entire apparatus expanded slightly and could not be heated between valve V6 and cell. Prior to each spectral measurement, the temperature was allowed to equilibrate for 20 minutes. No sample degradation was observed. At temperatures above *ca.* 110°C, the teflon o-ring started softening which made higher temperatures inaccessible. The cell for measurements at *low temperatures* consisted of two copper window holders, containing indium-sealed CaF₂ windows (5 mm thickness). The window holders were pushed against a circular lead seal by force of screws. After charging with Fe(CO)₅, the cell was mounted on a Displex He closed-cycle cryostat and protected by a high-vacuum shroud equipped with CaF₂ windows, and a solution was made by addition of gaseous xenon at low temperature *via* stainless steel tubing passing through the shroud (system similar to that shown in Fig. 3). Solutions were prepared with Fe(CO)₅ concentrations in the order of 10⁻³ mol dm⁻³, absorption maxima were kept well below unity. All spectra of a temperature series were normalised to an average area ($A_{av} = (\sum A_i)/n$, $i = 1$ to n) between

1970 cm^{-1} and 2050 cm^{-1} by the area under the spectral lines (A_i) between, using the normalisation factor $f = A_{\text{av}} / A_i$.

Table S1. Temperature / pressure conditions under which temperature-dependent IR-spectra were recorded

Temperature / °C	Pressure / psi	Density / (g cm^{-3}) ^a
28.4 - 28.4	2054 - 2054	14.67
36.5 - 36.5	2471 - 2470	14.67
45.1 - 45.1	2910 - 2909	14.67
53.6 - 53.7	3347 - 3349	14.67
61.4 - 61.5	3748 - 3749	14.67
70.1 - 70.2	4189 - 4190	14.67
78.3 - 73.4	4613 - 4612	14.67
86.3 - 86.3	5021 - 5022	14.67
94.8 - 94.9	5451 - 5461	14.67
103.2 - 103.3	5890 - 5882	14.67
112.8 - 112.9	6368 - 6375	14.67

^a density was assigned according to the pressure reading and the data available online at the NIST for Thermophysical Properties of Fluid Systems on Xenon.

Safety note: these experiments involve the use of high pressure and should be approached with due caution.

9. Spectra in liquid Xenon

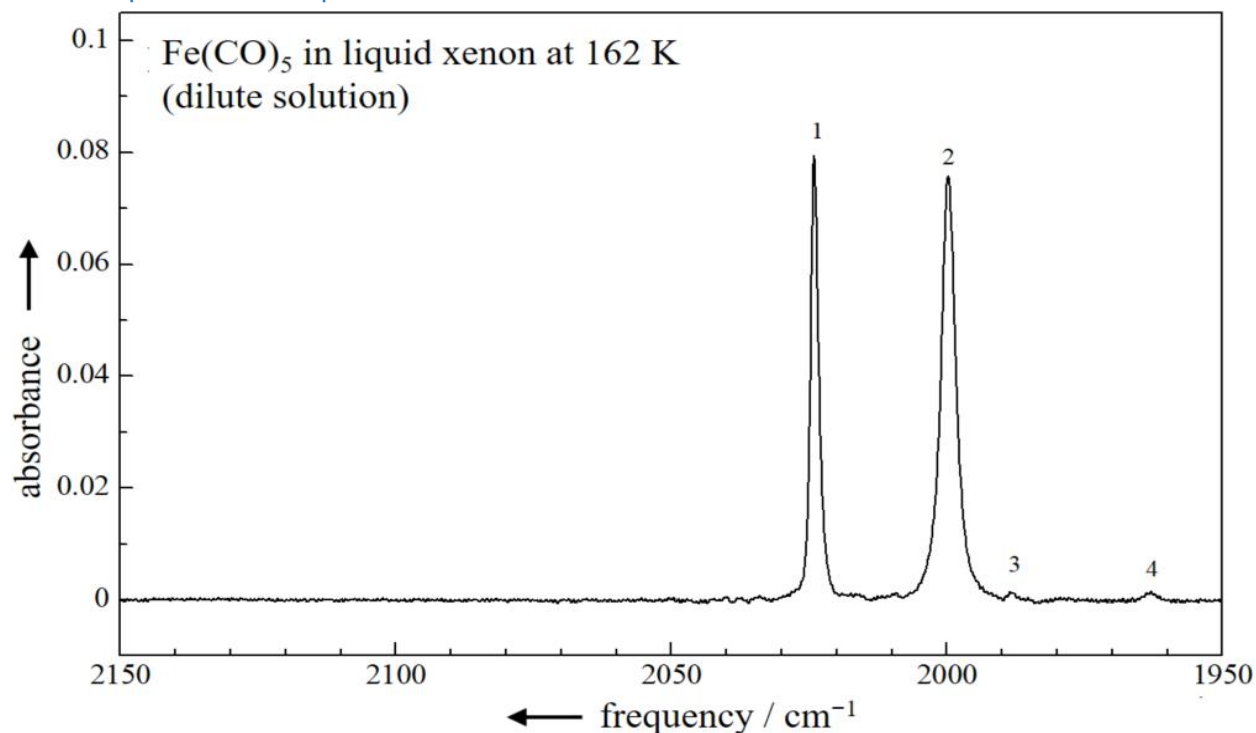


Fig. S4. FTIR spectrum (2150-1950 cm^{-1}) of $\text{Fe}(\text{CO})_5$ in liquid xenon at 162 K, dilute solution.

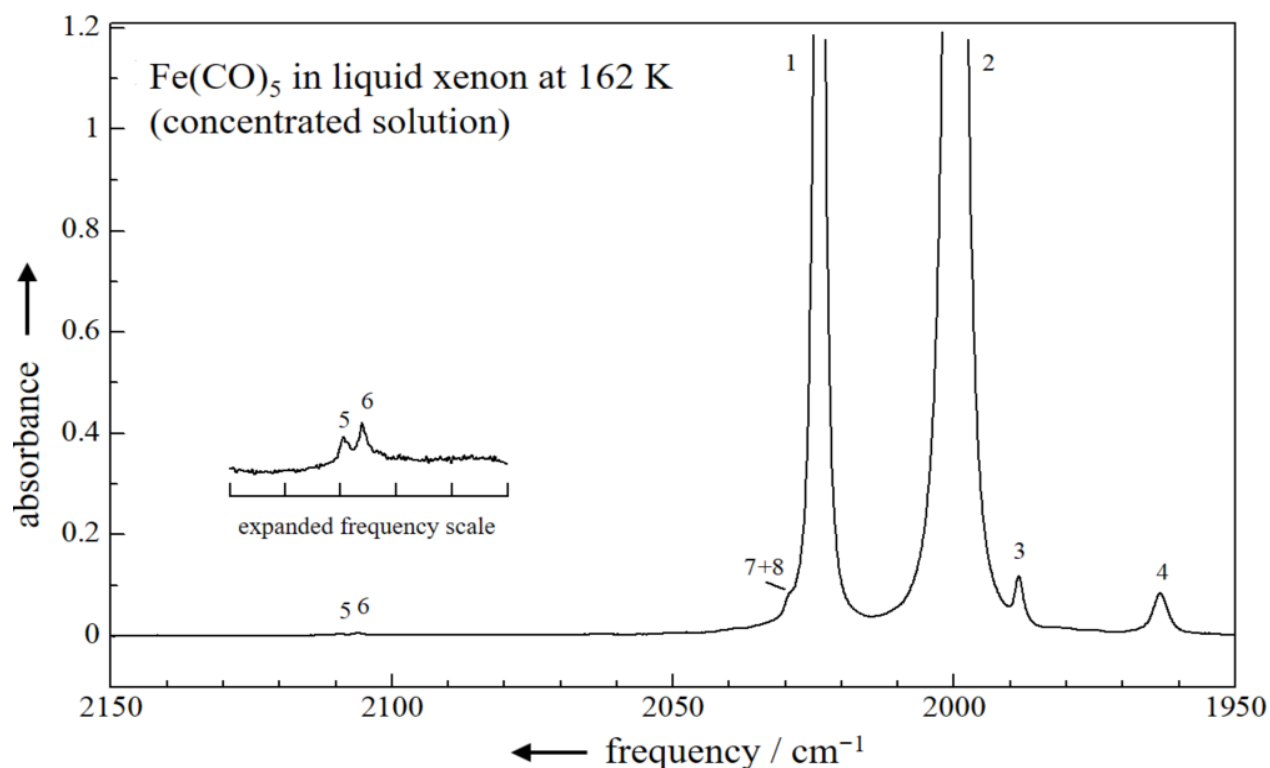


Fig. S5. FTIR spectrum (2150-1950 cm^{-1}) of $\text{Fe}(\text{CO})_5$ in liquid xenon at 162 K, concentrated solution.

The treatment of data for the derivation of the energy-factored force field is given below. The ligand sites in $\text{Fe}(\text{CO})_5$ are labelled 1, 2, 3 (equatorial positions, eq) and 4, 5 (axial positions, ax). According to this, the elements of the $\mathbf{K}_{\text{CO}}$ matrix take the following form: $k_{11} = k_{22} = k_{33} = k_{eq}$, $k_{44} = k_{55} = k_{ax}$, $k_{12} = k_{13} = k_{23} = k_{eq,eq}$, $k_{45} = k_{ax,ax}$, $k_{14} = k_{15} = k_{24} = k_{25} = k_{34} = k_{35} = k_{eq,ax}$.

The $\nu(\text{CO})$ vibrations of $\text{Fe}(\text{CO})_5$ in D_{3h} point group symmetry are: 2 a_1' (IR inactive), a_2'' (IR active), e' (IR active).

Samples of natural $\text{Fe}(\text{CO})_5$ contain primarily two stereo isotopomers, $\text{Fe}(\text{CO})_4(ax\text{-}^{13}\text{CO})$ and $\text{Fe}(\text{CO})_4(eq\text{-}^{13}\text{CO})$ with an abundance of 2.2 % and 3.3 %, respectively. They have the following $\nu(\text{CO})$ vibrational properties: $\text{Fe}(\text{CO})_4(ax\text{-}^{13}\text{CO})$ in C_{3v} point group symmetry, 3 a_1 , E (all IR active); $\text{Fe}(\text{CO})_4(eq\text{-}^{13}\text{CO})$ in C_{2v} point group symmetry, 3 a_1 , b_1 , b_2 (all IR active). Figure S4 shows next to the two bands of $\text{Fe}(\text{CO})_5$ (#1 and #2) two "isotope satellites" (#3 and #4). Curve fitting using Voigt profiles yields two intense bands of $\text{Fe}(\text{CO})_5$ at 2023.9 cm^{-1} (#1, a_2'' , rel. area 0.360, $w_G = 1.145 \text{ cm}^{-1}$, $w_L = 0.848 \text{ cm}^{-1}$) and 1999.6 cm^{-1} (#2, e' , at rel. area 0.640, $w_G = 1.897 \text{ cm}^{-1}$, $w_L = 1.816 \text{ cm}^{-1}$, which show no signs of broadening. Two isotopic satellites are assigned to $\text{Fe}(\text{CO})_4(ax\text{-}^{13}\text{CO})$ (#3, $\sim 1988.5 \text{ cm}^{-1}$; low frequency a_1) and $\text{Fe}(\text{CO})_4(eq\text{-}^{13}\text{CO})$ (#4, $\sim 1963.2 \text{ cm}^{-1}$, low frequency a_1). Furthermore, there are two weak bands (#5 and #6) in the high frequency region which are "satellites" of the high frequency a_1' vibration of $\text{Fe}(\text{CO})_5$. They are assigned to $\text{Fe}(\text{CO})_4(eq\text{-}^{13}\text{CO})$ (#5, 2109.4 cm^{-1} , high frequency a_1) and $\text{Fe}(\text{CO})_4(ax\text{-}^{13}\text{CO})$ (#6, 2106.1 cm^{-1} , high frequency a_1). At the high-frequency flank of the a_2'' band of $\text{Fe}(\text{CO})_5$ (#1), a

shoulder is discernible which we ascribe to the mid-frequency a_1 vibrations of $\text{Fe}(\text{CO})_4(ax\text{-}^{13}\text{CO})$ (#7) and $\text{Fe}(\text{CO})_4(eq\text{-}^{13}\text{CO})$ (#8).

These six observable frequencies (#1 to #6) are sufficient to determine the five CO force field parameters of $\text{Fe}(\text{CO})_5$. The calculations were carried out with the exact values of $a_1/2$ (0.97771) (i) and with the "practical" value (0.9772) used previously by Bor¹⁶ (ii). For comparison, Bor's values based on spectra in n-heptane are given (iii).

	(i)	(ii)	(iii)
$k_{\text{eq}} / \text{N}\cdot\text{m}^{-1}$	1653.2	1655.2	1657
$k_{\text{ax}} / \text{N}\cdot\text{m}^{-1}$	1696.7	1698.1	1695
$k_{\text{eq,eq}} / \text{N}\cdot\text{m}^{-1}$	38.4	39.9	40
$k_{\text{ax,ax}} / \text{N}\cdot\text{m}^{-1}$	42.0	43.4	41
$k_{\text{eq,ax}} / \text{N}\cdot\text{m}^{-1}$	29.5	28.0	28

Below are given the experimental values in comparison with those calculated.

$\text{Fe}(\text{CO})_5$ (D_{3h})	$\tilde{\nu}$ (exptl.) / cm^{-1}	$\tilde{\nu}$ (calcd.) / cm^{-1} (i) (ii)	
a_1'	(?) IR inactive	2114.9	2114.9
a_1'	(?) IR inactive	2028.3	2033.0
a_2''	2023.9 (#1)	2024.0	2023.9
e'	1999.6 (#2)	1999.4	1999.6

$\text{Fe}(\text{CO})_4(eq\text{-}^{13}\text{CO})$ (C_{2v})	$\tilde{\nu}$ (exptl.) / cm^{-1}	$\tilde{\nu}$ (calcd.) / cm^{-1} (i) (ii)	
a_1	2109.4 (#5)	2109.5	2109.4
a_1	(~2030, sh) ^a (#8)	2024.5	2028.9
b_1	(2023.9) ^b	2024.0	2023.9
b_2	(1999.6) ^c	1999.4	1999.6
a_1	1963.2 (#4)	1963.5	1963.2

^a overlap with #1, ^b coincides with #1 due to symmetry, ^c coincides due with #2 due to symmetry.

$\text{Fe}(\text{CO})_4(ax\text{-}^{13}\text{CO})$ (C_{3v})	$\tilde{\nu}$ (exptl.) / cm^{-1}	$\tilde{\nu}$ (calcd.) / cm^{-1} (i) (ii)	
a_1	2106.1 (#6)	2106.0	2106.1
a_1	(~2030, sh) ^a (#7)	2027.0	2030.5
e	(1999.6) ^b	1999.4	1999.6
a_1	1988.5 (#3)	1988.4	1988.5

^a overlap with #1, ^b coincidence with #2 due to symmetry.

Fe(CO)₅ (D_{3h})	Q_k	
	(i)	(ii)
a_1'	$0.3959(r_1 + r_2 + r_3) + 0.5147(r_4 + r_5)$	$0.3984(r_1 + r_2 + r_3) + 0.5117(r_4 + r_5)$
a_1'	$0.4203(r_1 + r_2 + r_3) - 0.4848(r_4 + r_5)$	$0.4178(r_1 + r_2 + r_3) - 0.4880(r_4 + r_5)$
a_2''	$0.7071(r_4 - r_5)$	$0.7071(r_4 - r_5)$
$e'(x)$	$0.8165(r_1) - 0.4082(r_2 + r_3)$	$0.8165(r_1) - 0.4082(r_2 + r_3)$
$e'(y)$	$0.7071(r_2 - r_3)$	$0.7071(r_2 - r_3)$

Fe(CO)₄(eq-¹³CO) (C_{2v})	*Q_k^a	
	(i)	(ii)
a_1	$0.2843(r_1) + 0.4041(r_2 + r_3) + 0.5444(r_4 + r_5)$	$0.2829(r_1) + 0.4052(r_2 + r_3) + 0.5439(r_4 + r_5)$
a_1	$0.1902(r_1) + 0.5327(r_2 + r_3) - 0.4451(r_4 + r_5)$	$0.2041(r_1) + 0.5286(r_2 + r_3) - 0.4469(r_4 + r_5)$
b_1	$0.7071(r_4 - r_5)$	$0.7071(r_4 - r_5)$
b_2	$0.7071(r_2 - r_3)$	$0.7071(r_2 - r_3)$
a_1	$0.9397(r_1) - 0.2301(r_2 + r_3) - 0.0746(r_4 + r_5)$	$0.9372(r_1) - 0.2375(r_2 + r_3) - 0.0668(r_4 + r_5)$

^a ¹³CO in Position 1. Die Koeffizienten von r_1 und r_2 bzw. von r_1 und r_3 sind zu vertauschen, wenn sich das ¹³CO in Position 2 bzw. 3 befindet.

Fe(CO)₄(ax-¹³CO) (C_{3v})	*Q_k^a	
	(i)	(ii)
a_1	$0.4332(r_1 + r_2 + r_3) + 0.3556(r_4) + 0.5574(r_5)$	$0.4383(r_1 + r_2 + r_3) + 0.3482(r_4) + 0.5501(r_5)$
a_1	$0.3526(r_1 + r_2 + r_3) - 0.0501(r_4) - 0.7902(r_5)$	$0.3538(r_1 + r_2 + r_3) - 0.0968(r_4) - 0.77843(r_5)$
$e(x)$	$0.8165(r_1) - 0.4082(r_2 + r_3)$	$0.8165(r_1) - 0.4082(r_2 + r_3)$
$e(y)$	$0.7071(r_2 - r_3)$	$0.7071(r_2 - r_3)$
a_1	$0.1461(r_1 + r_2 + r_3) - 0.9333(r_4) + 0.2547(r_5)$	$0.1269(r_1 + r_2 + r_3) - 0.9324(r_4) + 0.2868(r_5)$

^a ¹³CO in position 4. The coefficients r_4 and r_5 are to be swapped when ¹³CO is in position 5.

Fe(CO)₅, D_{3h}

$$S(a_1')_1 = 3^{-1/2}(r_1 + r_2 + r_3) = 0.5774(r_1 + r_2 + r_3)$$

$$S(a_1')_2 = 2^{-1/2}(r_4 + r_5) = 0.7071(r_4 + r_5)$$

$$S(a_2'') = Q(a'') = 2^{-1/2}(r_4 - r_5) = 0.7071(r_4 - r_5)$$

$$\begin{aligned}
S(e')_x = Q(e')_x &= 2 \times 6^{-1/2}(r_1) - 6^{-1/2}(r_2 + r_3) &= 0.8165(r_1) - 0.4082(r_2 + r_3) \\
S(e')_y = Q(e')_x &= 2^{-1/2}(r_2 - r_3) &= 0.7071(r_2 - r_3)
\end{aligned}$$

Fe(CO)₄(eq-¹³CO), C_{2v}, ¹³CO in Position 1

$$\begin{aligned}
S(a_1)_1 &= r_1 \\
S(a_1)_2 &= 2^{-1/2}(r_2 + r_3) &= 0.7071(r_2 + r_3) \\
S(a_1)_3 &= 2^{-1/2}(r_4 + r_5) &= 0.7071(r_4 + r_5) \\
S(b_1) = Q(b_1) &= 2^{-1/2}(r_4 - r_5) &= 0.7071(r_4 - r_5) \\
S(b_2) = Q(b_2) &= 2^{-1/2}(r_2 - r_3) &= 0.7071(r_2 - r_3)
\end{aligned}$$

Fe(CO)₄(ax-¹³CO), C_{3v}, ¹³CO in Position 4

$$\begin{aligned}
S(a_1)_1 &= 3^{-1/2}(r_1 + r_2 + r_3) &= 0.5774(r_1 + r_2 + r_3) \\
S(a_1)_2 &= r_4 \\
S(a_1)_3 &= r_5 \\
S(e)_x = Q(e)_x &= 2 \cdot 6^{-1/2}(r_1) - 6^{-1/2}(r_2 + r_3) &= 0.8165(r_1) - 0.4082(r_2 + r_3) \\
S(e)_y = Q(e)_x &= 2^{-1/2}(r_2 - r_3) &= 0.7071(r_2 - r_3)
\end{aligned}$$

10. Spectra in supercritical Xe - experimental versus simulated

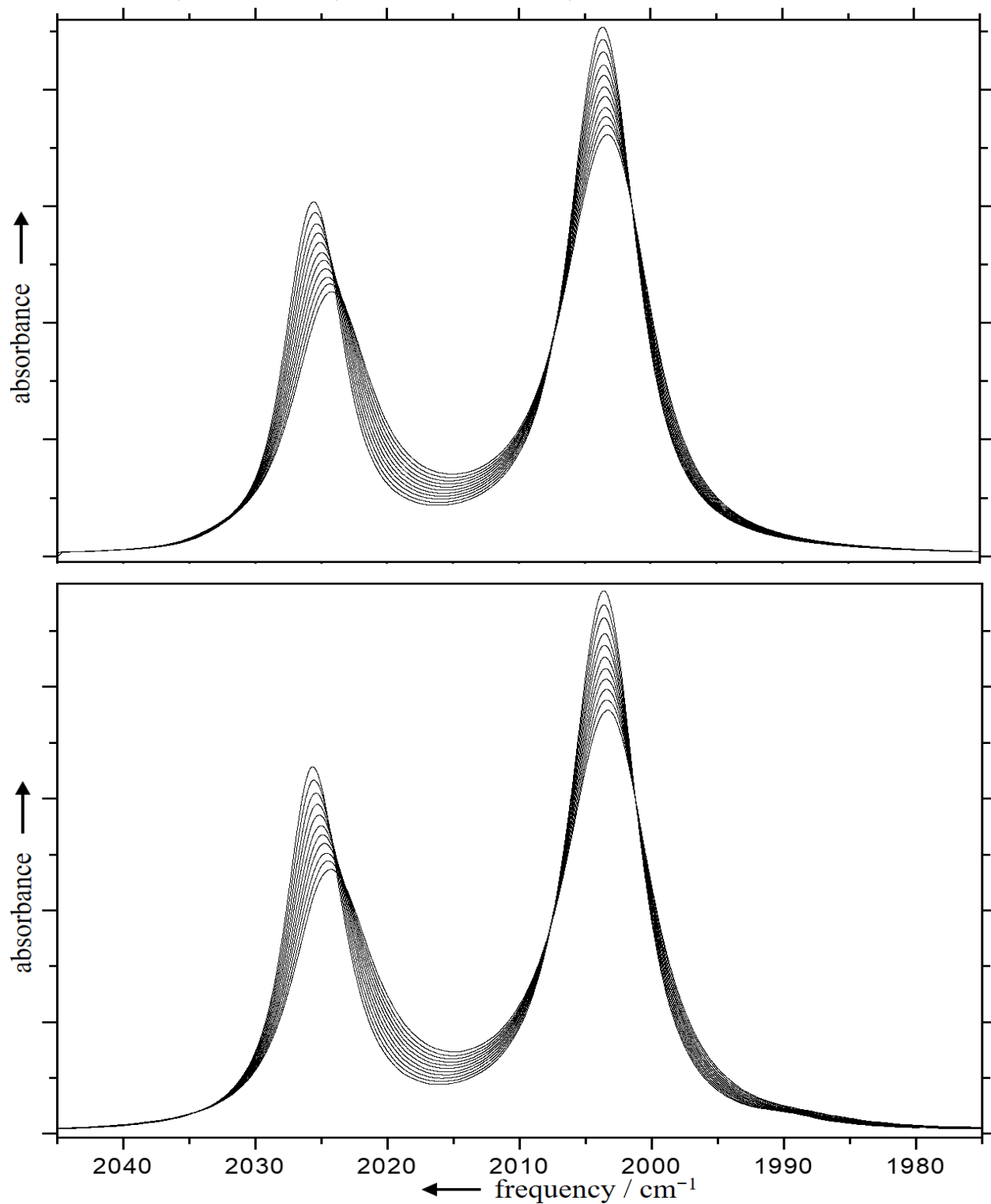


Fig. S6. 1975-2045 cm^{-1} section of the temperature-dependent IR spectra of $\text{Fe}(\text{CO})_5$ in supercritical xenon in the temperature interval 302 K to 386 K (*top*, simulated; *bottom* recorded at an optical resolution of 0.5 cm^{-1}).

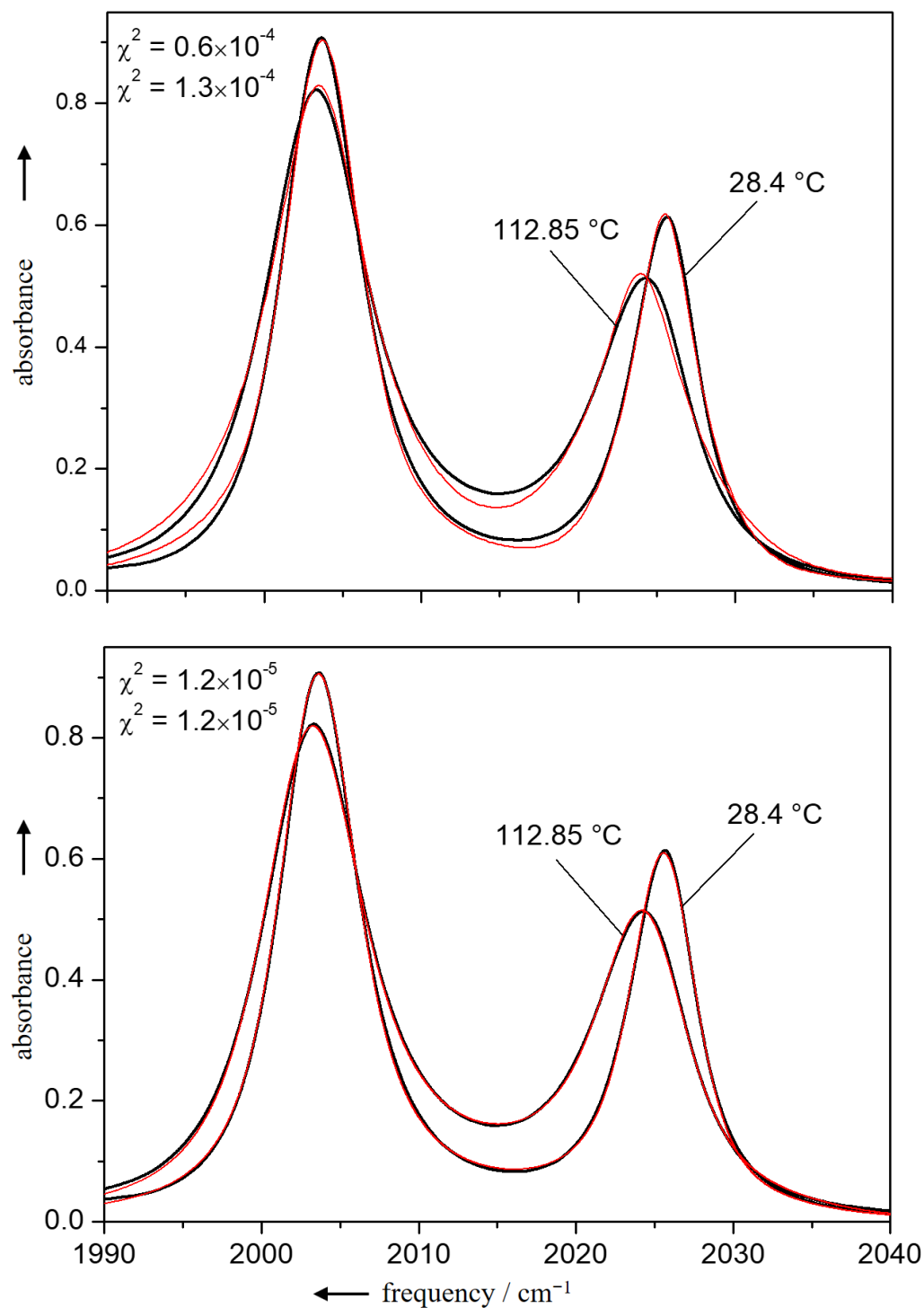


Fig. S7. Fit of experimentally determined spectra (—) by the sum of two Voigt profiles (—) (*top*) vs. the simulated spectra (—) (*bottom*) at ~302 K and ~386 K; the sum of χ^2 values (— vs. —) displayed top left.

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- [8] This SI unit differs from the formerly used unit $\text{mdyn} \cdot \text{\AA}^{-1}$ by a factor of 100: $1 \text{ mdyn} \cdot \text{\AA}^{-1} = 100 \text{ N} \cdot \text{m}^{-1}$.
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- [10] Calculated with $m(^{12}\text{C}) = 12.0000 \text{ g} \cdot \text{mol}^{-1}$, $m(^{16}\text{O}) = 15.994915 \text{ g} \cdot \text{mol}^{-1}$, and $m(^{13}\text{C}) = 13.003355 \text{ g} \cdot \text{mol}^{-1}$.
- [11] Numerical values can be obtained from the frequencies of all CO stretching vibrational modes of the unlabelled parent complex and of one of its partially ^{13}CO -labelled isotopomers.
- [12] In an early study of ^{13}CO -enriched $\text{Fe}(\text{CO})_5$, for example, a "practical" value of $a^{1/2} = 0.9772$ was used: see ref. 16.
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