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Supporting Material: On the Discrepancy between Theory and Experiment for the F-F Spin-spin Coupling Constant of Difluoroethyne†

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1 Derivation of the vibrational corrections

When describing the vibrational motion of a molecule and the influence of this motion on molecular properties, a simple approach is to use Taylor expansions. The molecular property of interest is expressed as an expansion in some set of generalised nuclear coordinates, all that is needed, in order to determine the vibrational correction, is a vibrational wavefunction of the molecule expressed in the same set of coordinates. Thus we'll briefly consider how to define an appropriate set of coordinates in which to express our vibrational wavefunction and consequently the expansion of the property surface.

In order to obtain a vibrational wavefunction, a potential energy surface for the nuclear motion is required, which is often expressed in terms of a Taylor expansion. For a set of displacement coordinates $\boldsymbol{\xi}$, implying $\boldsymbol{\xi} = \mathbf{0}$ at the equilibrium geometry, the potential energy surface can then be expanded around the equilibrium geometry *, as

$$\begin{aligned} V(\boldsymbol{\xi}) =& V_{eq} + \frac{1}{2}\sum_{i,j}^{3N} \frac{\partial^2 V}{\partial \xi_i \partial \xi_j}\Big|_{eq} \xi_i \xi_j \\ &+ \frac{1}{6}\sum_{i,j,k}^{3N} \frac{\partial^3 V}{\partial \xi_i \partial \xi_j \partial \xi_k}\Big|_{eq} \xi_i \xi_j \xi_k \ldots \end{aligned} \tag{1}$$

It is advantageous to introduce massweighted coordinates, $\boldsymbol{\eta} = \mathbf{m}^{\frac{1}{2}}\boldsymbol{\xi}$, where $\mathbf{m}$ is a diagonal matrix with the nuclear masses on the diagonal. Using those, the quadratic term of the potential can be written in matrix form as

$$\frac{1}{2}\boldsymbol{\eta}^{\mathbf{T}}\mathbf{F}\boldsymbol{\eta} \quad \text{where} \quad F_{i,j} = \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 V}{\partial \xi_i \partial \xi_j}\Big|_{eq} \tag{2}$$

Since the matrix $\mathbf{F}$ is real and symmetric, a unitary matrix $\mathbf{L}$ can be found so that $\mathbf{L^T F L} = \mathbf{D}$ is diagonal. $\mathbf{F}$ will have an eigenvalue that is zero for every translational and rotational degree of freedom (5 for a linear molecule, 6 otherwise). From the eigenvectors one can define normal coordinates, $\mathbf{Q} = \mathbf{L^T}\boldsymbol{\eta}$, and the quadratic term in the potential then becomes

$$V = \frac{1}{2}\boldsymbol{\eta}^{\mathbf{T}}\mathbf{F}\boldsymbol{\eta} = \frac{1}{2}\boldsymbol{\eta}^{\mathbf{T}}\mathbf{LDL^T}\boldsymbol{\eta} = \frac{1}{2}\mathbf{Q^T D Q} = \frac{1}{2}\sum_i D_{ii} Q_i^2 \tag{3}$$

The diagonal elements of $\mathbf{D}$ corresponding to vibrational degrees of freedom are related to the square of the corresponding harmonic frequency. In wavenumber units the harmonic frequency is given by

$$2\pi c \omega_i = \sqrt{\frac{\partial^2 V}{\partial Q_i^2}} = \sqrt{D_{ii}} \tag{4}$$

Another type of coordinate that is often encountered is the reduced normal coordinate, a unitless quantity we shall denote q and define from the above as

$$q_i = \sqrt{\frac{2\pi c \omega_i}{\hbar}} Q_i \tag{5}$$

In order to accurately describe vibrational motion, anharmonic terms in the expansion 1 have to be taken into account. In the above defined coordinates, one can define the cubic force constant as

$$k_{ijj} = \frac{1}{hc}\frac{\partial^3 V}{\partial q_i \partial q_j^2} = \frac{1}{\omega_j}\frac{\partial \omega_j^2}{\partial q_i} = 2\frac{\partial \omega_j}{\partial q_i}, \tag{6}$$

or alternatively in terms of Q coordinates:

$$K_{ijj} = \frac{1}{hc}\frac{\partial^3 V}{\partial Q_i \partial Q_j^2} = \frac{2\pi c}{\hbar}\cdot 2\omega_j \frac{\partial \omega_j}{Q_i} = \left(\frac{2\pi c}{\hbar}\right)^{3/2} \omega_j \sqrt{\omega_i} k_{ijj} \tag{7}$$

The cubic force constants, k_{ijj}, can be calculated, as described in ref[2], from analytic harmonic force constants by noting that

$$\frac{\partial \omega_j^2}{\partial q_i} = \frac{1}{(2\pi c)^2}\frac{\partial D_{jj}}{\partial q_i} = \frac{1}{(2\pi c)^2}\left(\mathbf{L^T}\frac{\partial \mathbf{F}}{\partial q_i}\mathbf{L}\right)_{jj} \tag{8}$$

and then differentiating the force constant matrix numerically.†

The vibrational motion of the molecule is then described on the basis of an harmonic oscillator in each normal coordinate, while the the higher order terms in the expansion of the

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* Åstrand et al.[1] have described how to handle a general expansion point.

† Since transforming with $\mathbf{L}$ will in general not diagonalize a force constant matrix $\mathbf{F}$ calculated at a displaced geometry, the above procedure can also yield cubic force constants with three different indexes, which, however, are not needed for the present purpose.

potential are added as perturbations:

$$\hat{H}^{(0)} = \sum_i \hat{H}_i = \sum_i -\frac{\hbar^2}{2}\frac{\partial^2}{\partial Q_i^2} + 2\pi^2 c^2 \omega_i^2 Q_i^2 \quad (9)$$

$$\hat{H}^{(1)} = \frac{1}{6}\sum_{i,j,k} hcK_{i,j,k} Q_i Q_j Q_k \quad (10)$$

$$\vdots \qquad \vdots \quad (11)$$

The a zero-order wavefunction is then a product of harmonic oscillator functions $\chi^i_{v_i}(Q_i)$

$$X^{(0)}_{v_1v_2v_3\ldots} = \prod_{n=1} \chi^n_{v_n}(Q_n) \qquad E^{(0)}_{v_1v_2v_3\ldots} = \sum_{n=1} hc\omega_n(v_n + \tfrac{1}{2}) \quad (12)$$

For the purpose of the derivations of vibrational corrections to properties one needs only to consider first order corrections to the wavefunction of the type

$$X^{(1)} = \sum_i (c^i_+ \chi^i_{v_i+1} + c^i_- \chi^i_{v_i-1}) \prod_{j\neq i} \chi^j_{v_j} \quad (13)$$

The remaining terms of the first-order correction can be found in references[3] and[1]. Using the orthogonality of the harmonic oscillator functions and normal modes the coefficients c_+, c_- can be found to be

$$c^i_\pm = \mp\frac{1}{6}\frac{K_{iii}\left\langle \chi^i_{v_i\pm1}|Q_i^3|\chi^i_{v_i}\right\rangle}{\omega_i} \mp \frac{1}{2}\frac{\sum_{j\neq i} K_{ijj}\left\langle \chi^j_{v_j}|Q_j^2|\chi^j_{v_j}\right\rangle \left\langle \chi^i_{v_i\pm1}|Q_i|\chi^i_{v_i}\right\rangle}{\omega_i} \quad (14)$$

The vibrationally corrected value of the property is

$$P_{v_1v_2v_3\cdots} = \langle X_{v_1v_2v_3\cdots}|P(\boldsymbol{\xi})|X_{v_1v_2v_3\cdots}\rangle \quad (15)$$

The property surface is expressed as a Taylor expansion in normal coordinates Q

$$P(\boldsymbol{\xi}) = P_{eq} + \sum_i \frac{\partial P}{\partial Q_i}\Big|_{eq} Q_i + \frac{1}{2}\sum_{i,j}\frac{\partial^2 P}{\partial Q_i \partial Q_j}\Big|_{eq} Q_i Q_j + \ldots \quad (16)$$

As the vibrational corrections to properties are then expressed using both an expansion of the vibrational wavefunction in orders of perturbation theory and a Taylor expansion of the property surface, and thus one needs to truncate both in an even fashion. In order to do so, each contribution to the vibrational correction is considered to have an order equal to the sum of the order of the term in the Taylor expansion and the order in the vibrational wavefunction to which the matrix element is evaluated, i.e. for a contribution of the n'th order term in the Taylor expansion to the m'th order vibrational correction, one needs to evaluate the expectation value of Q^n to $m-n$'th order. Using this definition we see that the first order vibrational correction vanishes, since $\langle Q_i\rangle^{(0)} = 0$ and thus to first non-vanishing order one obtains

$$\Delta P^{vib} = \sum_i \frac{\partial P}{\partial Q_i}\langle Q_i\rangle^{(1)} + \frac{1}{2}\sum_{i,j}\frac{\partial^2 P}{\partial Q_i \partial Q_j}\langle Q_i Q_j\rangle^{(0)} \quad (17)$$

which is the equation employed in this paper. If we evaluate the integrals, we see that

$$\langle Q_i\rangle^{(1)} = 2\left(c^i_+ \langle \chi^i_{v_i+1}|Q_i|\chi^i_{v_i}\rangle + c^i_+ \langle \chi^i_{v_i-1}|Q_i|\chi^i_{v_i}\rangle\right) \quad (18)$$

$$= -\left(\frac{\hbar}{4\pi c\omega_i}\right)^2 \left(\frac{K_{iii}}{\omega_i}((v_i+1)^2 - v_i^2) + \sum_{j\neq i}\frac{K_{ijj}}{\omega_j} 2(v_j + \tfrac{1}{2})((v_i+1) - v_i)\right) \quad (19)$$

$$\langle Q_i Q_j\rangle^{(0)} = \delta_{ij}\frac{\hbar}{4\pi c\omega_i} 2(v_i + \tfrac{1}{2}) \quad (20)$$

Inserting this yields

$$\Delta^{vib} P = -\sum_i \left(\frac{\hbar}{4\pi c\omega_i}\right)^2 \frac{\partial P}{\partial Q_i}\left(\sum_j \frac{K_{ijj}}{\omega_j} 2(v_j + \tfrac{1}{2})\right) + \sum_i \frac{\hbar}{4\pi c\omega_i}\frac{\partial^2 P}{\partial Q_i^2}(v_i + \tfrac{1}{2}) \quad (21)$$

which is in principle valid for a molecule in a arbitrary vibrational state, though the description of vibrational corrections using perturbed harmonic oscillators is in general only valid for low lying vibrational states. It should be reasonably good for the ground state, giving the well known expression for the zero-point vibrational correction

$$\Delta^{ZPVC} P = -\sum_i \left(\frac{\hbar}{4\pi c\omega_i}\right)^2 \frac{\partial P}{\partial Q_i}\left(\sum_j \frac{K_{ijj}}{\omega_j}\right) + \sum_i \frac{\hbar}{8\pi c\omega_i}\frac{\partial^2 P}{\partial Q_i^2} \quad (22)$$

We can also try to take temperature in account in a simple way by using the temperature averaged excitation level of a harmonic oscillator[4]

$$\left\langle v_i + \tfrac{1}{2}\right\rangle^T = \frac{\sum_v (v+\frac{1}{2}) e^{-\frac{hc\omega_i v}{kT}}}{\sum_v e^{-\frac{hc\omega_i v}{kT}}} = \tfrac{1}{2}\coth\left(\frac{hc\omega_i}{2kT}\right) \quad (23)$$

Inserting this gives

$$\Delta^T P = \sum_i -\left(\frac{\hbar}{4\pi c\omega_i}\right)^2 \frac{\partial P}{\partial Q_i}\left(\sum_j \frac{K_{ijj}}{\omega_j}\coth\left(\frac{hc\omega_j}{2kT}\right)\right) + \sum_i \frac{\hbar}{8\pi c\omega_i}\frac{\partial^2 P}{\partial Q_i^2}\coth\left(\frac{hc\omega_i}{2kT}\right) \quad (24)$$

2 Data

Table S1: Equilibrium distances calculated at CCSD(T).

Basis Set	RCC/Å	RCF/Å
cc-pVDZ	1.20886	1.29963
cc-pVTZ	1.18895	1.28507
cc-pVQZ	1.18656	1.28305
cc-pV5Z	1.18506	1.28198
cc-pVDZ (fc)	1.20967	1.30036
cc-pVTZ (fc)	1.19274	1.28861
cc-pVQZ(fc)	1.18913	1.28585
cc-pV5Z (fc)	1.18851	1.28511
aug-cc-pVTZ	1.18884	1.28435
aug-cc-pVQZ	1.18685	1.28255
aug-cc-pV5Z	1.18506	1.28118
cc-pCVDZ	1.20683	1.29918
cc-pCVTZ	1.18954	1.28661
cc-pCVQZ	1.18658	1.28362
cc-pCV5Z	1.18591	1.28291
aug-cc-pCVTZ	1.19014	1.28771
aug-cc-pCVQZ	1.18698	1.28400
aug-cc-pCV5Z	1.18609	1.28310

Which step length is appropriate for the numerically differentiation of the harmonic force constants has been investigated by calculating the cubic force constants of the $^{12}C^{12}C$ isotopomer using step lengths of 0.01, 0.05 and 0.10 times the reduced normal coordinate. These results are summarized in Table S3. The cubic force constants calculated using different step lengths do not differ substantially, so it can be expected that results obtained with step lengths in this range are reliable and a value of 0.05 q has been used in the following for the quadratic and cubic force field of the $^{13}C^{12}C$ isotopomer.

Table S2: The harmonic frequencies in cm^{-1} obtained for $F^{12}C^{12}CF$ at CCSD(T)/cc-pCVQZ level of theory.

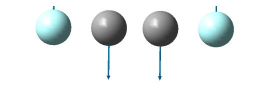
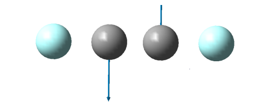
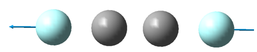
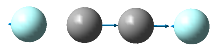
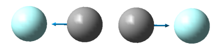
Normal mode		Frequency
Π_u		274.95
Π_g		279.00
Σ_g (1)		790.77
Σ_u		1373.90
Σ_g (2)		2528.18

Table S3: The reduced normal coordinate cubic force constants k_{ijk} of $F^{12}C^{12}CF$ in cm^{-1} calculated at CCSD(T)/cc-pCVQZ using different step lengths.

normal modes			step lengths dq		
i	j	k	0.01	0.05	0.1
Π_u	Π_u	$\Sigma_g(1)$	120.63	120.63	120.64
Π_u	Π_u	$\Sigma_g(1)$	120.63	120.63	120.64
Π_g	Π_g	$\Sigma_g(1)$	201.09	201.09	201.10
Π_g	Π_g	$\Sigma_g(1)$	201.09	201.09	201.10
$\Sigma_g(1)$	$\Sigma_g(1)$	$\Sigma_g(1)$	-119.94	-119.94	-119.95
Π_u	Π_g	Σ_u	-135.26	-135.26	-135.28
Π_u	Π_g	Σ_u	-135.26	-135.26	-135.28
$\Sigma_g(1)$	Σ_u	Σ_u	-235.53	-235.54	-235.56
Π_u	Π_u	$\Sigma_g(2)$	-152.03	-152.03	-152.04
Π_u	Π_u	$\Sigma_g(2)$	-152.03	-152.03	-152.04
Π_g	Π_g	$\Sigma_g(2)$	171.72	171.74	171.82
Π_g	Π_g	$\Sigma_g(2)$	171.72	171.74	171.82
$\Sigma_g(1)$	$\Sigma_g(1)$	$\Sigma_g(2)$	47.57	47.57	47.57
Σ_u	Σ_u	$\Sigma_g(2)$	228.19	228.19	228.20
$\Sigma_g(1)$	$\Sigma_g(2)$	$\Sigma_g(2)$	-262.37	-262.37	-262.38
$\Sigma_g(2)$	$\Sigma_g(2)$	$\Sigma_g(2)$	-413.53	-413.54	-413.57

Table S4: Nuclear spin-spin coupling constants calculated at the SOPPA level. The geometry used is that obtained at the CCSD(T)/cc-pCVQZ level. Results are in Hz.

Basis set	J_{FC}	J_{SD}	J_{DSO}	J_{PSO}	J
ccJ-pVDZ	11.491	38.331	-1.826	-45.942	2.054
ccJ-pVTZ	8.072	34.747	-1.862	-47.235	-6.278
ccJ-pVQZ	6.921	33.488	-1.871	-46.970	-8.432
ccJ-pV5Z	5.930	32.054	-1.866	-48.217	-12.098
aug-ccJ-pVDZ	6.771	31.710	-1.825	-46.260	-9.604
aug-ccJ-pVTZ	6.239	31.997	-1.862	-48.309	-11.936
aug-ccJ-pVQZ	5.951	31.772	-1.871	-48.643	-12.791
aug-ccJ-pV5Z	5.755	31.592	-1.866	-48.759	-13.277

Table S5: Nuclear spin-spin coupling constants calculated at the SOPPA(CCSD) level. The geometry used is that obtained at the CCSD(T)/cc-pCVQZ level. Results are in Hz.

Basis set	J_{FC}	J_{SD}	J_{DSO}	J_{PSO}	J
ccJ-pVDZ	11.153	36.697	-1.812	-47.667	-1.628
ccJ-pVTZ	8.264	33.753	-1.846	-48.790	-8.620
ccJ-pVQZ	7.411	32.838	-1.855	-48.729	-10.335
ccJ-pV5Z	6.595	31.630	-1.850	-50.172	-13.797
aug-ccJ-pVDZ	6.715	30.625	-1.813	-47.498	-11.970
aug-ccJ-pVTZ	6.559	31.217	-1.847	-49.722	-13.793
aug-ccJ-pVQZ	6.515	31.242	-1.855	-50.382	-14.480
aug-ccJ-pV5Z	6.455	31.220	-1.850	-50.769	-14.944

Table S6: The PSO term calculated er various correlation levels and with a number of basis sets. The results show, that each methods does converge in the basis set, and thus the difference

	HF	SOPPA	SOPPA(CCSD)	CCSD	CCSD(T)	CC3
ccJ-pVDZ	-17.756	-45.942	-47.667	-30.344	-36.062	-35.018
ccJ-pVTZ	-18.136	-47.235	-48.790	-31.298	-37.354	-36.690
ccJ-pVQZ	-18.664	-46.970	-48.729	-30.956	-36.912	-36.377
ccJ-pV5Z	-20.134	-48.217	-50.172	-32.291	-38.276	
aug-ccJ-pVDZ	-19.852	-46.260	-47.498	-31.603	-36.942	-36.256
aug-ccJ-pVTZ	-20.344	-48.309	-49.722	-32.803	-38.776	-38.215
aug-ccJ-pVQZ	-20.836	-48.643	-50.382	-32.829	-38.803	-38.330
aug-ccJ-pV5Z		-48.759	-50.769	-32.907		

Table S7: The ZPVC to the SSCC from each normal mode using numerical derivatives at CCSD/ccJ-pVQZ. Results are in Hz. The contributions from the Π modes are per individual mode, not for the set of degenerate modes.

Mode	J_{FC}	J_{SD}	J_{DSO}	J_{PSO}	J
Π(1)	0.252	0.598	0.008	-0.918	-0.060
Π(2)	0.448	0.780	0.008	-1.234	0.002
Σ(1)	0.039	-0.001	-0.004	-0.144	0.002
Σ(2)	-0.029	-0.078	-0.002	-0.206	-0.315
Σ(3)	0.177	0.636	-0.001	0.990	-0.110
Total	1.588	3.314	0.025	-3.664	1.263

Table S8: The ZPVC to the SSCC from each normal mode using numerical derivatives at CCSD/aug-ccJ-pVQZ. Results are in Hz. The contributions from the Π modes are per individual mode, not for the set of degenerate modes.

Mode	J_{FC}	J_{SD}	J_{DSO}	J_{PSO}	J
Π(1)	0.286	0.636	0.008	-0.830	0.100
Π(2)	0.497	0.832	0.006	-1.098	0.237
Σ(1)	0.037	0.005	-0.005	-0.119	-0.082
Σ(2)	-0.026	-0.064	-0.002	-0.177	-0.269
Σ(3)	0.171	0.624	-0.001	0.982	1.776
Total	1.749	3.501	0.020	-3.170	2.099

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