Supporting Information

Double Proton Transfer Across a Table: The Formic Acid Dimer–Fluorobenzene Complex

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S1 Summary of experimental and theoretical methods

The spectra of the PhF-FAD complexes were measured by using CP-FTMW spectroscopy in the frequency range of 2 – 8 GHz with the COMPACT instrument in Hamburg; the spectrometer design has been described elsewhere in detail.[1] The samples of PhF and FA were placed into two separated reservoirs at room temperature. Neon with a backing pressure of 3 bars was used as a carrier gas. PhF and FA were seeded into the carrier gas, after which the gas mixture was supersonically expanded into the vacuum chamber through a pulsed nozzle. The spectra of $^{13}$C singly substituted isotopologues were measured in natural abundance while the deuterated spectra were measured with the isotopically enriched FA. The isotopic purity of commercial DCOOH is 98%. In order to obtain the complexes containing HCOOD species, a rough 1:1 mixture of D$_2$O and HCOOH was placed in the sample reservoir instead of the pure HCOOH. All the chemicals were obtained from Sigma Aldrich and used without further purification. All the rotational transitions were assigned using the AABS package,[2, 3] and the spectroscopic parameters were fitted with Pickett’s SPFIT program,[4] within the $I^r$ -representation of Watson’s $S$ reduction. The tunneling patterns were fitted using a two-state proton transfer-rotation coupled Hamiltonian, including semirigid rotor terms for each torsional state, common centrifugal distortion, the splitting energy difference ($\Delta E_{01}$), and the Coriolis coupling terms $F_{bc}$, $F_{ca}$ (see Ref. [5] for details). The $r_s$ coordinates were obtained using the KRA package. The AABS, SPFIT, and KRA software can be found at the PROSPE website.[6]

A preliminary conformational search for the PhF-FAD cluster was conducted using the CREST software.[7] Ten low energy structures found were then re-optimized at the PBEh-3c[8] level of theory. Out of these structures only three unique structures were left, which were once again re-optimized at the gCP-B3LYP-D3BJ/def2-TZVP level of theory.[9][11] These structures are given in Table S23.

The PhF-FAD structures were optimized using the B3LYP-D3BJ[10][13] and B2PLYP[15] levels of theory with the def2-TZVP basis set[13] and geometrical counterpoise (gCP) correction[9] to account for basis set superposition error (BSSE). Structures of the monomers PhF and FAD were also optimized at B2PLYP/def2-TZVP approximation, the resulting electron densities were used to generate the CHELPG charges[10] for PhF.

Relaxed PES scans for FAD and PhF-FAD were carried out at PBEh-3c[8] and DFT/def2-TZVP (DFT = B3LYP,[17] B3LYP, mPW1LYP,[18] X3LYP[19]) levels of theory. The calculations for DFT/def2-TZVP levels of theory for PhF-FAD were performed only in the QM/MM approach[20] with PhF represented by a MM force field. PBEh-3c calculations for PhF-FAD were performed by treating PhF both quantum-chemically and via the MM approach.

To obtain a force field for QM/MM calculations, training and test sets for structures of FAD in different stages of proton transfer were randomly displaced with respect to the PhF plane. Then interaction energies were computed at the SAPT2/aug-cc-pVDZ level of theory.[21][23] The Lennard-Jones potential[24] parameters were fitted to reproduce the energy $E_{\text{int}}^{\text{SAPT2}} - E_{\text{PBEh-3c/MM}}^{\text{total}} < 2000$ cm$^{-1}$, where the first term is the total interaction energy from SAPT2/aug-cc-pVDZ calculations, and the second is the electrostatic and induction interaction of FAD with PhF represented as a set of CHELPG atomic charges. The training set consisted of 479 points, while the test set was composed of 215 structures, the resulting RMSD were 133 cm$^{-1}$ and 116 cm$^{-1}$ for training and test sets, respectively.

In addition to that, we have calculated the total interaction energy of the PhF with FAD at the PBEh-3c optimized geometry at SAPT2 level of theory with aug-cc-pVDZ and aug-cc-pVTZ basis sets (SAPT2/aug-cc-pVDZ///PBEh-3c and SAPT2/aug-cc-pVTZ///PBEh-3c, respectively). The interaction energies in these two cases were found to be 1633 cm$^{-1}$ (20 kJ/mol) and 1867 cm$^{-1}$ (22 kJ/mol), respectively.

The proton transfer dynamics was computed in the framework of an effective one-dimensional Schrödinger equation with the Hamiltonian[25]

$$\hat{H} = -\frac{\hbar^2}{2} \frac{d^2}{d\xi^2} G(\xi) \frac{d}{d\xi} + V(\xi) + \text{ZPVE}(\xi) ,$$

where

$$\xi = (r(O1H1) + r(O4H2) - r(O3H1) - r(O2H2))/\sqrt{8}$$  \hspace{1cm} (1)
is the proton transfer coordinate, $G$ is the inverse effective mass, $V$ is the PES obtained from a relaxed scan, and ZPVE is the zero-point vibrational energy term for other degrees of freedom in the harmonic oscillator approximation (see Refs. [26] and [25] for a detailed description of the procedure). The parameters for the Hamiltonian were extracted from one-dimensional PES scans and the Hessians computed in every point of the scan.

All the quantum-chemical calculations were done with the Orca 4 program package,\cite{27} except for SAPT2 calculations, which were performed using the Psi4 software.\cite{28} The computations were done using the Maxwell cluster operated at Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany.
## S2 Experimental parameters of the PhF-FAD complex

Table S1: Experimental and theoretical rotational parameters of the PhF-FAD complex.

|                          | Experiment[^a] | Theory         |          |          |
|--------------------------|----------------|----------------|----------|----------|
|                          | Parent(0^+ )   | Parent(0^- )   | B3LYP-D3BJ[^b] | B2PLYP[^b] | PBEh-3c   |
| **A [MHz]**              | 902.68022(20)  | 902.67985(22)  | 903.6    | 900.1    | 915.0     |
| **B [MHz]**              | 700.65306(20)  | 700.64869(19)  | 704.4    | 655.0    | 721.9     |
| **C [MHz]**              | 539.71027(21)  | 539.70937(20)  | 534.0    | 509.2    | 553.1     |
| **D_J [kHz]**            | 0.3434(14)     |                |          |          |
| **D_JK [kHz]**           | 0.5467(13)     |                |          |          |
| **D_K [kHz]**            | -0.2474(14)    |                |          |          |
| **d_1 [kHz]**            | -0.08985(18)   |                |          |          |
| **d_2 [kHz]**            | 0.024958(60)   |                |          |          |
| **ΔE_{01} [MHz]**        | 267.6080(13)   |                |          |          |
| **F_{bc} [MHz]**         | 15.57228(16)   |                |          |          |
| **F_{ca} [MHz]**         | 17.3378(17)    |                |          |          |
| **μ_a/μ_b/μ_c**          | intra-/intra-/inter[^c] | 0.9/1.2/0.2 | 1.0/1.2/0.1 | 1.0/1.1/0.1 |
| **σ[^d] [kHz]**          | 5.358          |                |          |          |
| **N[^e]**                | 460            |                |          |          |

[^a] Standard deviations within parentheses are expressed in units of the last two digits.
[^b] Calculated using def2-TZVP basis set and geometrical counterpoise (gCP) correction.
[^c] intra- denotes intra-state transition; inter- denotes inter-state transition.
[^d] Root-mean-square deviation of the fit.
[^e] Number of the lines in the fit.
Table S2: Experimental spectroscopic parameters of the symmetric $^{13}$C PhF-FAD species with the proton transfer motion (see Fig. S2 for atom numbering). All the other spectroscopic parameters (given in Table S1 but not given here) are fixed to the values of the parent species (see Table S1). Standard deviations within parentheses are expressed in units of the last two digits.

|       | $^{13}$C1$_{0+}$  | $^{13}$C1$_{0-}$  | $^{13}$C2$_{0+}$  | $^{13}$C2$_{0-}$  |
|-------|-------------------|-------------------|-------------------|-------------------|
|       | $^{13}$C1$_{0+}$  | $^{13}$C1$_{0-}$  | $^{13}$C2$_{0+}$  | $^{13}$C2$_{0-}$  |
| A [MHz] | 900.2625(22) | 894.3558(30) | 699.952(13) | 699.734(10) |
| B [MHz] | 695.5769(21) | 695.5883(18) | 536.2553(11) | 536.27529(91) |
| C [MHz] | 535.91732(41) | 535.92394(38) | 536.2553(11) | 536.27529(91) |
| σ$^{[a]}$ [kHz] | 9.816 | 10.452 | 26 | 26 |
| N$^{[b]}$ | 40 | 40 | 40 | 40 |

$^{[a]}$ Root-mean-square deviation of the fit.

$^{[b]}$ Number of lines in the fit.

Table S3: Experimental spectroscopic parameters of the asymmetric $^{13}$C PhF-FAD species with the quenched proton transfer motion (see Fig. S2 for atom numbering). All the other spectroscopic parameters (given in Table S1 but not given here) are fixed to the values of the parent species (see Table S1). Standard deviations within parentheses are expressed in units of the last two digits.

|       | $^{13}$C5  | $^{13}$C6  | $^{13}$C7  | $^{13}$C8  |
|-------|-----------|-----------|-----------|-----------|
| A [MHz] | 900.6303(54) | 903.9802(59) | 900.841(13) | 904.1467(95) |
| B [MHz] | 698.9391(16) | 700.8726(18) | 696.9423(60) | 697.7193(22) |
| C [MHz] | 536.29898(61) | 535.3830(12) | 534.7894(15) | 534.1916(15) |
| D$^{[a]}$ [kHz] | 0.2070(51) | 0.239(12) | 0.1510(85) | 0.033(18) |
| σ$^{[a]}$ [kHz] | 4.320 | 7.577 | 2.348 | 11.969 |
| N$^{[b]}$ | 22 | 16 | 18 | 16 |

$^{[a]}$ Root-mean-square deviation of the fit.

$^{[b]}$ Number of lines in the fit.
Table S4: Experimental spectroscopic parameters of the symmetric deuterated PhF-FAD species
with the proton transfer motion (see Fig. S2 for atom numbering). Standard deviations within
parentheses are expressed in units of the last two digits.

|       | D1D2o⁺ | D1D2o⁻ | D1H2o⁺ | D1H2o⁻ | H1D2o⁺ | H1D2o⁻ |
|-------|--------|--------|--------|--------|--------|--------|
| A [MHz]| 877.68910(94) | 877.68868(98) | 894.55379(94) | 894.5534(10) | 885.7724(12) | 885.7718(12) |
| B [MHz]| 694.16145(92) | 694.16355(92) | 694.23633(82) | 694.23748(86) | 700.4922(10) | 700.4929(10) |
| C [MHz]| 526.89542(97) | 526.89439(96) | 533.00999(96) | 533.00859(94) | 533.4951(11) | 533.4940(11) |
| $D_J$ [kHz]| 0.3582(41) | 0.3484(36) | 0.301(10) | 0.550(19) | 0.3355(44) |
| $D_{JK}$ [kHz]| 0.267(17) | 0.301(10) | 0.550(19) |
| $D_K$ [kHz]| −0.322(23) | −0.322(23) |
| $d_1$ [kHz]| −0.01074(28) | −0.0949(23) | −0.0932(29) |
| $d_2$ [kHz]| 0.0306(12) | 0.02943(89) | 0.0252(11) |
| $\Delta E_{01}$ [MHz]| 275.7992(84) | 274.0545(77) | 269.2596(74) |
| $F_{bc}$ [MHz]| 15.55419(64) | 15.64630(66) | 15.44167(65) |
| $F_{ca}$ [MHz]| 15.8785(98) | 16.1730(98) | 17.102(10) |
| $\sigma$ [kHz]| 8.391 | 6.895 | 7.652 |
| $N$ [kHz]| 8.391 | 6.895 | 7.652 |

[a] Root-mean-square deviation of the fit.
[b] Number of lines in the fit.
Table S5: Experimental spectroscopic parameters of the deuterated PhF-FAD species with the quenched proton transfer motion (see Fig. S2 for atom numbering). All the other spectroscopic parameters (given in Table S1 but not given here) are fixed to the values of the parent species (see Table S1). Standard deviations within parentheses are expressed in units of the last two digits.

|       | D3D4       | D3H4       | H3D4       |
|-------|------------|------------|------------|
| A [MHz]| 896.244(58)| 900.1446(18)| 899.5134(23)|
| B [MHz]| 694.499(27)| 698.0696(15)| 698.4309(11)|
| C [MHz]| 533.0517(64)| 535.53613(64)| 534.85848(83)|
| D_J [kHz]| 0.088(35)  | 0.342(13)  | 0.287(13)  |
| D_JK [kHz]| 0.666(79)  | 0.97(10)   |            |
| d_L [kHz]|           | -0.1093(75)| -0.0816(74)|
| σ[a] [kHz]| 6.634      | 7.248      | 8.642      |
| N      | 13         | 31         | 33         |

[a] Root-mean-square deviation of the fit.
[b] Number of the lines in the fit.
### S3 Linelists for PhF-FAD and its isotopologues

#### Table S6: Linelist for PhF-FAD parent species.

| J' Ka' Kc' v' | J'' Ka'' Kc'' v'' | obs/MHz  | obs-cal/MHz |
|---------------|-------------------|----------|-------------|
| 2 1 2 0       | 1 0 1 0           | 2517.3952| 0.0005      |
| 2 0 2 0       | 1 0 1 0           | 2412.3232| 0.0003      |
| 2 1 2 0       | 1 1 1 0           | 2351.4586| 0.0047      |
| 2 0 2 0       | 1 1 1 0           | 2210.3815| -0.0005     |
| 3 0 3 0       | 2 1 2 0           | 3396.1894| 0.0025      |
| 3 1 3 0       | 2 1 2 0           | 3436.2063| 0.0000      |
| 3 0 3 0       | 2 0 2 0           | 3501.2587| 0.0000      |
| 3 1 3 0       | 2 0 2 0           | 3541.2797| 0.0014      |
| 4 0 4 0       | 3 1 3 0           | 4521.0764| 0.0019      |
| 4 1 4 0       | 3 1 3 0           | 4533.5928| 0.0002      |
| 4 0 4 0       | 3 0 3 0           | 4561.0976| 0.0036      |
| 4 1 4 0       | 3 0 3 0           | 4573.6166| 0.0045      |
| 5 0 5 0       | 4 1 4 0           | 5613.6607| 0.0020      |
| 5 1 5 0       | 4 1 4 0           | 5617.1678| 0.0030      |
| 5 0 5 0       | 4 0 4 0           | 5626.1785| 0.0017      |
| 5 1 5 0       | 4 0 4 0           | 5629.6881| 0.0052      |
| 6 0 6 0       | 5 1 5 0           | 6693.7986| 0.0038      |
| 6 1 6 0       | 5 1 5 0           | 6694.7160| 0.0035      |
| 6 0 6 0       | 5 0 5 0           | 6697.3038| 0.0029      |
| 6 1 6 0       | 5 0 5 0           | 6698.2213| 0.0027      |
| 7 0 7 0       | 6 1 6 0           | 7769.9335| 0.0008      |
| 7 1 7 0       | 6 1 6 0           | 7770.1624| 0.0003      |
| 7 0 7 0       | 6 0 6 0           | 7770.8530| 0.0025      |
| 7 1 7 0       | 6 0 6 0           | 7771.0826| 0.0026      |
| 4 0 4 1       | 3 1 3 1           | 4519.5784| 0.0012      |
| 4 1 4 1       | 3 1 3 1           | 4531.6649| -0.0150     |
| 4 0 4 1       | 3 0 3 1           | 4558.3951| 0.0025      |
| 4 1 4 1       | 3 0 3 1           | 4570.4993| 0.0038      |
| 5 0 5 1       | 4 1 4 1           | 5611.5391| 0.0004      |
| 5 1 5 1       | 4 1 4 1           | 5614.9223| 0.0020      |
| 5 0 5 1       | 4 0 4 1           | 5623.6423| 0.0008      |
| 5 1 5 1       | 4 0 4 1           | 5627.0237| 0.0006      |
| 6 0 6 1       | 5 1 5 1           | 6691.4831| 0.0004      |
| 6 1 6 1       | 5 1 5 1           | 6692.3686| 0.0015      |
| 6 0 6 1       | 5 0 5 1           | 6694.8658| 0.0016      |
| 6 1 6 1       | 5 0 5 1           | 6695.7498| 0.0011      |
| 7 0 7 1       | 6 1 6 1           | 7767.5729| -0.013      |
| 7 1 7 1       | 6 1 6 1           | 7767.7937| -0.0020     |
| 7 0 7 1       | 6 0 6 1           | 7768.4579| -0.0008     |
| 7 1 7 1       | 6 0 6 1           | 7768.6780| -0.0022     |
| 3 0 3 1       | 2 1 2 1           | 3396.9965| -0.0025     |
| 3 1 3 1       | 2 1 2 1           | 3435.8122| -0.0023     |
| 3 0 3 1       | 2 0 2 1           | 3498.6345| -0.0004     |
| 3 1 3 1       | 2 0 2 1           | 3537.4512| 0.0007      |
| 2 0 2 1       | 1 1 1 1           | 2203.2280| -0.0013     |
| 2 1 2 1       | 1 1 1 1           | 2304.8667| 0.0014      |
| 2 0 2 1       | 1 0 1 1           | 2410.6080| 0.0009      |
| 2 1 2 1       | 1 0 1 1           | 2512.2471| 0.0041      |
| 2 1 1 0       | 1 1 0 0           | 2653.3511| -0.0051     |
| 3 1 2 0       | 2 1 1 0           | 3910.1750| -0.0030     |
| 4 1 3 0       | 3 1 2 0           | 5094.1452| -0.0007     |
| 5 1 4 0       | 4 1 3 0           | 6181.9189| 0.0052      |
| 6 1 5 0       | 5 1 4 0           | 7228.1794| 0.0021      |
| 2 1 1 1       | 1 1 0 1           | 2640.7167| 0.0048      |
| 3 1 2 1       | 2 1 1 1           | 3905.8636| -0.0021     |
| 4 1 3 1       | 3 1 2 1           | 5087.2215| -0.0009     |
| 5 1 4 1       | 4 1 3 1           | 6174.0074| 0.0030      |
| 6 1 5 1 | 5 1 4 1 | 7220.3592 | 0.0001 |
| 3 2 2 1 | 2 2 1 1 | 3677.7569 | -0.0022 |
| 3 2 1 1 | 2 2 0 1 | 3931.8125 | 0.0021 |
| 4 2 3 1 | 3 2 2 1 | 4924.1256 | -0.0058 |
| 4 2 2 1 | 3 2 1 1 | 5291.1644 | -0.0030 |
| 5 2 4 1 | 4 2 3 1 | 6048.4979 | -0.0017 |
| 5 2 3 1 | 4 2 2 1 | 6582.4461 | -0.0054 |
| 6 2 4 1 | 5 2 3 1 | 7773.7501 | 0.0012 |
| 6 2 5 1 | 5 2 4 1 | 7159.7555 | 0.0029 |
| 3 2 2 0 | 2 2 1 0 | 3723.8538 | 0.0006 |
| 3 2 1 0 | 2 2 0 0 | 3979.1090 | -0.0078 |
| 4 2 3 0 | 3 2 2 0 | 4907.1731 | -0.0001 |
| 4 2 2 0 | 3 2 1 0 | 5276.3881 | 0.0012 |
| 5 2 4 0 | 4 2 3 0 | 6052.7160 | 0.0034 |
| 5 2 3 0 | 4 2 2 0 | 6590.4475 | -0.0041 |
| 6 2 5 0 | 5 2 4 0 | 7165.7684 | 0.0000 |
| 6 2 4 0 | 5 2 3 0 | 7785.1263 | -0.0011 |
| 4 3 2 0 | 3 3 1 0 | 5063.2574 | -0.0008 |
| 4 3 1 0 | 3 3 0 0 | 5146.2794 | 0.0060 |
| 5 3 3 0 | 4 3 2 0 | 6308.4133 | -0.0005 |
| 5 3 2 0 | 4 3 1 0 | 6613.6966 | -0.0067 |
| 6 3 4 0 | 5 3 3 0 | 7513.0557 | 0.0071 |
| 6 3 3 0 | 5 3 2 0 | 7945.0037 | 0.0057 |
| 4 3 2 1 | 3 3 1 1 | 5062.4793 | -0.0054 |
| 4 3 1 1 | 3 3 0 1 | 5145.6994 | -0.0002 |
| 5 3 3 1 | 4 3 2 1 | 6245.3064 | 0.0076 |
| 5 3 2 1 | 4 3 1 1 | 6550.2900 | 0.0178 |
| 6 3 4 1 | 5 3 3 1 | 7516.5231 | 0.0029 |
| 6 3 3 1 | 5 3 2 1 | 7946.8272 | 0.0036 |
| 5 4 2 1 | 4 4 1 1 | 6345.4339 | -0.0024 |
| 5 4 1 1 | 4 4 0 1 | 6369.8989 | 0.0032 |
| 6 4 3 1 | 5 4 2 1 | 7656.5948 | 0.0028 |
| 6 4 2 1 | 5 4 1 1 | 7739.2531 | -0.0049 |
| 5 4 2 0 | 4 4 1 0 | 6354.4540 | -0.0008 |
| 5 4 1 0 | 4 4 0 0 | 6378.5626 | 0.0017 |
| 6 4 3 0 | 5 4 2 0 | 7645.5760 | 0.0019 |
| 6 4 2 0 | 5 4 1 0 | 7727.4095 | -0.0009 |
| 6 5 2 0 | 5 5 1 0 | 7624.0299 | 0.0008 |
| 6 5 1 0 | 5 5 0 0 | 7629.2192 | -0.0029 |
| 6 5 2 1 | 5 5 1 1 | 7612.7917 | 0.0032 |
| 6 5 1 1 | 5 5 0 1 | 7618.1478 | 0.0010 |
| 5 1 4 0 | 5 1 5 0 | 2099.5091 | -0.0057 |
| 6 1 5 0 | 6 1 6 0 | 2632.9818 | 0.0021 |
| 7 1 6 0 | 7 1 7 0 | 3143.6082 | -0.0047 |
| 8 1 7 0 | 8 1 8 0 | 3644.0540 | -0.0124 |
| 9 1 8 0 | 9 1 9 0 | 4140.5901 | 0.0123 |
| 6 1 5 1 | 6 1 6 1 | 2608.2392 | 0.0006 |
| 7 1 6 1 | 7 1 7 1 | 3113.9304 | 0.0070 |
| 9 1 8 1 | 9 1 9 1 | 4101.8843 | 0.0082 |
| 7 2 5 1 | 7 2 6 1 | 2440.2100 | -0.0070 |
| 8 2 6 1 | 8 2 7 1 | 3001.2523 | 0.0113 |
| 9 2 7 1 | 9 2 8 1 | 3525.1181 | 0.0028 |
| 10 2 8 1 | 10 2 9 1 | 4030.5702 | 0.0017 |
| 8 3 5 1 | 8 3 6 1 | 2105.2159 | -0.0005 |
| 9 3 6 1 | 9 3 7 1 | 2768.2856 | 0.0037 |
| 10 3 7 0 | 10 3 8 0 | 3392.4127 | -0.0050 |
| 11 3 8 1 | 11 3 9 1 | 3916.7331 | -0.0001 |
| 6 3 4 1 | 6 1 5 1 | 2219.1531 | 0.0045 |
| 7 3 5 1 | 7 1 6 1 | 2614.1259 | 0.0034 |
| 8 3 6 1 | 8 1 7 1 | 3067.5197 | -0.0031 |
| 7 2 6 1 | 7 0 7 1 | 3124.6309 | 0.0008 |
| 2 2 0 1 | 1 0 1 1 | 3681.3182 | 0.0023 |
| 3 2 1 1 | 2 0 2 1 | 5202.5213 | 0.0021 |
| 4 2 2 1 | 3 0 3 1 | 6995.0403 | -0.0113 |
| 6 2 5 1 | 6 0 6 1 | 2642.4099 | 0.0109 |
| 8 2 7 1 | 8 0 8 1 | 3612.9005 | 0.0080 |
| 9 2 8 1 | 9 0 9 1 | 4102.7231 | -0.0140 |
| 9 3 7 1 | 9 1 8 1 | 3547.6520 | 0.0007 |
| 10 3 8 1 | 10 1 9 1 | 4037.6671 | -0.0024 |
| 12 3 10 1 | 12 1 11 1 | 5023.1904 | -0.0077 |
| 10 3 7 1 | 10 3 8 1 | 3369.1557 | 0.0029 |
| 8 3 5 0 | 8 3 6 0 | 2116.1008 | -0.0011 |
| 9 3 6 0 | 9 3 7 0 | 2785.7116 | -0.0036 |
| 5 2 4 0 | 5 0 5 0 | 2199.8311 | -0.0036 |
| 6 2 5 0 | 6 0 6 0 | 2668.3067 | 0.0044 |
| 7 2 6 0 | 7 0 7 0 | 3154.6936 | -0.0009 |
| 9 2 8 0 | 9 0 9 0 | 4141.4647 | 0.0001 |
| 10 2 9 0 | 10 0 10 0 | 4635.7176 | -0.0125 |
| 11 2 10 0 | 11 0 11 0 | 5129.6979 | -0.0025 |
| 13 2 12 0 | 13 0 13 0 | 6116.6249 | 0.0134 |
| 6 3 4 0 | 6 1 5 0 | 2243.1773 | -0.0005 |
| 7 3 5 0 | 7 1 6 0 | 2638.4351 | 0.0037 |
| 8 3 6 0 | 8 1 7 0 | 3094.3566 | 0.0010 |
| 9 3 7 0 | 9 1 8 0 | 3577.8093 | -0.0034 |
| 10 3 8 0 | 10 1 9 0 | 4071.3720 | -0.0094 |
| 6 4 3 0 | 6 2 4 0 | 2441.5011 | 0.0074 |
| 7 4 4 0 | 7 2 5 0 | 2477.0069 | 0.0009 |
| 5 4 2 0 | 5 2 3 0 | 2581.0416 | -0.0053 |
| 8 4 5 0 | 8 2 6 0 | 2700.0081 | 0.0029 |
| 4 4 1 0 | 4 2 2 0 | 2817.0371 | -0.0067 |
| 9 4 6 0 | 9 2 7 0 | 3062.1486 | 0.0053 |
| 10 4 7 0 | 10 2 8 0 | 3504.4653 | 0.0019 |
| 7 2 5 0 | 7 2 6 0 | 2459.2639 | -0.0003 |
| 8 2 6 0 | 8 2 7 0 | 3026.0018 | -0.0008 |
| 9 2 7 0 | 9 2 8 0 | 3554.5840 | 0.0000 |
| 10 2 8 0 | 10 2 9 0 | 4064.0826 | -0.0092 |
| 6 4 3 1 | 6 2 4 1 | 2493.0590 | -0.0111 |
| 5 4 2 1 | 5 2 3 1 | 2610.2198 | 0.0028 |
| 8 4 5 1 | 8 2 6 1 | 2674.1388 | -0.0027 |
| 2 2 0 0 | 1 0 1 0 | 3680.2122 | 0.0011 |
| 3 2 1 0 | 2 0 2 0 | 5247.0045 | -0.0004 |
| 4 2 2 0 | 3 0 3 0 | 7022.1368 | 0.0037 |
| 10 1 9 0 | 10 1 10 0 | 4635.4963 | 0.0004 |
| 11 1 10 0 | 11 1 11 0 | 5129.6324 | -0.0081 |
| 12 1 11 1 | 12 1 12 1 | 5572.0029 | -0.0072 |
| 12 1 11 1 | 12 0 12 1 | 5572.0029 | -0.0072 |
| 12 2 11 1 | 12 1 12 1 | 5572.0029 | -0.0072 |
| 13 1 12 0 | 13 1 13 0 | 6116.6199 | 0.0103 |
| 13 1 12 0 | 13 0 13 0 | 6116.6199 | 0.0103 |
| 13 2 12 0 | 13 0 13 0 | 6116.6199 | 0.0103 |
| 13 2 12 0 | 13 1 13 0 | 6116.6199 | 0.0103 |
| 3 3 0 0 | 2 1 1 0 | 5789.1479 | -0.0011 |
| 3 3 1 0 | 2 1 2 0 | 6273.1145 | 0.0013 |
| 4 3 1 0 | 3 1 2 0 | 7025.2503 | 0.0058 |
| 4 3 2 0 | 3 1 3 0 | 7900.1586 | -0.0064 |
| 3 3 0 1 | 2 1 1 1 | 5798.6646 | 0.0015 |
| 4 3 1 1 | 3 1 2 1 | 7038.5011 | 0.0042 |
| 2 2 1 0 | 1 1 0 0 | 3252.6629 | -0.0057 |
| 3 2 2 0 | 2 1 1 0 | 4323.1638 | -0.0018 |
| 4 2 3 0 | 3 1 2 0 | 5320.1586 | -0.0023 |
| 5 2 4 0 | 4 1 3 0 | 6278.7303 | 0.0027 |
| 6 2 5 0 | 5 1 4 0 | 7262.5840 | 0.0019 |
| 2 2 1 1 | 1 1 0 1 | 3251.2940 | -0.0024 |
| 3 2 2 1 | 2 1 1 1 | 4288.3486 | 0.0048 |
| 4 2 3 1 | 3 1 2 1 | 5306.6124 | 0.0029 |
| 5 2 4 1 | 4 1 3 1 | 6267.8873 | 0.0004 |
|  6 | 2 | 5 | 1 | 7 | 253.6421 | 0.0071 |
|  3 | 1 | 1 | 2 | 0 | 5108.7894 | -0.0029 |
|  4 | 3 | 2 | 1 | 1 | 6239.4587 | -0.0080 |
|  5 | 3 | 3 | 1 | 2 | 7193.5995 | 0.0014 |
|  3 | 1 | 0 | 2 | 0 | 5110.2938 | -0.0030 |
|  4 | 3 | 0 | 2 | 1 | 6194.4423 | 0.0040 |
|  5 | 3 | 0 | 2 | 2 | 7226.4642 | -0.0009 |
|  3 | 1 | 2 | 2 | 1 | 3310.8630 | -0.0026 |
|  4 | 1 | 3 | 2 | 0 | 4681.1579 | -0.0003 |
|  5 | 1 | 4 | 2 | 0 | 5955.9002 | 0.0015 |
|  6 | 1 | 5 | 2 | 4 | 7131.3659 | 0.0024 |
|  3 | 1 | 2 | 2 | 1 | 3295.2775 | -0.0035 |
|  4 | 1 | 3 | 2 | 0 | 4704.7355 | -0.0088 |
|  5 | 1 | 4 | 2 | 0 | 5954.6165 | -0.0008 |
|  6 | 1 | 5 | 2 | 4 | 7126.4753 | -0.0013 |
|  4 | 4 | 1 | 3 | 0 | 6945.0497 | -0.0013 |
|  4 | 4 | 0 | 3 | 0 | 6945.9744 | 0.0006 |
|  4 | 4 | 0 | 3 | 0 | 6965.7246 | -0.0038 |
|  4 | 2 | 1 | 3 | 1 | 4114.1864 | 0.0009 |
|  5 | 2 | 3 | 1 | 4 | 5634.1502 | -0.0020 |
|  6 | 2 | 4 | 1 | 5 | 7162.5926 | -0.0098 |
|  4 | 2 | 2 | 3 | 0 | 4145.2117 | 0.0049 |
|  5 | 2 | 3 | 0 | 4 | 6572.4010 | 0.0006 |
|  6 | 2 | 4 | 0 | 3 | 7149.1197 | 0.0058 |
|  2 | 2 | 0 | 3 | 1 | 3478.2745 | 0.0043 |
|  3 | 2 | 1 | 3 | 0 | 5141.9336 | 0.0005 |
|  4 | 2 | 2 | 3 | 0 | 6982.1214 | 0.0078 |
|  2 | 2 | 0 | 3 | 1 | 3473.9411 | 0.0030 |
|  3 | 2 | 1 | 1 | 2 | 5100.8826 | -0.0006 |
|  4 | 2 | 2 | 1 | 3 | 6956.2369 | 0.0007 |
|  3 | 3 | 0 | 2 | 2 | 5189.8363 | -0.0003 |
|  4 | 3 | 1 | 2 | 0 | 6612.2625 | 0.0056 |
|  3 | 3 | 0 | 1 | 2 | 5188.0769 | -0.0015 |
|  4 | 3 | 1 | 1 | 2 | 6656.0112 | -0.0075 |
|  5 | 3 | 1 | 4 | 0 | 4343.0571 | 0.0019 |
|  6 | 3 | 4 | 1 | 4 | 5489.6791 | -0.0006 |
|  5 | 3 | 3 | 4 | 0 | 4406.1707 | -0.0001 |
|  7 | 3 | 5 | 0 | 6 | 6489.2867 | -0.0102 |
|  5 | 3 | 2 | 0 | 4 | 6481.0070 | 0.0040 |
|  6 | 3 | 0 | 5 | 4 | 6404.5520 | 0.0059 |
|  5 | 3 | 2 | 1 | 4 | 4750.9210 | 0.0005 |
|  6 | 3 | 1 | 5 | 4 | 6352.3103 | 0.0023 |
|  7 | 3 | 4 | 1 | 6 | 7959.3248 | 0.0014 |
|  8 | 3 | 6 | 1 | 7 | 7036.7050 | -0.0016 |
|  3 | 3 | 0 | 2 | 2 | 6378.1868 | 0.0017 |
|  4 | 3 | 0 | 3 | 0 | 7940.1834 | -0.0010 |
|  3 | 3 | 1 | 2 | 0 | 6379.5005 | -0.0006 |
|  4 | 3 | 2 | 3 | 0 | 7943.3476 | -0.0033 |
|  6 | 4 | 3 | 0 | 6 | 2077.5565 | -0.0025 |
|  7 | 4 | 0 | 7 | 3 | 2306.6915 | 0.0006 |
|  8 | 4 | 5 | 0 | 8 | 2634.8200 | 0.0018 |
|  9 | 4 | 6 | 0 | 9 | 3039.7893 | 0.0010 |
| 10 | 4 | 7 | 0 | 10 | 3497.4008 | -0.0041 |
| 10 | 4 | 6 | 0 | 10 | 2459.3475 | -0.0059 |
| 11 | 4 | 8 | 0 | 11 | 3982.8313 | -0.0006 |
| 12 | 4 | 9 | 0 | 12 | 4479.5527 | -0.0021 |
|  6 | 4 | 3 | 1 | 6 | 2139.1430 | 0.0006 |
|  7 | 4 | 1 | 7 | 3 | 2277.8987 | 0.0026 |
|  8 | 4 | 5 | 1 | 8 | 2610.9447 | 0.0001 |
|  9 | 4 | 6 | 1 | 9 | 3015.6882 | -0.0015 |
| 10 | 4 | 6 | 1 | 10 | 2448.2456 | 0.0057 |
| 11 | 4 | 8 | 1 | 11 | 3954.2109 | 0.0016 |
| 12 | 3 | 5 | 1 | 8 | 2168.4164 | 0.0029 |
6 3 4 1 6 2 5 1 2185.8732 0.0006
7 3 5 1 7 2 6 1 2603.6343 -0.0029
8 3 6 1 8 2 7 1 3064.4603 -0.0002
9 3 6 1 9 2 7 1 2789.9743 0.0046
9 3 7 1 9 2 8 1 3546.8082 0.0052
10 3 7 1 10 2 8 1 3376.0284 0.0054
10 3 8 1 10 2 9 1 4037.4369 -0.0017
11 3 8 1 11 2 9 1 3918.7941 0.0056
11 3 9 1 11 2 10 1 4530.3057 0.0114
12 3 9 1 12 2 10 1 4436.0884 0.0036
8 3 5 0 8 2 6 0 2181.2887 -0.0001
6 3 4 0 6 2 5 0 2208.7732 0.0001
7 3 5 0 7 2 6 0 2627.5817 0.0025
9 3 6 0 9 2 7 0 2808.0660 -0.0042
8 3 6 0 8 2 7 0 3091.1904 0.0007
9 3 7 0 9 2 8 0 3576.9362 -0.0027
10 3 7 0 10 2 8 0 3399.4796 0.0035
10 3 8 0 10 2 9 0 4071.1669 0.0167
11 3 8 0 11 2 9 0 3946.5480 0.0000
12 3 9 0 12 2 10 0 4467.2523 -0.0106
12 3 10 0 12 2 11 0 5063.8160 0.0000
6 4 2 0 5 5 1 0 5344.8317 0.0081
7 4 3 0 6 5 2 0 6994.2467 -0.0008
7 4 4 0 6 5 1 0 6513.0475 0.0010
8 4 5 0 7 5 2 0 7680.5983 0.0090
6 4 3 1 5 5 0 1 5237.7992 -0.0049
6 4 2 1 5 5 1 1 5348.8046 0.0010
7 4 3 1 6 5 2 1 6910.0540 -0.0075
8 4 5 1 7 5 2 1 7602.7471 -0.0137
11 5 6 0 11 4 7 0 2113.6486 0.0078
6 5 1 0 6 4 2 0 2284.9392 -0.0022
5 5 0 0 5 4 1 0 2383.1298 0.0000
6 5 2 0 6 4 3 0 2388.3993 0.0009
5 5 1 0 5 4 2 0 2409.9437 0.0003
7 5 3 0 7 4 4 0 2415.3855 -0.0044
8 5 4 0 8 4 5 0 2528.1119 -0.0074
9 5 5 0 9 4 6 0 2737.5526 -0.0031
10 5 6 0 10 4 7 0 3044.5128 -0.0032
11 5 7 0 11 4 8 0 3436.7517 0.0006
12 5 7 0 12 4 8 0 2717.7437 -0.0068
12 5 8 0 12 4 9 0 3888.8864 0.0104
7 5 2 1 7 4 3 1 2044.8925 0.0021
6 5 1 1 6 4 2 1 2269.9050 -0.0016
6 5 2 1 6 4 3 1 2374.4222 0.0013
5 5 0 1 5 4 1 1 2391.0174 -0.0005
5 5 1 1 5 4 2 1 2418.2243 -0.0002
7 5 3 1 7 4 4 1 2489.8301 0.0011
9 5 5 1 9 4 6 1 2708.9271 -0.0039
10 5 6 1 10 4 7 1 3021.3112 -0.0036
11 5 7 1 11 4 8 1 3413.9985 -0.0020
12 5 8 1 12 4 9 1 3864.9913 -0.0017
12 5 7 1 12 4 8 1 2708.5454 0.0082
5 2 4 0 5 1 5 0 2196.3405 0.0117
7 2 5 0 7 1 6 0 2470.1157 -0.0006
6 2 5 0 6 1 6 0 2667.3860 0.0015
8 2 6 0 8 1 7 0 3029.1638 -0.0047
7 2 6 0 7 1 7 0 3154.4634 -0.0017
9 2 7 0 9 1 8 0 3555.4567 -0.0009
8 2 7 0 8 1 8 0 3647.2288 -0.0036
10 2 8 0 10 1 9 0 4064.3223 -0.0007
9 2 8 0 9 1 9 0 4141.4651 0.0136
11 2 9 0 11 1 10 0 4565.4967 0.0031
10 2 9 0 10 1 10 0 4635.7177 -0.0093
11 2 10 0 11 1 11 0 5129.6979 -0.0018
| 5 2 4 1 5 1 5 1 | 2174.1297  0.0007 |
| 7 2 5 1 7 1 6 1 | 2450.7013  -0.0009 |
| 6 2 5 1 6 1 6 1 | 2641.5226  0.0080 |
| 8 2 6 1 8 1 7 1 | 3004.3182  -0.0077 |
| 7 2 6 1 7 1 7 1 | 3124.4076  -0.0010 |
| 9 2 7 1 9 1 8 1 | 3525.9646  0.0011 |
| 9 2 8 1 9 1 9 1 | 4102.7228  -0.0015 |
| 8 2 7 1 8 1 8 1 | 3612.8341  -0.0046 |
| 10 2 8 1 10 1 9 1 | 4030.7988  0.0043 |
| 10 2 9 1 10 1 10 1 | 4592.7287  0.0007 |
| 11 2 9 1 11 1 10 1 | 4528.3043  0.0068 |
| 12 2 10 1 12 1 11 1 | 5022.6114  0.0019 |
| 5 1 4 1 5 0 5 1 | 2083.6289  0.0008 |
| 6 1 5 1 6 0 6 1 | 2609.1241  0.0010 |
| 7 1 6 1 7 0 7 1 | 3114.1485  0.0036 |
| 8 1 7 1 8 0 8 1 | 3609.8280  -0.0021 |
| 9 1 8 1 9 0 9 1 | 4101.8853  -0.0035 |
| 5 1 4 0 5 0 5 0 | 2103.0245  0.0035 |
| 6 1 5 0 6 0 6 0 | 2633.8981  0.0005 |
| 7 1 6 0 7 0 7 0 | 3143.8427  0.0002 |
| 8 1 7 0 8 0 8 0 | 3644.1194  -0.0025 |
| 9 1 8 0 9 0 9 0 | 4140.5909  0.0002 |
| 10 1 9 0 10 0 10 0 | 4635.4963  -0.0025 |
| 8 6 2 0 8 5 3 0 | 2768.8790  0.0019 |
| 8 6 3 0 8 5 4 0 | 2859.3836  -0.0022 |
| 7 6 1 0 7 5 2 0 | 2869.3096  0.0000 |
| 9 6 4 0 9 5 5 0 | 2869.6785  -0.0103 |
| 7 6 2 0 7 5 3 0 | 2899.8645  0.0066 |
| 6 6 0 0 6 5 1 0 | 2940.6205  -0.0002 |
| 6 6 1 0 6 5 2 0 | 2946.2818  0.0006 |
| 10 6 5 0 10 5 6 0 | 2964.6065  -0.0066 |
| 12 6 7 0 12 5 8 0 | 3441.5458  -0.0042 |
| 10 6 4 1 10 5 5 1 | 2145.9999  0.0041 |
| 13 6 7 1 13 5 8 1 | 2344.2865  0.0070 |
| 9 6 3 1 9 5 4 1 | 2464.3894  0.0080 |
| 8 6 2 1 8 5 3 1 | 2729.0985  -0.0007 |
| 8 6 3 1 8 5 4 1 | 2821.4587  -0.0047 |
| 7 6 1 1 7 5 2 1 | 2877.9041  -0.0010 |
| 7 6 2 1 7 5 3 1 | 2909.2193  0.0004 |
| 6 6 0 1 6 5 1 1 | 2950.9138  -0.0027 |
| 6 6 1 1 6 5 2 1 | 2956.7539  -0.0032 |
| 10 6 5 1 10 5 6 1 | 3124.9973  0.0066 |
| 11 6 6 1 11 5 7 1 | 3127.8870  -0.0061 |
| 10 7 3 0 10 6 4 0 | 3251.4957  0.0070 |
| 10 7 4 0 10 6 5 0 | 3317.4444  -0.0116 |
| 9 7 2 0 9 6 3 0 | 3347.7279  0.0056 |
| 9 7 3 0 9 6 4 0 | 3375.5044  -0.0011 |
| 12 7 6 0 12 6 7 0 | 3391.4311  -0.0084 |
| 8 7 1 0 8 6 2 0 | 3433.7199  0.0003 |
| 8 7 2 0 8 6 3 0 | 3440.0356  0.0085 |
| 7 7 0 0 7 6 1 0 | 3488.2371  0.0137 |
| 7 7 1 0 7 6 2 0 | 3489.1663  -0.0102 |
| 14 7 8 0 14 6 9 0 | 3828.4692  -0.0020 |
| 12 7 5 1 12 6 6 1 | 2514.7286  0.0113 |
| 10 7 3 1 10 6 4 1 | 3182.6310  0.0114 |
| 10 7 4 1 10 6 5 1 | 3250.9841  -0.0083 |
| 9 7 2 1 9 6 3 1 | 3355.3119  -0.0060 |
| 9 7 3 1 9 6 4 1 | 3384.1864  -0.0030 |
| 8 7 1 1 8 6 2 1 | 3446.5997  -0.0019 |
| 8 7 2 1 8 6 3 1 | 3453.2218  -0.0060 |
| 7 7 0 1 7 6 1 1 | 3500.0550  0.0017 |
| 7 7 1 1 7 6 2 1 | 3501.0592  -0.0065 |
| 4 2 3 1 3 3 0 1 | 3413.8109  -0.0012 |
| 5 2 4 1 4 3 1 1 | 4316.6125  0.0002 |
|   |   |   |   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|---|---|---|
|   |   |   |   |   |   |   |   |   |   |   |
| 6 | 2 | 5 | 1 | 5 | 3 | 2 | 1 | 4926.0864 | -0.0064 |
| 4 | 2 | 3 | 0 | 3 | 3 | 0 | 0 | 3441.1900 | 0.0001 |
| 5 | 2 | 4 | 0 | 4 | 3 | 1 | 0 | 4347.6244 | -0.0044 |
| 6 | 2 | 5 | 0 | 5 | 3 | 2 | 0 | 4899.6921 | -0.0017 |
| 9 | 8 | 2 | 0 | 9 | 7 | 3 | 0 | 3986.7109 | -0.0078 |
| 10 | 8 | 2 | 0 | 10 | 7 | 3 | 0 | 3917.2684 | 0.0001 |
| 11 | 8 | 3 | 0 | 11 | 7 | 4 | 0 | 3820.9551 | 0.0088 |
| 11 | 8 | 4 | 0 | 11 | 7 | 5 | 0 | 3840.1560 | -0.0161 |
| 9 | 8 | 1 | 1 | 9 | 7 | 2 | 1 | 4000.1863 | -0.0054 |
| 9 | 8 | 2 | 1 | 9 | 7 | 3 | 1 | 4001.2086 | -0.0175 |
| 10 | 8 | 2 | 1 | 10 | 7 | 3 | 1 | 3932.4379 | 0.0005 |
| 10 | 8 | 3 | 1 | 10 | 7 | 4 | 1 | 3937.8769 | -0.0038 |
| 11 | 8 | 4 | 1 | 11 | 7 | 5 | 1 | 3846.0779 | -0.0091 |
| 5 | 4 | 0 | 1 | 5 | 1 | 4 | 0 | 3930.6967 | 0.0000 |
| 5 | 4 | 1 | 1 | 5 | 1 | 4 | 1 | 3949.8301 | 0.0022 |
| 6 | 4 | 2 | 1 | 6 | 1 | 5 | 1 | 4468.7353 | 0.0084 |
| 11 | 9 | 2 | 0 | 11 | 8 | 3 | 0 | 4474.1516 | 0.0068 |
| 12 | 9 | 3 | 0 | 12 | 8 | 4 | 0 | 4393.4816 | 0.0078 |
| 12 | 9 | 4 | 0 | 12 | 8 | 5 | 0 | 4395.2775 | 0.0071 |
| 11 | 9 | 2 | 1 | 11 | 8 | 3 | 1 | 4490.9178 | -0.0024 |
| 12 | 9 | 3 | 1 | 12 | 8 | 4 | 1 | 4410.3526 | -0.0007 |
| 12 | 9 | 4 | 1 | 12 | 8 | 5 | 1 | 4412.6376 | -0.0095 |
| 9 | 9 | 0 | 1 | 9 | 8 | 1 | 1 | 4591.2786 | 0.0059 |
| 9 | 9 | 1 | 1 | 9 | 8 | 2 | 1 | 4591.2786 | 0.0059 |
| 11 | 10 | 1 | 11 | 0 | 11 | 1 | 5082.4439 | -0.0058 |
| 11 | 2 | 10 | 1 | 11 | 1 | 1 | 1 | 5082.5010 | -0.0065 |
| 11 | 10 | 2 | 1 | 11 | 9 | 3 | 1 | 5096.1755 | -0.0040 |
| 10 | 10 | 1 | 10 | 9 | 2 | 0 | 5119.7507 | 0.0150 |
| 10 | 10 | 0 | 10 | 9 | 1 | 0 | 5119.7507 | 0.0150 |
| 4 | 4 | 1 | 0 | 3 | 3 | 1 | 1 | 6697.6696 | 0.0090 |
| 5 | 4 | 1 | 0 | 4 | 3 | 1 | 1 | 7917.4016 | -0.0041 |
| 5 | 4 | 2 | 0 | 4 | 3 | 2 | 1 | 7989.6371 | 0.0065 |
| 2 | 1 | 1 | 1 | 1 | 0 | 1 | 0 | 3272.7862 | -0.0152 |
| 3 | 1 | 2 | 1 | 2 | 0 | 2 | 0 | 4766.3498 | 0.0054 |
| 4 | 1 | 3 | 1 | 3 | 0 | 3 | 0 | 6352.3103 | 0.0022 |
| 5 | 1 | 4 | 1 | 4 | 0 | 4 | 0 | 7965.2181 | -0.0004 |
| 3 | 3 | 0 | 1 | 2 | 2 | 0 | 0 | 5391.2584 | 0.0048 |
| 4 | 3 | 1 | 1 | 3 | 2 | 1 | 0 | 6557.8389 | 0.0025 |
| 4 | 3 | 2 | 1 | 3 | 2 | 2 | 0 | 6776.7781 | -0.0033 |
| 4 | 3 | 1 | 0 | 3 | 2 | 1 | 1 | 6074.9407 | -0.0015 |
| 4 | 3 | 2 | 0 | 3 | 2 | 2 | 1 | 6292.6086 | -0.0121 |
| 5 | 3 | 2 | 0 | 4 | 2 | 2 | 1 | 7397.4747 | -0.0034 |
| 2 | 2 | 1 | 0 | 1 | 1 | 1 | 1 | 3144.5774 | -0.0032 |
| 3 | 2 | 1 | 0 | 2 | 1 | 1 | 1 | 4386.5178 | -0.0084 |
| 4 | 2 | 2 | 0 | 3 | 1 | 2 | 1 | 5757.0510 | 0.0035 |
| 5 | 2 | 3 | 0 | 4 | 1 | 3 | 1 | 7260.2720 | -0.0047 |
| 5 | 2 | 4 | 0 | 4 | 1 | 4 | 1 | 7555.9584 | -0.0014 |
| 2 | 1 | 1 | 0 | 1 | 0 | 1 | 1 | 2752.6463 | 0.0003 |
| 3 | 1 | 2 | 0 | 2 | 0 | 2 | 1 | 4252.2143 | -0.0025 |
| 5 | 1 | 4 | 0 | 4 | 0 | 4 | 1 | 7471.2508 | 0.0019 |
| 4 | 4 | 0 | 1 | 3 | 3 | 0 | 0 | 7213.0447 | 0.0030 |
| 5 | 2 | 3 | 1 | 4 | 3 | 1 | 0 | 5798.6644 | -0.0124 |
| 6 | 2 | 4 | 1 | 5 | 3 | 2 | 0 | 6958.7220 | -0.0003 |
| 7 | 2 | 5 | 1 | 6 | 3 | 3 | 0 | 7872.6665 | -0.0099 |
| 2 | 2 | 0 | 1 | 1 | 1 | 0 | 0 | 3582.0246 | -0.0015 |
| 3 | 2 | 1 | 2 | 1 | 2 | 1 | 0 | 5043.7541 | 0.0035 |
| 4 | 2 | 3 | 1 | 3 | 1 | 3 | 0 | 6531.6740 | -0.0016 |
| 7 | 5 | 2 | 0 | 7 | 4 | 4 | 1 | 2281.1113 | -0.0040 |
| 8 | 5 | 3 | 0 | 8 | 4 | 5 | 1 | 2461.8373 | 0.0041 |
| 7 | 5 | 3 | 1 | 7 | 4 | 3 | 0 | 2180.1442 | -0.0036 |
| 6 | 5 | 2 | 1 | 6 | 4 | 2 | 0 | 2530.9849 | 0.0003 |
| 10 | 6 | 5 | 1 | 10 | 5 | 5 | 0 | 2192.5746 | 0.0184 |
| 9 | 6 | 4 | 1 | 9 | 5 | 4 | 0 | 2562.1822 | -0.0092 |
|    |    |    |    |    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|----|----|----|----|
| 8  | 6  | 3  | 1  | 8  | 5  | 3  | 0  | 2996.6313 | 0.0121 |
| 6  | 6  | 1  | 1  | 6  | 5  | 1  | 0  | 3202.8107 | 0.0105 |
| 2  | 1  | 1  | 0  | 1  | 1  | 1  | 1  | 2545.2724 | 0.0042 |
| 3  | 1  | 2  | 0  | 2  | 1  | 2  | 1  | 4150.5736 | -0.0074 |
| 3  | 2  | 1  | 0  | 2  | 2  | 1  | 1  | 3775.9354 | -0.0062 |
| 4  | 2  | 2  | 0  | 3  | 2  | 2  | 1  | 5374.5599 | -0.0094 |
| 3  | 2  | 2  | 1  | 2  | 2  | 0  | 0  | 3880.9345 | 0.0002 |
| 4  | 2  | 3  | 1  | 3  | 2  | 1  | 0  | 4825.9571 | 0.0082 |
| 3  | 1  | 2  | 1  | 2  | 2  | 0  | 0  | 3498.4505 | -0.0057 |
| 4  | 1  | 3  | 1  | 3  | 2  | 1  | 0  | 4606.5655 | 0.0036 |
| 5  | 1  | 4  | 1  | 4  | 2  | 2  | 0  | 5504.1782 | -0.0012 |
| 3  | 2  | 2  | 1  | 2  | 0  | 2  | 0  | 5148.8365 | 0.0140 |
| 4  | 3  | 2  | 1  | 3  | 3  | 0  | 0  | 5310.7865 | -0.0115 |
| 5  | 3  | 3  | 1  | 4  | 3  | 1  | 0  | 6409.8267 | 0.0034 |
| 6  | 3  | 4  | 1  | 5  | 3  | 2  | 0  | 7312.6402 | 0.0000 |
| 5  | 3  | 2  | 0  | 4  | 3  | 2  | 1  | 6449.1761 | -0.0026 |
| 4  | 3  | 2  | 1  | 3  | 1  | 2  | 0  | 7189.7676 | -0.0014 |
| 6  | 4  | 2  | 0  | 5  | 4  | 2  | 1  | 7500.0332 | 0.0048 |
| 6  | 4  | 3  | 1  | 5  | 4  | 1  | 0  | 7883.9733 | -0.0007 |
Table S7: Linelist for PhF-FAD $^{13}$C1 isotopologue.

| $J'$ $K_a'$ $K_{c'}$ $v'$ | $J''$ $K_a''$ $K_{c''}$ $v''$ | obs/MHz   | obs-cal/MHz |
|---------------------------|---------------------------|-----------|-------------|
| 6 0 6 1 5 1 5 1           | 6645.3335                | 0.0007    |
| 6 1 6 1 5 1 5 1           | 6646.2775                | -0.0124   |
| 6 0 6 1 5 0 5 1           | 6648.9394                | -0.0030   |
| 6 1 6 1 5 0 5 1           | 6649.8916                | -0.0081   |
| 6 0 6 0 5 1 5 0           | 6647.5640                | 0.0007    |
| 6 1 6 0 5 1 5 0           | 6648.5612                | 0.0031    |
| 6 0 6 0 5 0 5 0           | 6651.3126                | 0.0023    |
| 6 1 6 0 5 0 5 0           | 6652.3177                | 0.0125    |
| 5 0 5 1 4 1 4 1           | 5572.7172                | 0.0120    |
| 5 1 5 1 4 1 4 1           | 5576.3231                | 0.0081    |
| 5 0 5 1 4 0 4 1           | 5585.4479                | 0.0019    |
| 5 1 5 1 4 0 4 1           | 5589.0544                | -0.0013   |
| 5 0 5 0 4 1 4 0           | 5574.7504                | 0.0086    |
| 5 1 5 0 4 1 4 0           | 5578.4772                | -0.0115   |
| 5 0 5 0 4 0 4 0           | 5591.6824                | 0.0042    |
| 5 1 5 0 4 0 4 0           | 5587.9297                | -0.0014   |
| 4 1 4 1 3 1 3 1           | 4500.4630                | 0.0243    |
| 4 0 4 1 3 0 3 1           | 4527.9922                | 0.0090    |
| 4 1 4 1 3 0 3 1           | 4540.7222                | -0.0016   |
| 4 0 4 0 3 1 3 0           | 4489.0863                | -0.0045   |
| 4 1 4 0 3 1 3 0           | 4502.2842                | 0.0039    |
| 4 0 4 0 3 0 3 0           | 4530.6576                | 0.0045    |
| 3 0 3 0 2 1 2 0           | 3370.6458                | -0.0012   |
| 3 1 3 0 2 1 2 0           | 3412.2106                | 0.0013    |
| 3 1 3 0 2 0 2 0           | 3519.8170                | 0.0067    |
| 3 0 3 1 2 0 2 1           | 3475.6485                | -0.0029   |
| 3 1 3 1 2 1 2 1           | 3411.9014                | -0.0289   |
| 3 0 3 1 2 1 2 1           | 3371.6453                | 0.0002    |
| 2 0 2 0 1 0 1 0           | 2395.9920                | 0.0043    |
| 2 1 1 0 1 1 0 0           | 2634.4951                | -0.0023   |
| 4 1 3 0 3 1 2 0           | 5060.9381                | 0.0122    |
| 5 1 4 0 4 1 3 0           | 6143.3004                | -0.0159   |
| 6 1 5 1 5 1 4 1           | 7174.7055                | 0.0173    |
| 6 1 5 0 5 1 4 0           | 7182.4895                | -0.0208   |
| 7 1 7 1 6 1 6 1           | 7714.1650                | -0.0099   |
| 3 2 1 1 2 2 0 1           | 3901.7158                | -0.0020   |
| 3 2 1 0 2 2 0 0           | 3950.8177                | 0.0025    |
| 3 2 2 0 2 1 1 0           | 4304.4171                | 0.0051    |
| 4 2 3 1 3 1 2 1           | 5280.4984                | 0.0008    |
Table S8: Linelist for PhF-FAD $^{13}$C2 isotopologue.

| $J'$ | $K_a'$ | $K_c'$ | $v'$ | $J''$ | $K_a''$ | $K_c''$ | $v''$ | obs/MHz  | obs-cal/MHz |
|------|--------|--------|------|-------|--------|--------|------|----------|--------------|
| 7    | 0      | 7      | 1    | 6     | 1      | 6      | 1    | 7719.9492 | 0.0036       |
| 7    | 1      | 7      | 1    | 6     | 1      | 6      | 1    | 7720.1119 | -0.0073      |
| 7    | 0      | 7      | 1    | 6     | 0      | 6      | 1    | 7720.6610 | -0.0034      |
| 6    | 0      | 6      | 1    | 5     | 1      | 5      | 1    | 6650.9295 | 0.0040       |
| 6    | 1      | 6      | 1    | 5     | 1      | 5      | 1    | 6651.6468 | 0.0024       |
| 6    | 0      | 6      | 1    | 5     | 0      | 5      | 1    | 6653.7681 | -0.0050      |
| 6    | 1      | 6      | 1    | 5     | 0      | 5      | 1    | 6654.4860 | -0.0060      |
| 6    | 0      | 6      | 0    | 5     | 1      | 5      | 0    | 6653.1771 | 0.0077       |
| 6    | 1      | 6      | 0    | 5     | 0      | 5      | 0    | 6656.8512 | 0.0194       |
| 5    | 0      | 5      | 1    | 4     | 1      | 4      | 1    | 5578.4772 | -0.0093      |
| 5    | 1      | 5      | 1    | 4     | 1      | 4      | 1    | 5581.3513 | 0.0169       |
| 5    | 0      | 5      | 1    | 4     | 0      | 4      | 1    | 5589.0544 | 0.0052       |
| 5    | 1      | 5      | 1    | 4     | 0      | 4      | 1    | 5591.8911 | -0.0058      |
| 5    | 0      | 5      | 0    | 4     | 1      | 4      | 0    | 5580.6369 | 0.0002       |
| 5    | 1      | 5      | 0    | 4     | 1      | 4      | 0    | 5583.5426 | -0.0191      |
| 5    | 0      | 5      | 0    | 4     | 0      | 4      | 0    | 5591.4734 | -0.0104      |
| 5    | 1      | 5      | 0    | 4     | 0      | 4      | 0    | 5594.4034 | -0.0054      |
| 4    | 1      | 4      | 1    | 3     | 0      | 3      | 1    | 4540.6800 | 0.0195       |
| 4    | 1      | 4      | 0    | 3     | 0      | 3      | 0    | 4543.5491 | -0.0078      |
| 3    | 1      | 3      | 1    | 2     | 1      | 2      | 1    | 3417.2108 | -0.0146      |
| 3    | 0      | 3      | 0    | 2     | 0      | 2      | 0    | 3480.0806 | 0.0117       |
| 3    | 1      | 3      | 1    | 2     | 0      | 2      | 1    | 3512.5706 | -0.0101      |
| 3    | 2      | 2      | 0    | 2     | 1      | 1      | 0    | 4288.0896 | -0.0031      |
| 4    | 2      | 3      | 0    | 3     | 1      | 2      | 0    | 5277.1801 | 0.0029       |
| 5    | 2      | 4      | 1    | 4     | 1      | 3      | 1    | 6220.6564 | -0.0108      |
| 6    | 2      | 5      | 1    | 5     | 1      | 4      | 1    | 7204.7648 | 0.0161       |
**Table S9: Linelist for PhF-FAD $^{13}$C3 isotopologue.**

| $J'$ $K_a'$ $K_c'$ $v'$ | $J''$ $K_a''$ $K_c''$ $v''$ | obs/MHz   | obs-cal/MHz |
|--------------------------|--------------------------|-----------|-------------|
| 7 0 7 1 6 1 6 1          | 7745.6817 0.0105         |
| 7 1 7 1 6 1 6 1          | 7745.8788 -0.0055        |
| 7 0 7 1 6 0 6 1          | 7746.5425 0.0153         |
| 7 1 7 1 6 0 6 1          | 7746.7367 -0.0035        |
| 7 0 7 0 6 1 6 0          | 7748.0097 -0.0030        |
| 7 1 7 0 6 1 6 0          | 7748.2338 0.0012         |
| 7 0 7 0 6 0 6 0          | 7748.8962 -0.0011        |
| 7 1 7 0 6 0 6 0          | 7749.1082 -0.0089        |
| 6 0 6 1 5 1 5 1          | 6672.7473 -0.0001        |
| 6 1 6 1 5 1 5 1          | 6673.6034 -0.0001        |
| 6 0 6 1 5 0 5 1          | 6676.0375 -0.0008        |
| 6 1 6 1 5 0 5 1          | 6676.8924 -0.0018        |
| 6 0 6 0 5 1 5 0          | 6675.0355 -0.0042        |
| 6 1 6 0 5 1 5 0          | 6675.9276 0.0032         |
| 6 0 6 0 5 0 5 0          | 6678.4407 0.0004         |
| 6 1 6 0 5 0 5 0          | 6679.3228 -0.0020        |
| 5 0 5 1 4 1 4 1          | 5596.0429 -0.0009        |
| 5 1 5 1 4 1 4 1          | 5599.3378 0.0031         |
| 5 0 5 1 4 0 4 1          | 5607.8880 -0.0002        |
| 5 1 5 1 4 0 4 1          | 5611.1671 -0.0118        |
| 5 0 5 0 4 1 4 0          | 5598.1595 0.0068         |
| 5 1 5 0 4 1 4 0          | 5601.5618 0.0086         |
| 5 0 5 0 4 0 4 0          | 5610.3575 -0.0126        |
| 4 0 4 1 3 1 3 1          | 4507.4713 -0.0062        |
| 4 1 4 1 3 1 3 1          | 4519.3226 0.0006         |
| 4 1 4 1 3 0 3 1          | 4557.5138 -0.0118        |
| 4 0 4 0 3 1 3 0          | 4509.0061 0.0078         |
| 3 0 3 1 2 0 2 1          | 3489.0982 -0.0042        |
| 3 1 3 1 2 0 2 1          | 3527.3283 0.0222         |
| 3 0 3 0 2 1 2 0          | 3387.7946 -0.0024        |
| 3 1 3 0 2 1 2 0          | 3427.1112 0.0067         |
| 4 1 4 0 3 1 3 0          | 4521.2269 0.0111         |
| 3 1 2 1 2 1 1 1          | 3897.5871 0.0024         |
| 3 1 2 0 2 1 1 0          | 3901.8451 -0.0113        |
| 4 1 3 1 3 1 2 1          | 5075.1351 0.0068         |
| 4 1 3 0 3 1 2 0          | 5081.9084 0.0078         |
| 5 1 4 1 4 1 3 1          | 6157.8957 -0.0056        |
| 6 1 5 1 5 1 4 1          | 7200.9563 -0.0070        |
Table S10: Linelist for PhF-FAD $^{13}$C4 isotopologue.

| $J'$ | $K_a'$ | $K_c'$ | $v'$ | $J''$ | $K_a''$ | $K_c''$ | $v''$ | obs/MHz | obs-cal/MHz |
|------|--------|--------|------|------|--------|--------|------|---------|-------------|
| 6    | 0      | 6      | 1    | 5    | 1      | 5      | 1    | 6639.3604| -0.0044     |
| 6    | 1      | 6      | 1    | 5    | 1      | 5      | 1    | 6640.3673| 0.0020      |
| 6    | 0      | 6      | 1    | 5    | 0      | 5      | 1    | 6643.1152| 0.0063      |
| 6    | 1      | 6      | 1    | 5    | 0      | 5      | 1    | 6644.1100| 0.0006      |
| 6    | 0      | 6      | 0    | 5    | 1      | 5      | 0    | 6641.6238| -0.0016     |
| 6    | 1      | 6      | 0    | 5    | 1      | 5      | 0    | 6642.6664| -0.0003     |
| 6    | 0      | 6      | 0    | 5    | 0      | 5      | 0    | 6645.5094| -0.0071     |
| 5    | 0      | 5      | 1    | 4    | 1      | 4      | 1    | 5567.5432| 0.0053      |
| 5    | 1      | 5      | 1    | 4    | 1      | 4      | 1    | 5571.2777| -0.0041     |
| 5    | 0      | 5      | 1    | 4    | 0      | 4      | 1    | 5580.6369| -0.0144     |
| 5    | 1      | 5      | 1    | 4    | 0      | 4      | 1    | 5584.3961| 0.0007      |
| 5    | 0      | 5      | 0    | 4    | 1      | 4      | 0    | 5569.5884| 0.0034      |
| 5    | 1      | 5      | 0    | 4    | 1      | 4      | 0    | 5573.4842| 0.0081      |
| 5    | 0      | 5      | 0    | 4    | 0      | 4      | 0    | 5583.1712| -0.0013     |
| 5    | 1      | 5      | 0    | 4    | 0      | 4      | 0    | 5587.0610| -0.0026     |
| 4    | 0      | 4      | 0    | 3    | 1      | 3      | 0    | 4484.4843| -0.0067     |
| 4    | 1      | 4      | 0    | 3    | 1      | 3      | 0    | 4498.0852| 0.0065      |
| 4    | 0      | 4      | 0    | 3    | 0      | 3      | 0    | 4526.9600| -0.0033     |
| 4    | 1      | 4      | 1    | 3    | 1      | 3      | 1    | 4496.2397| 0.0051      |
| 4    | 0      | 4      | 1    | 3    | 0      | 3      | 1    | 4524.2695| 0.0077      |
| 3    | 0      | 3      | 0    | 2    | 1      | 2      | 0    | 3366.3098| -0.0047     |
| 3    | 1      | 3      | 0    | 2    | 1      | 2      | 0    | 3408.7884| 0.0014      |
| 3    | 0      | 3      | 0    | 2    | 0      | 2      | 0    | 3475.4129| 0.0018      |
| 3    | 1      | 3      | 0    | 2    | 0      | 2      | 0    | 3517.8733| -0.0101     |
| 3    | 1      | 3      | 1    | 2    | 0      | 2      | 1    | 3513.9346| -0.0059     |
| 2    | 0      | 2      | 1    | 1    | 0      | 1      | 1    | 2391.8581| -0.0060     |
| 2    | 0      | 2      | 0    | 1    | 0      | 1      | 0    | 2393.5734| 0.0025      |
| 2    | 1      | 2      | 0    | 1    | 0      | 1      | 0    | 2502.6745| 0.0071      |
| 5    | 1      | 4      | 0    | 4    | 1      | 3      | 0    | 6138.6072| 0.0020      |
| 6    | 1      | 5      | 0    | 5    | 1      | 4      | 0    | 7177.1635| -0.0003     |
| 3    | 2      | 2      | 0    | 2    | 1      | 1      | 0    | 4304.4171| -0.0084     |
| 4    | 2      | 3      | 1    | 3    | 1      | 2      | 1    | 5279.6151| 0.0023      |
| 6    | 2      | 5      | 0    | 5    | 1      | 4      | 0    | 7215.1412| 0.0114      |
Table S11: Linelist for PhF-FAD $^{13}$C5 isotopologue.

| $J'$  $K_a'$ $K_c'$ | $J''$  $K_a''$ $K_c''$ | obs/MHz   | obs-cal/MHz |
|---------------------|------------------------|-----------|-------------|
| 3 0 3               | 2 0 2                  | 3491.0809 | -0.0063     |
| 4 0 4               | 3 0 3                  | 4548.9283 | -0.0071     |
| 5 0 5               | 4 0 4                  | 5611.8325 | 0.0011      |
| 6 0 6               | 5 0 5                  | 6680.7381 | 0.0104      |
| 7 0 7               | 6 0 6                  | 7752.0542 | 0.0008      |
| 2 1 2               | 1 1 1                  | 2307.8341 | 0.0047      |
| 2 1 1               | 1 1 0                  | 2633.1100 | 0.0004      |
| 3 1 3               | 2 1 2                  | 3426.1525 | 0.0049      |
| 4 1 4               | 3 1 3                  | 4521.3067 | 0.0040      |
| 5 1 5               | 4 1 4                  | 5602.7096 | -0.0020     |
| 6 1 6               | 5 1 5                  | 6678.0870 | -0.0022     |
| 7 1 7               | 6 1 6                  | 7751.3458 | -0.0005     |
| 3 0 3               | 2 1 2                  | 3385.8111 | 0.0000      |
| 4 0 4               | 3 1 3                  | 4508.5954 | -0.0036     |
| 5 0 5               | 4 1 4                  | 5599.1232 | -0.0045     |
| 6 0 6               | 5 1 5                  | 6677.1380 | -0.0057     |
| 7 0 7               | 6 1 6                  | 7751.1082 | 0.0003      |
| 3 1 3               | 2 0 2                  | 3531.4227 | -0.0009     |
| 4 1 4               | 3 0 3                  | 4561.6465 | 0.0074      |
| 5 1 5               | 4 0 4                  | 5615.4184 | 0.0030      |
| 6 1 6               | 5 0 5                  | 6681.6711 | -0.0022     |
| 7 1 7               | 6 0 6                  | 7752.2919 | 0.0000      |
Table S12: Linelist for PhF-FAD $^{13}$C6 isotopologue.

| J' | Ka' | Kc' | J'' | Ka'' | Kc'' | obs/MHz   | obs-cal/MHz |
|----|-----|-----|-----|------|------|-----------|-------------|
| 6  | 0   | 6   | 5   | 1    | 5    | 6669.7197 | -0.0075     |
| 6  | 1   | 6   | 5   | 1    | 5    | 6670.6510 | 0.0031      |
| 6  | 0   | 6   | 5   | 0    | 5    | 6673.2340 | -0.0076     |
| 6  | 1   | 6   | 5   | 0    | 5    | 6674.1643 | 0.0020      |
| 7  | 0   | 7   | 6   | 1    | 6    | 7741.8081 | -0.0047     |
| 7  | 1   | 7   | 6   | 1    | 6    | 7742.0400 | -0.0033     |
| 7  | 0   | 7   | 6   | 0    | 6    | 7742.7372 | 0.0036      |
| 7  | 1   | 7   | 6   | 0    | 6    | 7742.9743 | 0.0101      |
| 5  | 0   | 5   | 4   | 0    | 4    | 5606.1722 | 0.0049      |
| 2  | 1   | 1   | 2   | 1    | 1    | 2307.0029 | -0.0110     |
| 2  | 1   | 1   | 1   | 0    |      | 2637.9952 | 0.0021      |
| 3  | 1   | 2   | 2   | 1    | 1    | 3901.3461 | 0.0053      |
| 4  | 1   | 3   | 3   | 1    | 2    | 5079.5263 | -0.0094     |
| 5  | 1   | 5   | 4   | 1    | 4    | 5597.1423 | 0.0061      |
| 5  | 1   | 4   | 4   | 1    | 3    | 6162.6825 | 0.0144      |
| 6  | 1   | 5   | 5   | 1    | 4    | 7204.7648 | -0.0111     |
Table S13: Linelist for PhF-FAD $^{13}$C7 isotopologue.

| $J'\ Ka'\ Kc'$ | $J''\ Ka''\ Kc''$ | obs/MHz | obs-cal/MHz |
|----------------|--------------------|---------|-------------|
| 7 0 7 6 1 6    |                    | 7730.2324 | 0.0001 |
| 7 1 7 6 1 6    |                    | 7730.4872 | 0.0005 |
| 7 0 7 6 0 6    |                    | 7731.2301 | -0.0018 |
| 7 1 7 6 0 6    |                    | 7731.4889 | 0.0024 |
| 6 0 6 5 1 5    |                    | 6659.1841 | -0.0023 |
| 6 1 6 5 1 5    |                    | 6660.1885 | 0.0023 |
| 6 0 6 5 0 5    |                    | 6662.9402 | -0.0002 |
| 6 1 6 5 0 5    |                    | 6663.9375 | -0.0026 |
| 5 0 5 4 1 4    |                    | 5583.9631 | -0.0013 |
| 5 0 5 4 0 4    |                    | 5597.1421 | -0.0036 |
| 5 1 5 4 0 4    |                    | 5600.9058 | 0.0060 |
| 4 0 4 3 1 3    |                    | 4495.9555 | -0.0001 |
| 4 1 4 3 1 3    |                    | 4509.1402 | 0.0032 |
| 4 0 4 3 0 3    |                    | 4537.4070 | -0.0026 |
| 4 1 4 3 0 3    |                    | 4550.5916 | 0.0006 |
| 3 0 3 2 1 2    |                    | 3375.2997 | 0.0006 |
| 3 1 3 2 1 2    |                    | 3416.7518 | -0.0011 |
| 5 1 5 4 1 4    |                    | 5587.7185 | 0.0000 |
Table S14: Linelist for PhF-FAD $^{13}$C$^8$ isotopologue.

| $J'$ | $K_a'$ | $K_c'$ | $J''$ | $K_a''$ | $K_c''$ | obs/MHz       | obs-cal/MHz   |
|------|--------|--------|-------|---------|---------|---------------|--------------|
| 6    | 0      | 6      | 5     | 1       | 5       | 6654.4050     | 0.0034       |
| 6    | 1      | 6      | 5     | 1       | 5       | 6655.4393     | 0.0128       |
| 6    | 0      | 6      | 5     | 0       | 5       | 6658.2234     | -0.0164      |
| 6    | 1      | 6      | 5     | 0       | 5       | 6659.2601     | -0.0046      |
| 5    | 0      | 5      | 4     | 0       | 4       | 5593.6811     | 0.0191       |
| 3    | 1      | 3      | 2     | 1       | 2       | 3415.0236     | 0.0014       |
| 2    | 1      | 1      | 1     | 1       | 0       | 2627.3305     | -0.0179      |
| 4    | 1      | 4      | 3     | 1       | 3       | 4506.5123     | 0.0036       |
| 5    | 1      | 4      | 4     | 1       | 3       | 6148.8520     | 0.0099       |
| 4    | 1      | 4      | 3     | 0       | 3       | 4548.6523     | -0.0171      |
| 3    | 0      | 3      | 2     | 1       | 2       | 3372.8604     | -0.0009      |
| 3    | 1      | 3      | 2     | 0       | 2       | 3523.7428     | -0.0120      |
| 5    | 1      | 5      | 4     | 0       | 4       | 5597.5191     | 0.0187       |
| 4    | 0      | 4      | 3     | 1       | 3       | 4493.0564     | -0.0102      |
| 7    | 0      | 7      | 6     | 0       | 6       | 7725.3629     | -0.0091      |
| 3    | 2      | 1      | 2     | 2       | 0       | 3909.8705     | 0.0062       |
| J' Ka'  | Kc'   | v' J'' Ka'' Kc'' v'' | obs/MHz  | obs-cal/MHz |
|---------|-------|----------------------|----------|-------------|
| 2 1 2 0 | 1 1 1 0 | 2270.8976           | 0.0071   |
| 2 0 2 0 | 1 0 1 0 | 2365.3909           | −0.0158  |
| 2 1 1 0 | 1 1 0 0 | 2620.1624           | −0.0231  |
| 3 1 3 0 | 2 1 2 0 | 3365.2046           | 0.0022   |
| 3 0 3 0 | 2 0 2 0 | 3423.1664           | −0.0155  |
| 3 2 2 0 | 2 2 1 0 | 3666.0111           | 0.0164   |
| 3 1 2 0 | 2 1 1 0 | 3852.8353           | 0.0004   |
| 3 2 1 0 | 2 2 0 0 | 3936.2556           | 0.0000   |
| 4 1 4 0 | 3 1 3 0 | 4435.1687           | 0.0057   |
| 4 0 4 0 | 3 0 3 0 | 4457.2536           | 0.0048   |
| 4 2 3 0 | 3 2 2 0 | 4822.7209           | −0.0002  |
| 4 3 2 0 | 3 3 1 0 | 4996.0076           | 0.0126   |
| 4 1 3 0 | 3 1 2 0 | 4999.7052           | 0.0077   |
| 4 3 1 0 | 3 3 0 0 | 5096.1690           | 0.0012   |
| 4 2 2 0 | 3 2 1 0 | 5221.9305           | 0.0085   |
| 5 1 5 0 | 4 1 4 0 | 5491.9122           | 0.0036   |
| 5 0 5 0 | 4 0 4 0 | 5498.4676           | 0.0042   |
| 5 2 4 0 | 4 2 3 0 | 5938.4185           | 0.0025   |
| 5 1 4 0 | 4 1 3 0 | 6048.8128           | −0.0149  |
| 5 3 3 0 | 4 3 2 0 | 6216.0861           | −0.0047  |
| 5 4 2 0 | 4 4 1 0 | 6277.3447           | 0.0080   |
| 5 4 1 0 | 4 4 0 0 | 6310.5413           | 0.0114   |
| 5 2 3 0 | 4 2 2 0 | 6496.9537           | 0.0000   |
| 6 1 6 0 | 5 1 5 0 | 6543.4503           | 0.0059   |
| 6 0 6 0 | 5 0 5 0 | 6545.1637           | 0.0068   |
| 5 3 2 0 | 4 3 1 0 | 6557.5318           | 0.0014   |
| 6 2 5 0 | 5 2 4 0 | 7020.9298           | 0.0074   |
| 6 1 5 0 | 5 1 4 0 | 7068.3612           | −0.0104  |
| 6 3 4 0 | 5 3 3 0 | 7390.5739           | −0.0006  |
| 5 5 2 0 | 5 5 1 0 | 7533.8825           | −0.0032  |
| 6 5 1 0 | 5 5 0 0 | 7542.0081           | −0.0026  |
| 6 4 3 0 | 5 4 2 0 | 7548.4968           | −0.0106  |
| 7 1 7 0 | 6 1 6 0 | 7593.3428           | −0.0074  |
| 7 0 7 0 | 6 0 6 0 | 7593.7630           | −0.0024  |
| 6 2 4 0 | 5 2 3 0 | 7642.6548           | −0.0018  |
| 6 4 2 0 | 5 4 1 0 | 7648.6798           | −0.0147  |
| 6 3 3 0 | 5 3 2 0 | 7866.9636           | −0.0094  |
| 7 2 6 0 | 6 2 5 0 | 8083.3570           | −0.0048  |
| 7 3 5 0 | 6 3 4 0 | 8519.7560           | −0.0052  |
| 8 2 7 0 | 7 2 6 0 | 9136.7046           | 0.0113   |
| 8 1 7 0 | 7 1 6 0 | 9141.4402           | −0.0003  |
| 8 3 6 0 | 7 3 5 0 | 9610.8497           | −0.0015  |
| 2 1 2 1 | 1 1 1 1 | 2260.7583           | 0.0060   |
| 2 0 2 1 | 1 0 1 1 | 2364.1266           | 0.0036   |
| 2 1 1 1 | 1 1 0 1 | 2608.4665           | 0.0087   |
| 3 1 3 1 | 2 1 2 1 | 3364.8123           | 0.0008   |
| 3 0 3 1 | 2 0 2 1 | 3420.6514           | 0.0088   |
| 3 2 2 1 | 2 2 1 1 | 3625.7898           | 0.0191   |
| 3 1 2 1 | 2 1 1 1 | 3848.6902           | 0.0010   |
| 3 2 1 1 | 2 2 0 1 | 3894.9733           | −0.0045  |
| 4 1 4 1 | 3 1 3 1 | 4433.3241           | 0.0054   |
| 4 0 4 1 | 3 0 3 1 | 4454.6739           | 0.0035   |
| 4 2 3 1 | 3 2 2 1 | 4835.2806           | −0.0047  |
| 4 1 3 1 | 3 1 2 1 | 4993.0096           | 0.0079   |
| 4 3 2 1 | 3 3 1 1 | 4998.3576           | 0.0058   |
| 4 3 1 1 | 3 3 0 1 | 5098.9460           | −0.0122  |
| 4 2 2 1 | 3 2 1 1 | 5232.5229           | −0.0117  |
| 5 1 5 1 | 4 1 4 1 | 5489.7491 | 0.0005 |
| 5 0 5 1 | 4 0 4 1 | 5496.0572 | 0.0037 |
| 5 2 4 1 | 4 2 3 1 | 5934.1919 | 0.0006 |
| 5 1 4 1 | 4 1 3 1 | 6041.1068 | -0.0133 |
| 5 3 3 1 | 4 3 2 1 | 6155.8717 | -0.0069 |
| 5 4 2 1 | 4 4 1 1 | 6269.0790 | 0.0040 |
| 5 4 1 1 | 4 4 0 1 | 6302.8665 | -0.0003 |
| 5 2 3 1 | 4 2 2 1 | 6488.9728 | 0.0024 |
| 5 3 2 1 | 4 3 1 1 | 6497.2729 | 0.0037 |
| 6 1 6 1 | 5 1 5 1 | 6541.1951 | 0.0026 |
| 6 0 6 1 | 5 0 5 1 | 6542.8333 | 0.0008 |
| 6 2 5 1 | 5 2 4 1 | 7015.0725 | -0.0003 |
| 6 1 5 1 | 5 1 4 1 | 7060.9039 | 0.0106 |
| 6 3 4 1 | 5 3 3 1 | 7391.1173 | 0.0000 |
| 6 5 2 1 | 5 5 1 1 | 7522.9268 | -0.0105 |
| 6 5 1 1 | 5 5 0 1 | 7531.3606 | 0.0009 |
| 6 4 3 1 | 5 4 2 1 | 7575.8583 | 0.0036 |
| 7 1 7 1 | 6 1 6 1 | 7591.0802 | 0.0001 |
| 7 0 7 1 | 6 0 6 1 | 7591.4622 | -0.0143 |
| 6 2 4 1 | 5 2 3 1 | 7631.3449 | 0.0049 |
| 6 4 2 1 | 5 4 1 1 | 7677.3844 | 0.0072 |
| 6 3 3 1 | 5 3 2 1 | 7866.0067 | -0.0051 |
| 7 2 6 1 | 6 2 5 1 | 8077.0229 | 0.0007 |
| 7 1 6 1 | 6 1 5 1 | 8092.4675 | 0.0022 |
| 8 2 7 1 | 7 2 6 1 | 9130.2345 | 0.0019 |
| 7 3 4 1 | 6 3 3 1 | 9135.7493 | 0.0058 |
| 6 4 3 0 | 6 3 4 0 | 2003.2203 | -0.0048 |
| 5 2 4 0 | 5 1 5 0 | 2197.2364 | -0.0060 |
| 5 5 0 0 | 5 4 1 0 | 2216.8233 | 0.0128 |
| 5 5 1 0 | 5 4 2 0 | 2253.7151 | -0.0016 |
| 2 1 2 0 | 1 0 1 0 | 2454.2883 | 0.0110 |
| 6 1 5 0 | 6 0 6 0 | 2652.7172 | -0.0019 |
| 6 2 5 0 | 6 1 6 0 | 2874.7190 | -0.0014 |
| 7 1 6 0 | 7 0 7 0 | 3158.3951 | 0.0074 |
| 2 2 1 0 | 1 1 0 0 | 3164.4000 | -0.0024 |
| 7 2 6 0 | 7 1 7 0 | 3164.7344 | 0.0023 |
| 3 1 2 0 | 2 2 1 0 | 3308.6095 | -0.0085 |
| 3 0 3 0 | 2 1 2 0 | 3334.3007 | -0.0106 |
| 3 1 3 0 | 2 0 2 0 | 3454.0679 | -0.0049 |
| 3 2 2 0 | 2 1 1 0 | 4210.1926 | -0.0189 |
| 4 0 4 0 | 3 1 3 0 | 4426.3623 | 0.0045 |
| 4 1 4 0 | 3 0 3 0 | 4466.0603 | 0.0063 |
| 4 1 3 0 | 3 2 2 0 | 4642.3334 | 0.0125 |
| 3 3 1 0 | 2 2 0 0 | 4971.2633 | -0.0121 |
| 3 3 0 0 | 2 2 1 0 | 5063.3112 | 0.0001 |
| 4 2 3 0 | 3 1 2 0 | 5180.0957 | -0.0021 |
| 5 0 5 0 | 4 1 4 0 | 5489.6604 | 0.0023 |
| 5 1 5 0 | 4 0 4 0 | 5500.7185 | 0.0046 |
| 5 2 3 0 | 4 3 2 0 | 5887.8553 | -0.0054 |
| 5 1 4 0 | 4 2 3 0 | 5868.4202 | -0.0072 |
| 4 3 2 0 | 3 2 1 0 | 6031.0069 | -0.0079 |
| 5 2 4 0 | 4 1 3 0 | 6118.7992 | -0.0170 |
| 4 3 2 0 | 3 2 2 1 | 6138.2899 | -0.0101 |
| 4 3 1 0 | 3 2 2 0 | 6493.5044 | 0.0202 |
| 6 0 6 0 | 5 1 5 0 | 6542.9147 | 0.0083 |
| 6 1 6 0 | 5 0 5 0 | 6545.7039 | 0.0089 |
| 4 4 1 0 | 3 3 0 0 | 6759.5676 | 0.0098 |
| 4 4 0 0 | 3 3 1 0 | 6784.6185 | 0.0037 |
| 6 1 5 0 | 5 2 4 0 | 6998.3816 | -0.0015 |
| 5 3 3 0 | 4 2 2 0 | 7025.1894 | 0.0057 |
| 6 2 5 0 | 5 1 4 0 | 7090.9145 | 0.0036 |
| 6 2 4 0 | 5 3 3 0 | 7114.4402 | 0.0136 |
| 7 0 7 0 | 6 1 6 0 | 7593.2178 | -0.0095 |
| 7 1 7 0 | 6 0 6 0 | 7593.8853 | -0.0030 |
6 3 4 0 5 2 3 0 7918.8057 0.0011
5 4 2 0 4 3 1 0 7940.7163 -0.0102
7 1 6 0 6 2 5 0 8076.8967 0.0020
5 4 1 0 4 3 2 0 8099.1377 -0.0119
7 2 6 0 6 1 5 0 8105.9095 0.0082
5 5 1 0 4 4 0 0 8526.4862 0.0063
8 1 7 0 7 2 6 0 9134.9755 0.0022
2 0 2 1 1 1 1 1 2175.1017 -0.0090
6 3 4 1 6 2 5 1 2175.9313 0.0066
5 2 4 1 5 1 5 1 2176.0930 -0.0060
5 5 0 1 5 4 1 1 2223.7328 0.0083
5 5 1 1 5 4 2 1 2261.2988 0.0026
2 1 2 1 1 1 0 1 2269.9775 0.0080
6 2 5 1 6 1 6 1 2649.9663 -0.0132
2 2 1 1 1 1 0 1 3163.4820 0.0025
3 1 2 1 2 2 1 1 3293.6609 -0.0065
3 0 3 1 2 1 2 1 3334.9953 -0.0057
3 1 3 1 2 0 2 1 3450.4414 -0.0114
3 2 2 1 2 1 1 1 4180.7881 -0.0042
4 0 4 1 3 1 3 1 4424.8636 0.0036
4 1 4 1 3 0 3 1 4463.1316 0.0025
4 1 3 1 3 2 2 1 4660.8912 -0.0072
3 3 1 1 2 2 0 1 4969.6370 -0.0180
3 3 0 1 2 2 1 1 5061.5566 0.0080
4 2 3 1 3 1 2 1 5167.3843 -0.0041
5 0 5 1 4 1 4 1 5487.6030 0.0083
5 1 5 1 4 0 4 1 5498.2099 0.0026
5 2 3 1 4 3 2 1 5648.4774 0.0013
5 1 4 1 4 2 3 1 5866.7175 -0.0159
4 3 2 1 3 2 1 1 6073.0230 -0.0059
5 2 4 1 4 1 3 1 6108.5578 -0.0201
4 3 1 1 3 2 2 1 6534.7459 0.0096
6 0 6 1 5 1 5 1 6540.6822 0.0035
6 1 6 1 5 0 5 1 6543.3516 0.0053
4 4 1 1 3 3 0 1 6758.5817 0.0103
4 4 0 1 3 3 1 1 6783.9104 0.0103
6 1 5 1 5 2 4 1 6993.4490 0.0136
5 3 3 1 4 2 2 1 6996.3715 -0.0013
6 2 5 1 5 1 4 1 7082.5340 0.0033
6 2 4 1 5 3 3 1 7123.9541 0.0166
7 0 7 1 6 1 6 1 7590.9605 -0.0021
7 1 7 1 6 0 6 1 7591.5752 -0.0186
6 3 4 1 5 2 3 1 7898.5086 -0.0111
5 4 2 1 4 3 1 1 7928.6724 -0.0155
7 1 6 1 6 2 5 1 8070.8347 0.0069
5 4 1 1 4 3 2 1 8088.4165 0.0014
5 5 1 1 4 4 0 1 8525.6996 0.0058
Table S16: Linelist for PhF-FAD D1 isotopologue.

| J' Ka' Kc' v' | J'' Ka'' Kc'' v'' | obs/MHz   | obs-cal/MHz |
|---------------|------------------|-----------|-------------|
| 2 1 2 0 1 1 1 0 | 2289.1982       | 0.0033    |
| 2 0 2 0 1 0 1 0 | 2385.7180       | -0.0072   |
| 2 1 1 0 1 1 0 0 | 2627.5271       | 0.0022    |
| 3 1 3 0 2 1 2 0 | 3396.5683       | 0.0009    |
| 3 0 3 0 2 0 2 0 | 3460.9688       | -0.0127   |
| 3 2 2 0 2 2 1 0 | 3684.7500       | -0.0114   |
| 3 1 2 0 2 1 1 0 | 3870.5851       | 0.0015    |
| 3 2 1 0 2 2 0 0 | 3943.8787       | 0.0122    |
| 4 1 4 0 3 1 3 0 | 4480.5438       | 0.0026    |
| 4 0 4 0 3 0 3 0 | 4507.5750       | 0.0009    |
| 4 2 3 0 3 2 2 0 | 4854.5750       | -0.0029   |
| 4 3 2 0 3 3 1 0 | 5011.6913       | 0.0143    |
| 4 1 3 0 3 1 2 0 | 5040.4758       | -0.0092   |
| 4 3 1 0 3 3 0 0 | 5095.6432       | 0.0075    |
| 4 2 2 0 3 2 1 0 | 5222.5209       | 0.0084    |
| 5 1 5 0 4 1 4 0 | 5550.7708       | 0.0037    |
| 5 0 5 0 4 0 4 0 | 5559.5678       | 0.0028    |
| 5 2 4 0 4 2 3 0 | 5986.4285       | -0.0031   |
| 5 1 4 0 4 1 3 0 | 6114.0073       | -0.0111   |
| 5 3 3 0 4 3 2 0 | 6243.4760       | -0.0069   |
| 5 4 2 0 4 4 1 0 | 6290.3202       | 0.0060    |
| 5 4 1 0 4 4 0 0 | 6314.8215       | 0.0069    |
| 5 2 3 0 4 2 2 0 | 6524.6579       | 0.0000    |
| 5 3 2 0 4 3 1 0 | 6552.9060       | -0.0002   |
| 6 1 6 0 5 1 5 0 | 6615.0372       | -0.0035   |
| 6 0 6 0 5 0 5 0 | 6617.5487       | -0.0027   |
| 6 2 5 0 5 2 4 0 | 7085.8133       | 0.0000    |
| 6 1 5 0 5 1 4 0 | 7146.9407       | -0.0039   |
| 6 3 4 0 5 3 3 0 | 7434.2932       | -0.0023   |
| 6 5 2 0 5 5 1 0 | 7547.1628       | 0.0038    |
| 6 5 1 0 5 5 0 0 | 7552.4666       | 0.0080    |
| 6 4 3 0 5 4 2 0 | 7568.5252       | -0.0089   |
| 6 4 2 0 5 4 1 0 | 7651.9909       | 0.0044    |
| 7 1 7 0 6 1 6 0 | 7677.2589       | 0.0010    |
| 7 0 7 0 6 0 6 0 | 7677.9223       | 0.0008    |
| 6 2 4 0 5 2 3 0 | 7704.4590       | 0.0060    |
| 6 3 3 0 5 3 2 0 | 7867.1868       | -0.0060   |
| 7 2 6 0 6 2 5 0 | 8163.7616       | 0.0011    |
| 2 1 2 1 1 1 1 1 | 2278.5005       | 0.0008    |
| 2 0 2 1 1 0 1 1 | 2384.1501       | -0.0125   |
| 2 1 1 1 1 1 0 1 | 2615.1002       | 0.0071    |
| 3 1 3 1 2 1 2 1 | 3396.4367       | 0.0012    |
| 3 0 3 1 2 0 2 1 | 3458.3291       | -0.0133   |
| 3 1 2 1 2 1 1 1 | 3866.8322       | -0.0011   |
| 3 2 1 1 2 2 0 1 | 3894.2641       | -0.0105   |
| 4 1 4 1 3 1 3 1 | 4478.7277       | 0.0025    |
| 4 0 4 1 3 0 3 1 | 4504.8544       | 0.0005    |
| 4 2 3 1 3 2 2 1 | 4874.1697       | -0.0024   |
| 4 3 2 1 3 3 1 1 | 5011.3857       | 0.0060    |
| 4 1 3 1 3 1 2 1 | 5033.7921       | -0.0045   |
| 4 3 1 1 3 3 0 1 | 5095.8886       | -0.0038   |
| 4 2 2 1 3 2 1 1 | 5240.4034       | -0.0071   |
| 5 1 5 1 4 1 4 1 | 5548.5884       | 0.0101    |
| 5 0 5 1 4 0 4 1 | 5557.0399       | 0.0031    |
| 5 2 4 1 4 2 3 1 | 5982.6376       | -0.0017   |
| 5 1 4 1 4 1 3 1 | 6106.0715       | -0.0112   |
| 5 3 3 1 4 3 2 1 | 6178.6107       | 0.0042    |
| 5 4 2 1 | 4 4 1 1 | 6282.0687 | 0.0093 |
| 5 4 1 1 | 4 4 0 1 | 6307.1022 | 0.0104 |
| 5 3 2 1 | 4 3 1 1 | 6488.3825 | 0.0062 |
| 5 2 3 1 | 4 2 2 1 | 6517.4813 | 0.0064 |
| 6 1 6 1 | 5 1 5 1 | 6612.7301 | -0.0032 |
| 6 0 6 1 | 5 0 5 1 | 6615.1325 | -0.0027 |
| 6 2 5 1 | 5 2 4 1 | 7080.0265 | 0.0013 |
| 6 1 5 1 | 5 1 4 1 | 7139.0669 | 0.0024 |
| 6 3 4 1 | 5 3 3 1 | 7439.3338 | -0.0071 |
| 6 5 2 1 | 5 5 1 1 | 7536.8818 | 0.0010 |
| 6 5 1 1 | 5 5 0 1 | 7542.4087 | -0.0001 |
| 6 4 3 1 | 5 4 2 1 | 7580.2036 | -0.0045 |
| 6 4 2 1 | 5 4 1 1 | 7665.0607 | 0.0100 |
| 7 1 7 1 | 6 1 6 1 | 7674.9206 | -0.0010 |
| 7 0 7 1 | 6 0 6 1 | 7675.5533 | -0.0008 |
| 6 2 4 1 | 5 2 3 1 | 7693.3958 | 0.0040 |
| 6 3 3 1 | 5 3 2 1 | 7871.2994 | -0.0084 |
| 7 2 6 1 | 6 2 5 1 | 8157.3461 | -0.0021 |
| 7 1 6 1 | 6 1 5 1 | 8179.3374 | -0.0038 |
| 8 0 8 1 | 7 0 7 1 | 8736.6960 | 0.0060 |
| 2 0 2 0 | 1 1 1 0 | 2185.5500 | -0.0058 |
| 5 2 4 0 | 5 1 5 0 | 2192.5907 | 0.0002 |
| 6 5 1 0 | 6 4 2 0 | 2266.8192 | 0.0010 |
| 5 5 1 0 | 5 4 2 0 | 2393.5908 | -0.0065 |
| 7 5 3 0 | 7 4 4 0 | 2400.3885 | -0.0062 |
| 7 2 5 0 | 7 1 6 0 | 2470.2616 | -0.0101 |
| 2 1 2 0 | 1 0 1 0 | 2489.3556 | -0.0085 |
| 6 1 5 0 | 6 0 6 0 | 2630.8923 | -0.0006 |
| 7 1 6 0 | 7 0 7 0 | 3139.6276 | -0.0029 |
| 7 2 6 0 | 7 1 7 0 | 3149.8740 | 0.0082 |
| 2 2 1 0 | 1 1 0 0 | 3221.3370 | 0.0113 |
| 3 1 2 0 | 2 2 1 0 | 3276.7829 | 0.0000 |
| 3 0 3 0 | 2 1 2 0 | 3357.3382 | -0.0043 |
| 2 2 0 0 | 1 1 1 0 | 3447.5129 | -0.0011 |
| 3 1 3 0 | 2 0 2 0 | 3500.2023 | -0.0040 |
| 3 2 2 0 | 2 1 1 0 | 4278.5788 | 0.0166 |
| 4 0 4 0 | 3 1 3 0 | 4468.3519 | 0.0026 |
| 4 1 4 0 | 3 0 3 0 | 4519.7669 | 0.0009 |
| 4 1 3 0 | 3 2 2 0 | 4632.4883 | -0.0181 |
| 3 3 1 0 | 2 2 0 0 | 5062.4770 | 0.0101 |
| 3 3 0 0 | 2 2 1 0 | 5142.5625 | 0.0065 |
| 4 2 3 0 | 3 1 2 0 | 5262.5757 | 0.0190 |
| 5 0 5 0 | 4 1 4 0 | 5547.3821 | 0.0089 |
| 5 1 5 0 | 4 0 4 0 | 5562.9666 | -0.0022 |
| 5 2 3 0 | 4 3 2 0 | 5616.8848 | -0.0081 |
| 5 1 4 0 | 4 2 3 0 | 5891.9475 | 0.0006 |
| 4 3 2 0 | 3 2 1 0 | 6130.2588 | -0.0186 |
| 5 2 4 0 | 4 1 3 0 | 6208.4893 | -0.0138 |
| 4 3 1 0 | 3 2 2 0 | 6553.4164 | -0.0138 |
| 6 0 6 0 | 5 1 5 0 | 6614.1522 | -0.0053 |
| 6 1 6 0 | 5 0 5 0 | 6618.4328 | -0.0017 |
| 4 4 1 0 | 3 3 0 0 | 6881.8106 | 0.0098 |
| 4 4 0 0 | 3 3 1 0 | 6901.5782 | 0.0079 |
| 6 1 5 0 | 5 2 4 0 | 7052.4583 | -0.0016 |
| 6 2 4 0 | 5 3 3 0 | 7077.8707 | 0.0078 |
| 5 3 3 0 | 4 2 2 0 | 7151.2543 | 0.0063 |
| 6 2 5 0 | 5 1 4 0 | 7180.2937 | -0.0043 |
| 7 0 7 0 | 6 1 6 0 | 7677.0383 | 0.0000 |
| 7 1 7 0 | 6 0 6 0 | 7678.1427 | 0.0017 |
| 6 3 4 0 | 5 2 3 0 | 8060.8910 | 0.0054 |
| 5 4 2 0 | 4 3 1 0 | 8076.4658 | -0.0133 |
| 7 1 6 0 | 6 2 5 0 | 8153.3122 | 0.0064 |
| 7 2 6 0 | 6 1 5 0 | 8197.1148 | 0.0009 |
| 5 4 1 0 | 4 3 2 0 | 8204.7075 | -0.0004 |
|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 5 | 1 | 4 | 1 | 5 | 0 | 5 | 1 | 2082.8584 | 0.0006 |
| 5 | 2 | 4 | 1 | 5 | 1 | 5 | 1 | 2170.6326 | -0.0108 |
| 2 | 0 | 2 | 1 | 1 | 1 | 1 | 1 | 2178.7575 | -0.0042 |
| 6 | 3 | 4 | 1 | 6 | 2 | 5 | 1 | 2180.8848 | 0.0035 |
| 7 | 4 | 4 | 1 | 7 | 3 | 5 | 1 | 2268.7141 | -0.0024 |
| 2 | 1 | 2 | 1 | 1 | 0 | 1 | 1 | 2483.8935 | -0.0069 |
| 7 | 3 | 5 | 1 | 7 | 2 | 6 | 1 | 2599.7794 | 0.0004 |
| 6 | 1 | 5 | 1 | 6 | 0 | 6 | 1 | 2606.7777 | -0.0092 |
| 6 | 2 | 5 | 1 | 6 | 1 | 6 | 1 | 2637.9364 | 0.0011 |
| 7 | 6 | 2 | 1 | 7 | 5 | 3 | 1 | 2888.0776 | -0.0079 |
| 7 | 1 | 6 | 1 | 7 | 0 | 7 | 1 | 3110.5757 | 0.0018 |
| 2 | 1 | 1 | 1 | 1 | 0 | 1 | 1 | 3220.0391 | 0.0032 |
| 3 | 0 | 3 | 1 | 2 | 1 | 2 | 1 | 3358.6024 | -0.0022 |
| 2 | 2 | 0 | 1 | 1 | 1 | 1 | 1 | 3443.5177 | -0.0096 |
| 3 | 1 | 3 | 1 | 2 | 0 | 2 | 1 | 3496.1651 | -0.0082 |
| 3 | 2 | 2 | 1 | 2 | 1 | 1 | 1 | 4240.9426 | 0.0122 |
| 4 | 0 | 4 | 1 | 3 | 1 | 3 | 1 | 4467.0264 | 0.0034 |
| 4 | 1 | 4 | 1 | 3 | 0 | 3 | 1 | 4516.5520 | -0.0039 |
| 4 | 1 | 3 | 1 | 3 | 2 | 2 | 1 | 4659.6989 | -0.0006 |
| 3 | 2 | 1 | 1 | 2 | 1 | 2 | 1 | 5059.3060 | 0.0035 |
| 3 | 3 | 1 | 1 | 2 | 2 | 0 | 1 | 5060.9238 | -0.0098 |
| 3 | 3 | 0 | 1 | 2 | 2 | 1 | 1 | 5141.0252 | 0.0120 |
| 4 | 2 | 3 | 1 | 3 | 1 | 2 | 1 | 5248.2839 | 0.0148 |
| 5 | 0 | 5 | 1 | 4 | 1 | 4 | 1 | 5545.3313 | -0.0033 |
| 5 | 1 | 5 | 1 | 4 | 0 | 4 | 1 | 5560.2850 | 0.0046 |
| 5 | 2 | 3 | 1 | 4 | 3 | 2 | 1 | 5579.8424 | -0.0042 |
| 5 | 1 | 4 | 1 | 4 | 2 | 3 | 1 | 5891.6097 | -0.0005 |
| 4 | 3 | 2 | 1 | 3 | 2 | 1 | 1 | 6178.0339 | -0.0048 |
| 5 | 2 | 4 | 1 | 4 | 1 | 3 | 1 | 6197.1071 | -0.0048 |
| 6 | 3 | 3 | 1 | 5 | 4 | 2 | 1 | 6292.6110 | 0.0006 |
| 4 | 3 | 1 | 1 | 3 | 2 | 2 | 1 | 6600.9156 | -0.0023 |
| 6 | 0 | 6 | 1 | 5 | 1 | 5 | 1 | 6611.8880 | -0.0037 |
| 6 | 1 | 6 | 1 | 5 | 0 | 5 | 1 | 6615.9730 | -0.0038 |
| 4 | 4 | 1 | 1 | 3 | 3 | 0 | 1 | 6880.9197 | 0.0129 |
| 4 | 4 | 0 | 1 | 3 | 3 | 1 | 1 | 6900.9393 | 0.0065 |
| 6 | 1 | 5 | 1 | 5 | 2 | 4 | 1 | 7048.0380 | 0.0027 |
| 5 | 3 | 3 | 1 | 4 | 2 | 2 | 1 | 7116.2388 | 0.0040 |
| 6 | 2 | 5 | 1 | 5 | 1 | 4 | 1 | 7171.0502 | -0.0041 |
| 7 | 0 | 7 | 1 | 6 | 1 | 6 | 1 | 7674.7115 | -0.0010 |
| 7 | 1 | 7 | 1 | 6 | 0 | 6 | 1 | 7675.7611 | -0.0021 |
| 5 | 4 | 1 | 1 | 4 | 3 | 2 | 1 | 8196.6432 | -0.0016 |
| 8 | 0 | 8 | 1 | 7 | 1 | 7 | 1 | 8736.5032 | -0.0029 |
| 8 | 1 | 8 | 1 | 7 | 1 | 7 | 1 | 8736.5032 | -0.0029 |
Table S17: Linelist for PhF-FAD D2 isotopologue.

| J' Ka' Kc' v' | J'' Ka'' Kc'' v'' | obs/MHz | obs-cal/MHz |
|---------------|---------------------|---------|-------------|
| 2 1 2 0 1 1 1 0 | 2296.7598 | 0.0012 |
| 2 0 2 0 1 0 1 0 | 2391.6889 | -0.0050 |
| 2 1 1 0 1 1 0 0 | 2645.6868 | 0.0067 |
| 3 1 3 0 2 1 2 0 | 3404.2872 | 0.0006 |
| 3 0 3 0 2 0 2 0 | 3462.9471 | -0.0063 |
| 3 2 2 0 2 2 1 0 | 3704.5223 | 0.0085 |
| 3 1 2 0 2 1 1 0 | 3891.9683 | 0.0000 |
| 3 2 1 0 2 2 0 0 | 3971.4350 | -0.0008 |
| 4 1 4 0 3 1 3 0 | 4487.4808 | 0.0031 |
| 4 0 4 0 3 0 3 0 | 4510.0131 | 0.0037 |
| 4 2 3 0 3 2 2 0 | 4874.6291 | -0.0059 |
| 4 3 2 0 3 3 1 0 | 5046.7558 | 0.0064 |
| 4 1 3 0 3 1 2 0 | 5052.9051 | -0.0089 |
| 4 3 1 0 3 3 0 0 | 5145.8258 | 0.0030 |
| 4 2 2 0 3 2 1 0 | 5274.6219 | 0.0014 |
| 5 1 5 0 4 1 4 0 | 5557.3691 | 0.0021 |
| 5 0 5 0 4 0 4 0 | 5564.1058 | 0.0007 |
| 5 2 4 0 4 2 3 0 | 6003.8938 | 0.0008 |
| 5 1 4 0 4 1 3 0 | 6116.0211 | -0.0068 |
| 5 3 3 0 4 3 2 0 | 6280.1402 | -0.0061 |
| 5 4 1 0 4 4 0 0 | 6373.0490 | 0.0048 |
| 5 2 3 0 4 2 2 0 | 6562.1624 | -0.0106 |
| 6 0 6 0 5 0 5 0 | 6623.7474 | 0.0056 |
| 6 2 5 0 5 2 4 0 | 7099.9004 | -0.0012 |
| 6 1 5 0 5 1 4 0 | 7148.5293 | 0.0007 |
| 6 3 4 0 5 3 3 0 | 7468.4330 | 0.0084 |
| 6 5 2 0 5 5 1 0 | 7609.3784 | -0.0003 |
| 6 4 3 0 5 4 2 0 | 7624.3494 | -0.0010 |
| 7 1 7 0 6 1 6 0 | 7684.8971 | -0.0038 |
| 7 0 7 0 6 0 6 0 | 7685.3327 | -0.0010 |
| 6 4 2 0 5 4 1 0 | 7722.4035 | 0.0004 |
| 6 2 4 0 5 2 3 0 | 7722.9035 | -0.0092 |
| 6 3 3 0 5 3 2 0 | 7943.6782 | -0.0122 |
| 7 2 6 0 6 2 5 0 | 8175.6580 | 0.0042 |
| 7 3 5 0 6 3 4 0 | 8611.5518 | -0.0036 |
| 2 1 2 1 1 1 1 1 | 2286.7197 | 0.0049 |
| 2 0 2 1 1 0 1 1 | 2390.2304 | -0.0097 |
| 2 1 1 1 1 1 0 1 | 2633.6777 | -0.0013 |
| 3 1 3 1 2 1 2 1 | 3403.6465 | 0.0009 |
| 3 0 3 1 2 0 2 1 | 3460.4313 | -0.0122 |
| 3 2 2 1 2 2 1 1 | 3666.4146 | -0.0042 |
| 3 1 2 1 2 1 1 1 | 3887.2648 | 0.0012 |
| 3 2 1 1 2 2 0 1 | 3931.8211 | -0.0213 |
| 4 1 4 1 3 1 3 1 | 4485.5401 | 0.0030 |
| 4 0 4 1 3 0 3 1 | 4507.4486 | 0.0004 |
| 4 2 3 1 3 2 2 1 | 4885.0776 | -0.0002 |
| 4 1 3 1 3 1 2 1 | 5046.0228 | -0.0093 |
| 4 3 2 1 3 3 1 1 | 5048.6022 | 0.0061 |
| 4 2 2 1 3 2 1 1 | 5282.5987 | -0.0031 |
| 5 1 5 1 4 1 4 1 | 5555.1668 | 0.0166 |
| 5 0 5 1 4 0 4 1 | 5561.6882 | 0.0062 |
| 5 2 4 1 4 2 3 1 | 5999.2711 | 0.0023 |
| 5 1 4 1 4 1 3 1 | 6108.3814 | -0.0075 |
| 5 3 3 1 4 3 2 1 | 6221.3719 | 0.0039 |
| 5 4 2 1 4 4 1 1 | 6331.2748 | 0.0154 |
| 5 4 1 1 4 4 0 1 | 6364.3014 | 0.0116 |
| 5 2 3 1 4 2 2 1 | 6553.4164 | -0.0013 |
| 5 3 2 1 | 4 3 1 1 | 6558.0506 | 0.0081 |
| 6 1 6 1 | 5 1 5 1 | 6619.6789 | 0.0034 |
| 6 2 5 1 | 5 2 4 1 | 7093.8396 | 0.0033 |
| 6 1 5 1 | 5 1 4 1 | 7141.1132 | 0.0035 |
| 6 3 4 1 | 5 3 3 1 | 7467.6830 | 0.0105 |
| 6 5 2 1 | 5 5 1 1 | 7597.3726 | 0.0012 |
| 6 5 1 1 | 5 5 0 1 | 7605.5292 | -0.0115 |
| 6 4 3 1 | 5 4 2 1 | 7651.1254 | 0.0027 |
| 7 1 7 1 | 6 1 6 1 | 7682.5913 | -0.0040 |
| 7 0 7 1 | 6 0 6 1 | 7683.0066 | -0.0070 |
| 6 2 4 1 | 5 2 3 1 | 7711.3993 | 0.0023 |
| 6 4 2 1 | 5 4 1 1 | 7749.7918 | 0.0011 |
| 6 3 3 1 | 5 3 2 1 | 7940.6904 | -0.0094 |
| 7 2 6 1 | 6 2 5 1 | 8169.1985 | 0.0174 |
| 7 3 5 1 | 6 3 4 1 | 8603.3538 | 0.0028 |
| 5 2 4 0 | 5 1 5 0 | 2201.3290 | -0.0108 |
| 6 3 4 0 | 6 2 5 0 | 2202.3757 | 0.0033 |
| 2 0 2 0 | 1 1 1 0 | 2206.4844 | -0.0024 |
| 7 4 4 0 | 7 3 5 0 | 2272.8497 | -0.0010 |
| 2 1 2 0 | 1 0 1 0 | 2481.9610 | -0.0047 |
| 6 2 5 0 | 6 1 6 0 | 2679.2697 | -0.0031 |
| 7 6 1 0 | 7 5 2 0 | 2680.3869 | -0.0082 |
| 7 2 6 0 | 7 1 7 0 | 3170.0277 | 0.0019 |
| 2 2 1 0 | 1 1 0 0 | 3195.5261 | -0.0026 |
| 3 0 3 0 | 2 1 2 0 | 3372.6800 | -0.0016 |
| 2 2 0 0 | 1 1 1 0 | 3435.3493 | -0.0062 |
| 3 1 3 0 | 2 0 2 0 | 3494.5479 | -0.0105 |
| 3 2 2 0 | 2 1 1 0 | 4254.3816 | 0.0191 |
| 4 0 4 0 | 3 1 3 0 | 4478.4047 | 0.0003 |
| 4 1 4 0 | 3 0 3 0 | 4519.0861 | 0.0035 |
| 4 1 3 0 | 3 2 2 0 | 4690.5315 | 0.0115 |
| 3 3 1 0 | 2 2 0 0 | 5018.8143 | -0.0136 |
| 3 2 1 0 | 2 1 2 0 | 5110.0289 | -0.0039 |
| 3 3 0 0 | 2 2 1 0 | 5110.2824 | 0.0305 |
| 4 2 3 0 | 3 1 2 0 | 5237.0352 | 0.0059 |
| 5 0 5 0 | 4 1 4 0 | 5555.0492 | 0.0173 |
| 5 1 5 0 | 4 0 4 0 | 5566.4351 | -0.0050 |
| 5 2 3 0 | 4 3 2 0 | 5742.6480 | -0.0041 |
| 5 1 4 0 | 4 2 3 0 | 5931.9104 | -0.0023 |
| 4 3 2 0 | 3 2 1 0 | 6094.1356 | -0.0057 |
| 5 2 4 0 | 4 1 3 0 | 6187.9957 | -0.0123 |
| 4 3 1 0 | 3 2 2 0 | 6551.5810 | 0.0202 |
| 6 1 6 0 | 5 0 5 0 | 6624.3116 | 0.0079 |
| 4 4 1 0 | 3 3 0 0 | 6823.4047 | 0.0025 |
| 4 4 0 0 | 3 3 1 0 | 6848.1605 | 0.0012 |
| 6 1 5 0 | 5 2 4 0 | 7076.5484 | -0.0001 |
| 5 3 3 0 | 4 2 2 0 | 7099.6632 | -0.0040 |
| 6 2 5 0 | 5 1 4 0 | 7171.8827 | 0.0009 |
| 6 2 4 0 | 5 3 3 0 | 7185.4172 | -0.0013 |
| 7 0 7 0 | 6 1 6 0 | 7684.7698 | 0.0019 |
| 7 1 7 0 | 6 0 6 0 | 7685.4579 | 0.0050 |
| 5 4 1 0 | 4 3 2 0 | 8174.4546 | 0.0005 |
| 7 2 6 0 | 6 1 5 0 | 8199.0030 | -0.0039 |
| 5 5 1 0 | 4 4 0 0 | 8606.6218 | 0.0060 |
| 5 2 4 1 | 5 1 5 1 | 2179.9264 | -0.0043 |
| 2 0 2 1 | 1 1 1 1 | 2199.2126 | -0.0009 |
| 6 5 2 1 | 6 4 3 1 | 2225.3155 | -0.0017 |
| 5 5 0 1 | 5 4 1 1 | 2242.3517 | 0.0096 |
| 2 1 2 1 | 1 0 1 1 | 2477.7362 | -0.0034 |
| 6 1 5 1 | 6 0 6 1 | 2631.9906 | -0.0039 |
| 7 2 6 1 | 7 1 7 1 | 3140.6846 | 0.0073 |
| 2 2 1 1 | 1 1 0 1 | 3194.5109 | -0.0014 |
| 3 1 2 1 | 2 2 1 1 | 3326.4071 | -0.0231 |
| 3 0 3 1 | 2 1 2 1 | 3372.9425 | -0.0015 |

S31
| x | y | z | a | b | c | d | e | f |
|---|---|---|---|---|---|---|---|---|
| 2 | 2 | 0 | 1 | 1 | 1 | 1 | 1 | 1 |
| 3 | 1 | 3 | 1 | 2 | 0 | 2 | 1 | 1 |
| 3 | 2 | 1 | 0 | 2 | 1 | 1 | 1 | 1 |
| 4 | 0 | 4 | 1 | 3 | 1 | 3 | 1 | 1 |
| 4 | 1 | 4 | 1 | 3 | 0 | 3 | 1 | 1 |
| 4 | 1 | 3 | 1 | 3 | 2 | 2 | 1 | 1 |
| 3 | 3 | 1 | 1 | 2 | 2 | 0 | 1 | 1 |
| 3 | 3 | 0 | 1 | 2 | 2 | 1 | 1 | 1 |
| 4 | 2 | 3 | 1 | 3 | 1 | 2 | 1 | 1 |
| 5 | 0 | 5 | 1 | 4 | 1 | 4 | 1 | 1 |
| 5 | 1 | 5 | 1 | 4 | 0 | 4 | 1 | 1 |
| 5 | 1 | 4 | 1 | 4 | 2 | 3 | 1 | 1 |
| 4 | 3 | 2 | 1 | 3 | 2 | 1 | 1 | 1 |
| 5 | 2 | 4 | 1 | 4 | 1 | 3 | 1 | 1 |
| 4 | 3 | 1 | 1 | 3 | 2 | 2 | 1 | 1 |
| 5 | 0 | 6 | 1 | 5 | 1 | 5 | 1 | 1 |
| 4 | 4 | 1 | 1 | 3 | 3 | 0 | 1 | 1 |
| 4 | 4 | 0 | 1 | 3 | 3 | 1 | 1 | 1 |
| 6 | 1 | 5 | 1 | 5 | 2 | 4 | 1 | 1 |
| 6 | 2 | 5 | 1 | 5 | 1 | 4 | 1 | 1 |
| 6 | 2 | 4 | 1 | 5 | 3 | 3 | 1 | 1 |
| 7 | 0 | 7 | 1 | 6 | 1 | 6 | 1 | 1 |
| 7 | 1 | 7 | 1 | 6 | 0 | 6 | 1 | 1 |
| 6 | 3 | 4 | 1 | 5 | 2 | 3 | 1 | 1 |
| 5 | 4 | 2 | 1 | 4 | 3 | 1 | 1 | 1 |
| 7 | 1 | 6 | 1 | 6 | 2 | 5 | 1 | 1 |
| 5 | 4 | 1 | 1 | 4 | 3 | 2 | 1 | 1 |
| 7 | 2 | 6 | 1 | 6 | 1 | 5 | 1 | 1 |
| 5 | 5 | 1 | 1 | 4 | 4 | 0 | 1 | 1 |
| 5 | 5 | 0 | 1 | 4 | 4 | 1 | 1 | 1 |
| 6 | 1 | 6 | 0 | 5 | 1 | 5 | 0 | 1 |
| 6 | 1 | 6 | 1 | 5 | 0 | 5 | 1 | 1 |
| 6 | 0 | 6 | 0 | 5 | 1 | 5 | 0 | 1 |
| 6 | 0 | 6 | 1 | 5 | 0 | 5 | 1 | 1 |

S32
| $J'$  | $K_a'$ | $K_c'$ | $J''$ | $K_a''$ | $K_c''$ | obs/MHz    | obs-cal/MHz |
|-------|--------|--------|-------|---------|---------|------------|-------------|
| 4     | 1      | 4      | 3     | 1       | 3       | 4493.9896  | 0.0068      |
| 4     | 0      | 4      | 3     | 0       | 3       | 4521.8031  | -0.0034     |
| 5     | 1      | 5      | 4     | 1       | 4       | 5568.9718  | -0.0009     |
| 5     | 0      | 5      | 4     | 0       | 4       | 5578.1950  | -0.0125     |
| 6     | 1      | 6      | 5     | 1       | 5       | 6637.9313  | 0.0002      |
| 6     | 0      | 6      | 5     | 0       | 5       | 6640.6217  | 0.0044      |
| 4     | 0      | 4      | 3     | 1       | 3       | 4481.0959  | 0.0035      |
| 5     | 0      | 5      | 4     | 1       | 4       | 5565.3079  | -0.0092     |
| 5     | 1      | 5      | 4     | 0       | 4       | 5581.8722  | 0.0090      |
| 6     | 0      | 6      | 5     | 1       | 5       | 6636.9581  | -0.0035     |
| 6     | 1      | 6      | 5     | 0       | 5       | 6641.5945  | 0.0079      |
| 7     | 0      | 7      | 6     | 1       | 6       | 7704.5150  | -0.0073     |
| 7     | 1      | 7      | 6     | 0       | 6       | 7705.7427  | 0.0052      |
Table S19: Linelist for PhF-FAD D3 isotopologue.

| $J'$ | $K_a'$ | $K_c'$ | $J''$ | $K_a''$ | $K_c''$ | obs/MHz  | obs-cal/MHz |
|------|--------|--------|------|---------|---------|-----------|-------------|
| 3    | 0      | 3      | 2    | 0       | 2       | 3486.5421 | -0.0167     |
| 3    | 1      | 2      | 1    | 1       | 1       | 3890.5241 | -0.0026     |
| 4    | 1      | 4      | 3    | 1       | 3       | 4515.1573 | 0.0060      |
| 4    | 2      | 3      | 2    | 2       | 2       | 4880.7742 | 0.0005      |
| 5    | 1      | 5      | 4    | 1       | 4       | 5595.0730 | 0.0027      |
| 5    | 0      | 5      | 4    | 0       | 4       | 5604.2506 | 0.0057      |
| 5    | 1      | 4      | 4    | 1       | 3       | 6153.1186 | -0.0142     |
| 5    | 3      | 3      | 4    | 3       | 2       | 6267.7207 | 0.0085      |
| 5    | 4      | 1      | 4    | 4       | 0       | 6343.6289 | -0.0045     |
| 5    | 2      | 3      | 4    | 2       | 2       | 6555.5656 | 0.0053      |
| 6    | 1      | 6      | 5    | 1       | 5       | 6668.9514 | 0.0029      |
| 6    | 0      | 6      | 5    | 0       | 5       | 6671.6079 | 0.0004      |
| 6    | 2      | 5      | 5    | 2       | 4       | 7132.8943 | -0.0064     |
| 6    | 1      | 5      | 5    | 1       | 4       | 7196.2078 | -0.0102     |
| 6    | 3      | 4      | 5    | 3       | 3       | 7470.8073 | 0.0070      |
| 7    | 1      | 7      | 6    | 1       | 6       | 7740.7043 | -0.0001     |
| 7    | 0      | 7      | 6    | 0       | 6       | 7741.4180 | -0.0003     |
| 6    | 2      | 4      | 5    | 2       | 3       | 7745.0307 | 0.0094      |
| 3    | 1      | 3      | 2    | 0       | 2       | 3527.0997 | 0.0056      |
| 4    | 0      | 4      | 3    | 1       | 3       | 4502.3685 | 0.0060      |
| 4    | 1      | 4      | 3    | 0       | 3       | 4555.6880 | 0.0015      |
| 3    | 3      | 1      | 2    | 2       | 0       | 5086.8581 | -0.0097     |
| 5    | 0      | 5      | 4    | 1       | 4       | 5591.4588 | 0.0028      |
| 5    | 1      | 5      | 4    | 0       | 4       | 5607.8568 | -0.0022     |
| 5    | 1      | 4      | 4    | 2       | 3       | 5924.4274 | -0.0026     |
| 4    | 3      | 2      | 3    | 2       | 1       | 6200.3208 | 0.0115      |
| 6    | 0      | 6      | 5    | 1       | 5       | 6667.9952 | 0.0019      |
| 6    | 1      | 6      | 5    | 0       | 5       | 6672.5653 | 0.0025      |
| 6    | 1      | 5      | 5    | 2       | 4       | 7097.4631 | -0.0173     |
| 7    | 0      | 7      | 6    | 1       | 6       | 7740.4625 | -0.0007     |
| 7    | 1      | 7      | 6    | 0       | 6       | 7741.6636 | 0.0038      |
Table S20: Linelist for PhF-FAD D4 isotopologue.

| J'  | Ka'  | Kc'  | J'' | Ka'' | Kc'' | obs/MHz   | obs-cal/MHz |
|-----|------|------|-----|------|------|-----------|-------------|
| 3   | 1    | 2    | 1   | 1    | 1    | 3890.2622 | -0.0057     |
| 3   | 2    | 1    | 2   | 0    | 3    | 3916.4480 | -0.0003     |
| 4   | 0    | 4    | 3   | 0    | 3    | 4538.0770 | 0.0136      |
| 4   | 2    | 3    | 2   | 2    | 2    | 4878.7447 | -0.0017     |
| 4   | 1    | 3    | 1   | 2    | 0    | 5066.3481 | 0.0158      |
| 3   | 3    | 1    | 2   | 0    | 3    | 5083.0896 | -0.0003     |
| 4   | 3    | 1    | 3   | 0    | 3    | 5126.9019 | 0.0196      |
| 4   | 2    | 2    | 3   | 2    | 1    | 5269.3586 | -0.0129     |
| 5   | 1    | 5    | 4   | 1    | 4    | 5589.1823 | 0.0028      |
| 5   | 0    | 5    | 4   | 0    | 4    | 5598.1448 | 0.0016      |
| 5   | 2    | 4    | 4   | 2    | 3    | 6019.6376 | -0.0092     |
| 5   | 1    | 4    | 4   | 1    | 3    | 6148.4081 | -0.0166     |
| 5   | 2    | 3    | 2    | 4    | 2    | 6555.6525 | -0.0066     |
| 6   | 1    | 6    | 5   | 1    | 5    | 6661.6451 | 0.0027      |
| 6   | 0    | 6    | 5   | 0    | 5    | 6664.2200 | 0.0005      |
| 6   | 2    | 5    | 5   | 2    | 4    | 7127.6894 | -0.0065     |
| 6   | 1    | 5    | 5   | 1    | 4    | 7189.8135 | -0.0023     |
| 6   | 3    | 4    | 5   | 3    | 3    | 7468.6863 | 0.0048      |
| 7   | 1    | 7    | 6   | 1    | 6    | 7732.0207 | 0.0016      |
| 7   | 0    | 7    | 6   | 0    | 6    | 7732.7071 | 0.0016      |
| 6   | 2    | 4    | 5   | 2    | 3    | 7742.2915 | 0.0231      |
| 6   | 3    | 3    | 5   | 3    | 2    | 7913.2178 | -0.0031     |
| 3   | 2    | 2    | 2    | 1    | 1    | 4303.0534 | 0.0065      |
| 4   | 0    | 4    | 3    | 1    | 3    | 4498.2693 | 0.0013      |
| 5   | 0    | 5    | 4    | 1    | 4    | 5585.6872 | 0.0008      |
| 5   | 1    | 5    | 4    | 0    | 4    | 5601.6380 | 0.0018      |
| 5   | 1    | 4    | 4    | 2    | 3    | 5923.2177 | -0.0139     |
| 5   | 2    | 4    | 4    | 1    | 3    | 6244.8318 | -0.0081     |
| 6   | 0    | 6    | 5    | 1    | 5    | 6660.7253 | -0.0011     |
| 6   | 1    | 6    | 5    | 0    | 5    | 6665.1379 | 0.0024      |
| 6   | 2    | 5    | 5    | 1    | 4    | 7224.1026 | -0.0085     |
| 7   | 0    | 7    | 6    | 1    | 6    | 7731.7886 | -0.0008     |
| 7   | 1    | 7    | 6    | 0    | 6    | 7732.9354 | 0.0003      |
S4 Structure of the PhF-FAD complex

S4.1 Experimental \( r_s \) structure

Figure S1: Overlay of experimental \( r_s \) coordinates of the PhF-FAD complex with its theoretical \( r_e \) structure at the B3LYP-D3BJ/def2-TZVP level of theory.

Table S21: Experimental \( r_s \) coordinates of the PhF-FAD complex. Standard errors within parentheses are expressed in units of the last two digits.

|   | \( a \), Å |   | \( b \), Å |   | \( c \), Å |
|---|---|---|---|---|---|
| \( 0^+ \) | \( 0^- \) | \( 0^+ \) | \( 0^- \) | \( 0^+ \) | \( 0^- \) |
| C1 | 2.27088(72) 2.26766(71) | 1.2174(14) 1.2180(13) | 0.2677(62) 0.2644(62) |
| C2 | 0.8652(42) 0.9155(33) | 2.3017(16) 2.2733(14) | \( i \cdot 0.226(17) \) \( [a] \) | \( 0.285(11) \) |
| C3 | 1.0757(21) 1.1041(16) | 1.2509(18) 1.2289(15) | 0.2836(79) 0.051(35) |
| C4 | 2.51262(66) 2.50798(75) | 1.0761(16) 1.0847(18) | 0.2874(58) | 0.2534(75) |
| H1 | 2.54154(62) 2.54107(62) | 2.30242(69) 2.30317(69) | \( i \cdot 0.097(16) \) \( [a] \) | \( i \cdot 0.114(14) \) \( [a] \) |
| H2 | 0.4252(38) 0.4225(38) | 3.27405(49) 3.27449(49) | \( i \cdot 0.1720(95) \) \( [a] \) | \( i \cdot 0.1801(90) \) \( [a] \) |

\([a]\) Imaginary values are fixed to zero when calculating the structural parameters.
Table S22: Experimental ($r_s$) and theoretical ($r_e$) interatomic distances in the PhF-FAD complex. Theoretical values correspond to calculations done at the B3LYP-D3BJ/def2-TZVP level of theory. Standard errors within parentheses are expressed in units of the last two digits.

|       | $r_s(0^+)$, Å | $r_s(0^-)$, Å | $r_e$, Å |
|-------|---------------|---------------|---------|
| C1...C2 | 3.7989(26) | 3.7440(22) | 3.79   |
| C3...C4 | 2.7349(23) | 2.7137(34) | 2.75   |
| C1–H1  | 1.1499(21) | 1.1499(20) | 1.10   |
| C2–H2  | 1.0673(28) | 1.1517(37) | 1.10   |

S4.2 Theoretical calculations

Table S23: Cartesian coordinates of the equilibrium structures of the three lowest conformers of PhF-FAD complex at the gCP-B3LYP-D3BJ/def2-TZVP level of theory. The second and the third conformers are higher in energy than the first one by 0.5 and 0.6 kcal/mol, respectively.

|  | Rotational Constants: 903.63841634 704.39512718 533.98023625 MHz |
|---|---|---|---|---|
| C | -2.3831434912 | -0.3601444070 | -1.1016949413 |
| C | -1.7441131530 | 0.8713196942 | -0.1017280853 |
| C | -1.1684984300 | 1.2313143394 | 0.1883215000 |
| C | -1.2007288021 | 0.4134553957 | 1.3036285279 |
| C | -1.8459220677 | -0.8148858547 | 1.2018215698 |
| C | -2.4366692725 | -1.2033491916 | 0.0039787951 |
| H | -2.8341385368 | -0.662187104 | -0.0238434527 |
| H | -1.6806238877 | 1.5415038867 | -1.8642067634 |
| H | -0.7223498964 | 0.7333845094 | 2.2195430811 |
| H | -1.8769140760 | -1.471177650 | 2.0624930394 |
| H | -2.9361636023 | -2.1613174172 | -0.068812697 |
| F | -0.5395463505 | 2.4278258198 | 0.2784675244 |
| C | 0.9278552374 | -2.2513489566 | -0.2570546107 |
| O | 0.9891017672 | -1.5433123173 | -1.2451058827 |
| O | 1.3616308738 | -1.9542548025 | 0.9421466689 |
| H | 0.4871196160 | -3.2548333595 | -0.2938538794 |
| H | 1.7193908335 | -1.0149638804 | 0.9685160443 |
| C | 2.2910378954 | 1.2742338735 | -0.008581447 |
| C | 2.2502134126 | 0.5542398599 | 0.9751799179 |
| C | 1.2200527285 | -1.2234612039 |
| C | 2.647424072 | 2.3077935970 | 0.0463769388 |
| C | 1.5861558124 | 0.003072452 | -1.2525156851 |
| Rotational Constants: 1040.26429152 531.64886052 496.38944736 MHz |
| C | -0.5697225207 | -1.1643899281 | -0.7417102112 |
| C | -0.6541850128 | -1.9343369360 | 0.6096938876 |
| C | -1.5232536846 | -1.2282460851 | 1.4344934631 |
| C | -2.3085536274 | -2.0351675250 | 0.9158114470 |
| C | -2.2026452291 | 0.0924612124 | -0.4325835451 |
| C | -1.3465055678 | -0.5924882555 | -1.2768461713 |
| H | -2.1287901053 | -0.3191256752 | -2.3219581790 |
| F | -2.9597844883 | 1.0899248820 | -0.933395609 |
| H | -2.9943464416 | 0.3595025249 | 1.5356138221 |
| H | -1.5877292849 | -1.4680162594 | 2.4879344761 |
| H | -0.0385739129 | -2.7244188038 | 1.0196132503 |
| H | 0.1067077472 | -2.1595507769 | -1.3881634655 |
| C | 2.9264510131 | -0.6274480383 | -0.838117214 |
| O | 0.3730320359 | 0.2854686450 | -1.4243784888 |
| O | 2.8386049631 | -0.9018901968 | 0.4375445568 |
| H | 2.2422371266 | -0.2407885784 | 0.9091053091 |
| H | 3.5799327869 | -1.3362778477 | -1.3633022117 |
| X       | Y       | Z       |
|---------|---------|---------|
| C 0.6514296671 | 1.7287591396 | 1.0649032530 |
| O 1.2799620266 | 0.8672237245 | 1.6532034417 |
| O 0.7131213532 | 2.0001928101 | -0.2140022058 |
| H 1.3372115563 | 1.3715087337 | -0.6843206780 |
| H -0.0516415447 | 2.3882603095 | 1.5870184967 |

Rotational Constants: 1011.89413301 540.8005169 475.45131207 MHz

| X       | Y       | Z       |
|---------|---------|---------|
| C 2.0643876272 | -1.6020569586 | -0.3956671059 |
| C 1.1040340396 | -1.3828718177 | -1.3782933988 |
| C 0.6501253122 | -0.0914847267 | -1.6259630581 |
| C 1.5017447393 | 0.9830060548 | -0.8978685679 |
| C 2.1062954993 | 0.7353349560 | 0.0719398533 |
| C 2.5755878813 | -0.5381075479 | 0.3411572701 |
| H 3.3221229493 | -0.6828132776 | 1.1111462033 |
| F 2.5974746153 | 1.7735434537 | 0.7820330580 |
| H 0.8079439466 | 1.9967224291 | -1.0652799226 |
| H -0.1030839336 | 0.0809082208 | -2.3846735782 |
| H 0.7043215784 | -2.2165357911 | -1.9424840783 |
| H 2.4216310253 | -2.6059554850 | -0.2001595790 |
| C -2.7810454320 | 1.2597231247 | -0.5891538540 |
| O -2.9177782987 | 0.0861995805 | -0.8861429553 |
| O -2.0380042443 | 1.7377012828 | 0.3752451254 |
| H -1.5679744336 | 0.9969364122 | 0.8711237656 |
| H -3.2975760920 | 2.0569988401 | -1.138864186 |
| C -0.9473302556 | -1.4167573481 | 1.3675756061 |
| O -0.8338813214 | -0.2416991425 | 1.6639339658 |
| O -1.7203060967 | -1.9119882199 | 0.4326063918 |
| H -2.1902377006 | -1.1782759888 | -0.0642865495 |
| H -0.3882472178 | -2.2001938053 | 1.8920971141 |
Table S24: Equilibrium structure of the PhF-FAD complex at gCP-B2PLYP/def2-TZVP level of theory

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Rotational Constants: 900.10015152 655.01469538 509.22928855 MHz

C -2.370095364 -0.4618957943 -1.1932691838
C -1.7096449031 0.7595164022 -1.1041828470
C -1.2535875489 1.1693453959 0.1366471558
C -1.4234354531 0.4126706406 1.2826312829
C -2.0870190103 -0.8060676058 1.1751904308
C -2.5609892231 -1.2444988537 -0.0579903045
H -2.7325989177 -0.8007380347 -2.1541956773
H -1.5433120064 1.3843132633 -1.9701126700
H -1.0397840052 0.7738701009 2.2261433092
H -2.2294636881 -1.4121825207 -0.1340586227
F -0.6086295199 2.3543223890 0.2317239602
C 1.1897551198 -2.2561389356 -0.1897013655
O 1.2958258889 -1.5786129205 -1.1977937988
O 1.4546911702 -1.8738087402 1.035807313
H 0.8526448921 -3.2958592655 -0.2258582115
H 1.7429271201 -0.9141527207 1.0447910172
C 2.2413076926 1.3869648986 0.0351140059
O 2.1901074921 0.6892916293 1.0346851216
O 2.0023063122 0.9976898829 -1.1936741136
H 2.5070035766 2.4458292146 0.0811360404
H 1.7462149939 0.0301253958 -1.2080545329

S5 Adjusting the molecular mechanics (MM) force field for the QM/MM simulations

In the QM/MM approach, PhF was presented as a rigid molecule with a geometry being fixed at the B2PLYP/def2-TZVP structure. The interaction with the FAD was induction via electrostatic embedding and exchange+dispersion interactions modeled by the Lennard-Jones potential

$$V_{LJ,ij}(r_{ij}) = \varepsilon_{ij} \cdot \left( \left( \frac{r_{\text{min},ij}}{r_{ij}} \right)^{12} - 2 \left( \frac{r_{\text{min},ij}}{r_{ij}} \right)^{6} \right),$$

where \(V_{LJ,ij}\) is the interaction energy between atom numbers \(i\) and \(j\), \(r_{ij}\) is the distance between these atoms, \(\varepsilon_{ij} = \sqrt{\varepsilon_i \cdot \varepsilon_j}\) and \(r_{\text{min},ij} = \frac{1}{2}(r_i + r_j)\) with \(\varepsilon_i\) and \(r_i\) being the interaction energy and radius of the atom number \(i\).

The atomic charges of PhF were frozen at the CHELPG values at the B2PLYP/def2-TZVP level of theory. The only fitted values of the MM potential were the interaction energies and radii of the different atomic types (\(\varepsilon_i\) and \(r_i\)). The latter were parametrized to fit the SAPT2/aug-cc-pVDZ interaction energy of FAD with PhF. For this purpose, we have generated 860 randomly parallel-displaced structures (600 for the training set and 260 for the test set) on the basis of the B2PLYP/def2-TZVP geometries of PhF and FAD at the different stages of the double proton transfer reaction. To compensate for difference in the induction interaction in the electrostatic embedding QM/MM and in the SAPT2 calculations, we have performed the fitting for the corrected SAPT2/aug-cc-pVDZ interaction values:

$$E_{\text{SAPT2}}^{(\text{corr})} = E_{\text{SAPT2}}^{(\text{raw})} - (E_{\text{PBEh-3c/MM}}^{\text{charges}} - E_{\text{PBEh-3c/MM}}^{\text{no charges}}),$$

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Table S25: Initial and fitted interaction energies Lennard-Jones potential (Eq. 2) parameters for PhF-FAD dispersion/exchange interaction. The fitting aimed at reproducing the SAPT2/aug-cc-pVDZ interaction energies given by Eq. 3.

| Atom type | OPLS-AA | | Fit | |
|-----------|---------|----------------|---------|----------------|
|           | $\varepsilon$, kcal/mol | $r$, Å | $\varepsilon$, kcal/mol | $r$, Å |
| H         | -0.03   | 2.72           | -0.01   | 2.66           |
| H$_{ac}$  | 0.0     | 2.72           | 0.0     | 2.60           |
| H$_{al}$  | -0.02   | 2.72           | -0.03   | 2.54           |
| C$_F$     | -0.07   | 3.98           | -0.05   | 3.90           |
| C$_H$     | -0.07   | 3.98           | -0.09   | 3.91           |
| C$_{ac}$  | -0.105  | 4.21           | -0.03   | 3.58           |
| F         | -0.06   | 3.20           | -0.06   | 2.93           |
| O         | -0.19   | 3.34           | -0.21   | 3.29           |

where $E^{(\text{raw})}_{\text{SAPT2}}$ are the PhF-FAD interaction energies as produced by the SAPT2, $E^{\text{PBEh-3c/MM}}_{\text{charges}}$ are the total QM/MM energies of the same structure without any Lennard-Jones interaction. The $E^{\text{PBEh-3c/MM charges}}_{\text{PBEh-3c/MM}}$ values were computed with CHELPG charges on PhF, whilst $E^{\text{no charges}}_{\text{PBEh-3c/MM}}$ were obtained without charges on the PhF (i.e., in the case of non-interacting PhF and FAD). The $(E^{\text{PBEh-3c/MM charges}}_{\text{PBEh-3c/MM}} - E^{\text{no charges}}_{\text{PBEh-3c/MM}})$ correction is thus the induction interaction energy of PhF with FAD at the PBEh-3c/MM level of theory.

In order to remove a strong influence of highly energetic exchange repulsion on small PhF-FAD distances, only structures with energies $E^{(\text{corr})}_{\text{SAPT2}} < 2000$ cm$^{-1}$ were considered in the fitting. That left 479 and 215 structures from the training and test sets, respectively. The starting ($\varepsilon_i$, $r_i$) parameters were taken from the OPLS-AA [29, 30] force field. The initial root-mean-square deviations (RMSD) for training and test sets with these parameters were 538 and 451 cm$^{-1}$, respectively. After fitting, they have decreased to 133 and 116 cm$^{-1}$, respectively. The fitted Lennard-Jones potential has eight types of atoms considered:

- For PhF:
  - hydrogens (H),
  - fluorine (F),
  - $sp^2$ hybridized carbons connected to hydrogens (in the C–H fragments, C$_H$),
  - $sp^2$ hybridized carbon connected to fluorine (in the C–F fragment, C$_F$).
- For FAD:
  - acetic $sp^2$ hybridized carbon (C$_{ac}$),
  - aliphatic hydrogen (in the C–H fragment, H$_{al}$),
  - acetic hydrogen (in the O–H fragment, H$_{ac}$),
  - oxygens (O).

The initial OPLS-AA and fitted parameters are given in Table S25.
The reaction coordinate for proton transfer was

$$\xi = \frac{r(O1H1) + r(O4H2) - r(O3H1) - r(O2H2)}{\sqrt{8}},$$

(4)

see Fig. S2 for atom numbering.

Figure S2: The configuration of the PhF-FAD cluster with atom numbering and principal axes system.

Figure S3: Potential energy surfaces for the double proton transfer in FAD and PhF-FAD along the reaction coordinate given by Eq. 4 at different levels of theory.
Comparison of FAD and PhF-FAD at the PBEh-3c(/MM) level of theory

![Graphical representation of PES, effective mass, and wavefunction for FAD and PhF-FAD](image)

**Figure S4:** From top to bottom: theoretical potential energy surfaces (PES) with effective PES (PES+ZPVE), effective masses $\mu = G^{-1}$, and wavefunctions for the $0^+ / 0^-$ states of FAD and PhF-FAD along the reaction coordinate given by Eq. 4. The calculations were done at the PBEh-3c and PBEh-3c/MM levels of theory for FAD and PhF-FAD, respectively.
S7 An illustrative model for the decrease of the tunneling rate in PhF-FAD with respect to FAD

Let us imagine that the PhF-FAD has two coupled motions.

• The double proton transfer parametrized by internal coordinate $\xi$, and given by Hamiltonian

$$\hat{H}_{pt} = \hat{T}_{pt} + V_{pt}(\xi),$$

where $\hat{T}_{pt}$ and $V_{pt}(\xi)$ are the proton transfer kinetic energy and potential in the free FAD, respectively. The $V_{pt}$ is a standard double well potential (see Fig. S6 with $\xi = 0$ corresponding to the transition state. The two localized energy degenerate vibrational ground states in each well ($|a\rangle$ and $|b\rangle$) form the symmetric ($|+\rangle \approx (|a\rangle + |b\rangle)/\sqrt{2}$) and antisymmetric ($|-\rangle \approx (|a\rangle - |b\rangle)/\sqrt{2}$) eigenstates with energies $\hat{H}_{pt}|\pm\rangle = E^{(0)}_{\pm} |\pm\rangle$ and energy separation (tunneling splitting) of

$$\epsilon = E^{(0)}_{-} - E^{(0)}_{+} > 0.$$  

• The second motion is the environment mode of the same symmetry as the reaction coordinate $\xi$. This environmental mode is coupled to the proton transfer motion. In the case of PhF-FAD, this is an internal counter-rotation of FAD and PhF around the $a$-axis of the complex. This motion can be treated in a harmonic approximation with the Hamiltonian

$$\hat{H}_{env} = \hbar \omega (\hat{P}^2 + \hat{Q}^2),$$

where $\hat{P}$ and $\hat{Q}$ are the momentum and coordinate operators of this motion, and $\omega$ is the angular frequency of this vibration, which is taken to be independent of the $\xi$ (see Fig. S6). The eigenvalues/eigenstates of this Hamiltonian are given as $\hat{H}_{env}|v\rangle = \hbar \omega (v + 1/2)|v\rangle$, where $v = 0, 1, 2, \ldots$ is the vibrational quantum number.

The coupling between proton transfer and the environment mode is introduced as following: the equilibrium value of $Q$ will depend on $\xi$ as $Q_{eq} \approx \alpha \xi$, where $\alpha$ is the coupling coefficient, which can be positive or negative. This will lead to a modified potential energy for the environmental mode:

$$V_{env} \approx \frac{\hbar \omega}{2} (Q - \alpha \xi)^2 = \frac{\hbar \omega}{2} Q^2 - \hbar \omega \alpha \xi Q + \frac{\hbar \omega}{2} (\alpha \xi)^2.$$  

We will assume that the perturbation of the pure proton transfer potential $\frac{\hbar \omega}{2} (\alpha \xi)^2$ is too small compared to $V_{pt}(\xi)$, therefore this term can be ignored. This leads to a coupled Hamiltonian of the form:

$$\hat{H} = \hat{H}_{pt} + \hat{H}_{env} + \hat{W},$$

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where $\hat{W} = -\hbar \omega \alpha \xi Q$ is the linear coupling of the proton transfer with the environment motion.

We will calculate the new eigenvalues of $\hat{H}$ using second-order perturbation theory, where the eigenvalue $E_n$ for the Hamiltonian $\hat{H} = \hat{H}_0 + \hat{W}$ is given by the formula

$$E_n \approx E_n^{(0)} + \frac{\langle n | \hat{W} | n \rangle}{\varepsilon_n} + \sum_{m \neq n} \frac{|\langle m | \hat{W} | n \rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

expressed through the unperturbed Hamiltonian eigenvalues/eigenstates ($\hat{H}_0 |n\rangle = E_n^{(0)} |n\rangle$) and the perturbation operator ($\hat{W}$).

We are interested in the energy difference between the states $|+\rangle = |+\rangle |0\rangle$ and $|--\rangle = |--\rangle |0\rangle$ (i.e., the vibrational ground state of the system split by tunneling). In order to calculate the corrections, we need to know the following types of integrals.

- For the proton transfer, we need to know $\langle \pm | \xi | \pm \rangle$ and $\langle \pm | \xi | \mp \rangle$. $\xi$ is an antisymmetric coordinate, therefore for the symmetrized states $|\pm\rangle$ the first integral is going to be zero ($\langle \pm | \xi | \pm \rangle = 0$). This means that the first-order correction ($E_n^{(1)}$) for this system is zero. The second integral will have a non-zero value $\langle \pm | \xi | \mp \rangle = \xi_0$, where $|\xi_0| = |\langle a | \xi | a \rangle| = |\langle b | \xi | b \rangle|$ is the average position of a localized wavepacket in well $a$ or $b$.

- For the second motion, we need to know the integrals $\langle 0 | \hat{Q} | v \rangle$, which for the harmonic oscillator are well-known:

$$\langle 0 | \hat{Q} | v \rangle = \begin{cases} 0, & v \neq 1, \\ 1/\sqrt{2}, & v = 1. \end{cases}$$

By applying these formulas to the second-order perturbation of the states, we obtain the new energies of $|\pm0\rangle$ states:

$$E_{+0} = E_{+0}^{(0)} + \frac{\hbar \omega}{2} - \frac{A^2}{\hbar \omega + \epsilon},$$

and

$$E_{-0} = E_{-0}^{(0)} + \frac{\hbar \omega}{2} - \frac{A^2}{\hbar \omega - \epsilon},$$

where

$$A^2 = |\langle \pm0 | \hat{W} | \mp1 \rangle|^2 = \frac{1}{2} (\hbar \omega)^2 (\alpha \xi_0)^2.$$
The final formula can be reinterpreted in terms of the reorganization energy. The potential $FAD(\lambda)$ therefore the new splitting in the presence of the coupled environment will be lower than in the free FAD ($\Delta E < \epsilon$).

The splitting for FAD is much smaller than all the vibrational frequencies of PhF-FAD ($\epsilon \ll \hbar \omega$), therefore the new splitting in the presence of the coupled environment will be lower than in the free FAD ($\Delta E < \epsilon$).

The expression above can be further worked with. In practice, the anharmonic shift of the zero-point vibrational frequencies of PhF-FAD ($\epsilon$) is about 0.1 – 1 % of the bond length ($\xi_0$) from the equilibrium value of the bond length ($\xi_e$) is about 0.1 – 1 % of the bond length. Therefore we can expect the zero-point vibrationally averaged reorganization energy $\lambda_0 = 2\hbar \omega (\alpha \xi_0)^2$ to be close to its equilibrium analog

$$\lambda_0 = 2\hbar \omega (\alpha \xi_0)^2.$$ 

The expression above can be further worked with. In practice, the anharmonic shift of the zero-point vibrationally averaged position for the valence stretching vibrations ($\xi_0$) from the equilibrium value of the bond length ($\xi_e$) is about 0.1 – 1 % of the bond length. Therefore we can expect the zero-point vibrationally averaged reorganization energy $\lambda_0 = 2\hbar \omega (\alpha \xi_0)^2$ to be close to its equilibrium analog

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Figure S7: The physical meaning of the equilibrium reorganization energy ($\lambda_e$).

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