How Aromatic Fluorination Exchanges the Interaction Role of Pyridine with Carbonyl Compounds: The Formaldehyde Adduct

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Flexible model analysis

Complete reference 33

Figure S1. Conformers of the adduct pentafluoropyridine⋯formaldehyde and their MP2/6-311++G(2d,p) relative energies.

Figure S2. (a) Observed broadband FTMW spectrum (2-8 GHz) dominated by the signals of C5F5N (*) and CH2CO (*). (b) The 33,0 ← 23,1 transition assigned to C5F5N⋯H2CO (c) The 63,4 ← 52,3 transition recorded with the narrow band FP-FTMW spectrometer.

Figure S3. Comparison of the structures calculated for configuration C2 of the adduct pentafluoropyridine⋯formaldehyde at B3LYP-D3/6-311++G(2d,p), MP2/aug-cc-pVTZ, and CCSD/6-311++G(2d,p).

Figure S4. Electron density contours corresponding to the molecular graph shown in Figure 6a calculated using the CCSD/6-311++G(2d,p) wave function in the Cs symmetry plane (a) and a plane containing the RCP perpendicular to the previous one (b).

Figure S5. Comparison of the molecular graphs of the predicted configuration of form C2 of the complex pentafluoropyridine⋯formaldehyde calculated at MP2/aug-cc-pVTZ, and CCSD/6-311++G(2d,p).

Tables S1-S6. Rotational parameters and energies predicted for the most stable conformers of the pentafluoropyridine⋯formaldehyde adduct at different levels of theory.

Table S7. Comparison of the experimental rotational constants obtained from the analysis of the spectra of pentafluoropyridine with those from the previous work and the theoretical calculations at different levels of theory.

Table S8. Rotational constants obtained from the analysis of the spectra of pentafluoropyridine and its 13C and 15N isotopologues.

Table S9. Rotational parameters obtained from the semirigid rotor analysis of the 0+ and 0- torsion states of the pentafluoropyridine⋯formaldehyde adduct and their comparison with those from theoretical calculations at different levels of theory.

Table S10. Rotational constants obtained from the analysis of the spectra of the observed 13C and 15N isotopologues of the pentafluoropyridine⋯formaldehyde cluster.

Table S11. Comparison of the rotational constants (A, B, C), the moments of inertia (Ia, Ib, Ic), and the planar moments (Paa, Pbb, Pcc) of pentafluoropyridine, formaldehyde, and the pentafluoropyridine⋯formaldehyde adduct.

Table S12. Comparison of the r_s coordinates (in Å) of pentafluoropyridine with those from r_0 method and r_e coordinates predicted at different levels of theory.
Table S13. $r_s$ and $r_0$ structures of pentafluoropyridine ($C_{2v}$) calculated from the rotational constants given in Table S8, and compared with the $r_e$ structures predicted at different levels of theory.

Table S14. The $r_s$ coordinates (in Å) of pentafluoropyridine···formaldehyde and its comparison with the $r_0$ and $r_e$ coordinates for the most stable conformer C1.

Table S15. $r_0$ distances and angles of pentafluoropyridine···formaldehyde and their comparison with those from theoretical calculations.

Table S16. Comparison of the results of the energy decomposition analysis (Electrostatic, Exchange, Induction, Dispersion, HF, and SAPT values in kJ/mol) done with the DFT-SAPT method for the C$_5$F$_5$N···CH$_2$O and C$_5$H$_5$N···CH$_2$O complexes.

Tables S17-S27. Observed rotational transitions and residuals for the parent and isotopic species of pentafluoropyridine and pentafluoropyridine···formaldehyde.
Flexible model analysis

Meyer’s flexible model\cite{1} was used to deduce the potential energy function of the motion. The potential and structural relaxation parameters were adjusted to reproduce the differences of the experimental planar moments of inertia $\Delta P_{aa}$, $\Delta P_{bb}$, and $\Delta P_{cc}$ between the two observed states ($0^{+}$ and $0^{-}$). We tested both types of potential energy functions describing the H$_2$CO torsion pathway, the periodic two-fold double minimum function:

$$V(\alpha) = V_2 \left(1 - \cos(2\alpha)\right)/2 + V_4 \left(1 - \cos(4\alpha)\right)/2 \quad (1)$$

where $V_2$ gives the two-fold barrier size while $V_4$ shapes its width and the periodic function with minima at C1 and C2:

$$V(\alpha) = V_2 \left(1 - \cos(2\alpha)\right)/2 + V_4 \left(1 - \cos(4\alpha)\right)/2 + V_6 \left(1 - \cos(6\alpha)\right)/2 \quad (2)$$

where the $\alpha$ values of 0°, 180°, and 360° correspond to the equilibrium configuration C1 with H$_2$CO lying in the $\sigma_{bc}$ plane perpendicular to the ring and containing the nitrogen atom (see Figure 5). A negative value of $V_6$ in eqn. (2) leads to additional minima at 90° and 270° for the C2 configuration. Both (1) and (2) potential energy functions would predict the lowest energy torsional states as a doublet with a small energy difference as experimentally observed.

Theoretical calculations indicated that the intermolecular parameters undergo a considerable structural relaxation upon the internal rotation of formaldehyde. We have chosen to describe the variation of the $r(C_{12}N_{1})$ distance ($r(\alpha)$) and the $\angle C_{12}N_{1}C_{4}$ ($\beta(\alpha)$) and $\angle O_{13}C_{12}N_{1}$ ($\gamma(\alpha)$) angles (see Figure 5 for labeling) with the following equations to model the structural relaxations:

$$r(\alpha) = r(0) + r_2 \left(1 - \cos(2\alpha)\right)/2 + r_4 \left(1 - \cos(4\alpha)\right)/2 \quad (3)$$

$$\beta(\alpha) = \beta(0) + \beta_2 \left(1 - \cos(2\alpha)\right)/2 + \beta_4 \left(1 - \cos(4\alpha)\right)/2 \quad (4)$$

$$\gamma(\alpha) = \gamma(0) + \gamma_2 \left(1 - \cos(2\alpha)\right)/2 + \gamma_4 \left(1 - \cos(4\alpha)\right)/2 \quad (5)$$
The fixed structural parameters were taken from the $r_0$ structure. The potential function parameters for the function of eqn. (1) were initially adapted from the MP2/6-311++G(2d,p) \textit{ab initio} constrained calculations ($V_2 = 218$ cm$^{-1}$ and $V_4 = 30$ cm$^{-1}$), while the \textit{ab initio} structural relaxation parameters ($r_2 = 0.15$ Å, $r_4 = 0.006$ Å, $\beta_2 = -4.43^\circ$, $\beta_4 = -0.35^\circ$, $\gamma_2 = -1.88^\circ$, and $\gamma_4 = -0.03^\circ$) were used together with the $r_0$ results ($r(0) = 3.361$ Å, $\beta(0) = 91.48^\circ$ and $\gamma(0) = 71.20^\circ$). A reasonable agreement ($\Delta P_{aa} = 0.028$ uÅ$^2$, $\Delta P_{bb} = -0.001$ uÅ$^2$ and $\Delta P_{cc} = 0.001$ uÅ$^2$) with the experimental planar moments of inertia was reached using a scale factor for both potential parameters to give $V_2 = 155$ cm$^{-1}$ and $V_4 = 21$ cm$^{-1}$ with slight modifications of the relaxation parameters ($r_2 = 0.14$ Å, $r_4 = 0.006$ Å, $\beta_2 = -3.7^\circ$, $\beta_4 = -0.35^\circ$, $\gamma_2 = -2.40^\circ$, and $\gamma_4 = -0.03^\circ$). The potential energy function is shown in Figure 3 (black continous, trace 4).

When using the potential function (2) we started from the MP2/aug-cc-pVTZ parameters ($V_2 = 166$ cm$^{-1}$, $V_4 = 77$ cm$^{-1}$, and $V_6 = -18$ cm$^{-1}$) and proceeded in the same way as before using a common scale factor for the potential energy parameters. Assuming the same relaxation parameters determined before, the same degree of agreement between experimental and predicted parameters was obtained for values of the potential energy parameters of $V_2 = 132.8$ cm$^{-1}$, $V_4 = 32.7$ cm$^{-1}$, and $V_6 = 14.4$ cm$^{-1}$, with C2 structure being 118.4 cm$^{-1}$ higher than C1 and barriers of 145.8 cm$^{-1}$ (Figure 3, black dashed, trace 5). The C2 energies calculated at CCSD/6-311++G(2d,p) (138 cm$^{-1}$) is between the values of the energy of C2 estimated for potential function (1) of 155.0 cm$^{-1}$ or (2) of 118.0 cm$^{-1}$. The fact that both potential energy functions describe the experimental observations is not a surprise since the observed rotational constants reflect the energy profile and torsion dynamics near the C1 minimum and this is described practically in the same way in both models.

[1] R. Meyer, \textit{J. Mol. Spectrosc.} \textbf{1979}, \textit{76}, 266–300.
Complete reference 33
Gaussian 16, Revision A.03, Frisch, M. J.; Trucks, M. J.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.
Figure S1. Conformers of the adduct pentafluoropyridine···formaldehyde and their MP2/6-311++G(2d,p) relative energies. The conformers have been labeled C1, C2, etc., in order of increasing energy.
**Figure S2.** (a) Observed broadband FTMW spectrum (2-8 GHz) dominated by the spectra of C₅F₅N (*) and CH₂CO (*). (b) The 3₃,₀ ← 2₃,₁ transition assigned to C₅F₅N···H₂CO showing the F₊₁ ← F quadrupole coupling hyperfine components and the 0⁺/0⁻ doublets with an intensity ratio 1/3. (c) The 6₃,₄ ← 5₂,₃ transition recorded with the narrow band FP-FTMW spectrometer shows an additional Doppler doubling.
Figure S3. Comparison of the structures calculated for configuration C2 of the adduct pentafluoropyridine···formaldehyde at B3LYP-D3/6-311++G(2d,p), MP2/aug-cc-pVTZ, and CCSD/6-311++G(2d,p).
**Figure S4.** Electron density contours corresponding to the molecular graph shown in Figure 6a calculated using the CCSD/6-311++G(2d,p) wave function in the Cs symmetry plane (a) and a plane containing the RCP perpendicular to the previous one (b). The green, red and blue dots represent the location of the bond, ring, and cage critical points. The 2D contour plots provide clues on how the electron density changes around the isolated ring and cage critical points. In addition, the proximity of both critical points is an indication that the topological description is close to a catastrophic point.
**Figure S5.** Comparison of the molecular graphs of the predicted configuration of form C2 of the complex pentafluoropyridine····formaldehyde calculated at MP2/aug-cc-pVTZ, and CCSD/6-311++G(2d,p). The green, red and blue dots represent the location of the bond, ring, and cage critical points.
Table S1. Rotational parameters and energies predicted at B3LYP-D3/6-311G++(2d,p) level for the most stable conformers of the pentafluoropyridine···formaldehyde adduct. Form C2 corresponds to a saddle point at this level of theory.

| Parameters\(^a\) | C1        | C2        | C3        |
|------------------|-----------|-----------|-----------|
| A/MHz            | 791.12    | 813.25    | 909.03    |
| B/MHz            | 755.01    | 728.65    | 668.36    |
| C/MHz            | 554.58    | 578.47    | 477.10    |

|          |           |           |           |           |
|----------|-----------|-----------|-----------|
| \(P_{aa}\)/\(\mu\)\(^{2}\) | 470.92    | 472.90    | 629.74    |
| \(P_{bb}\)/\(\mu\)\(^{2}\) | 440.37    | 400.75    | 429.54    |
| \(P_{cc}\)/\(\mu\)\(^{2}\) | 198.45    | 220.68    | 126.41    |

|          |           |           |           |           |
|----------|-----------|-----------|-----------|
| \(\chi_{aa}\)/MHz | 2.21    | 2.21      | -0.60     |
| \(\chi_{bb}\)/MHz | -2.86   | -3.11     | -0.48     |
| \(\chi_{cc}\)/MHz | 0.65    | 0.91      | 1.08      |
| \(\chi_{ab}\)/MHz | 0.00    | 0.00      | 2.74      |
| \(\chi_{ac}\)/MHz | 0.00    | 0.00      | 1.56      |
| \(\chi_{bc}\)/MHz | 2.44    | 2.29      | -1.58     |

|          |           |           |           |
|----------|-----------|-----------|-----------|
|          |           |           |           |
| 1.5(\(\chi_{aa}\))/MHz | 3.32    | 3.31      | -0.91     |
| 0.25(\(\chi_{bb}\)-\(\chi_{cc}\))/MHz | -0.88   | -1.00     | -0.39     |

|          |           |           |           |
|----------|-----------|-----------|-----------|
|          |           |           |           |
| |\(\mu_{a}\)|/D | 0.0       | 0.0       | 3.14      |
| |\(\mu_{b}\)|/D | 1.6       | 1.4       | 1.1       |
| |\(\mu_{c}\)|/D | 0.4       | 0.4       | 1.0       |

|          |           |           |           |
|----------|-----------|-----------|-----------|
|          |           |           |           |
| \(E/h\) | -859.252389 | -859.251225 | -859.250958 |
| \(\Delta E/cm^{-1}\) | 0.0       | 255.5     | 314.13    |
| \(\Delta E/kJmol^{-1}\) | 0.0       | 3.06      | 3.76      |
| \(C_{E}(BSSE)/kJmol^{-1}\) | -19.0     | -15.8     | -15.5     |

\(^a\) A, B and C are the rotational constants; \(P_{\alpha\alpha}\) (\(\alpha = a, b\) or \(c\)) are the planar moments of inertia derived from the moments of inertia \(I_{\alpha}\) as for example \(P_{cc} = (I_{a} + I_{b} - I_{c})/2\); \(\chi_{\alpha\beta}\) (\(\alpha,\beta = a, b, c\)) are the \(^{14}\)N nuclear quadrupole coupling constants. \(E\) are the electronic energies; \(\Delta E\) are the energies relative to the most stable conformer C1. \(C_{E}(BSSE)\) is the BSSE corrected complexation energy calculated using counterpoise procedure.
Table S2. Rotational parameters and energies predicted at B3LYP-D3BJ/6-311G++(2d,p) level for the most stable conformers of the pentafluoropyridine···formaldehyde adduct. Form C2 corresponds to a saddle point at this level of theory.

| Parameters$^a$ | C1   | C2   | C3   |
|---------------|------|------|------|
| $A$/MHz       | 785.77 | 813.25 | 909.03 |
| $B$/MHz       | 750.98 | 728.65 | 668.36 |
| $C$/MHz       | 554.53 | 578.47 | 477.10 |
| $P_{aa}$/uÅ²  | 470.58 | 472.90 | 629.74 |
| $P_{bb}$/uÅ²  | 440.79 | 400.75 | 429.54 |
| $P_{cc}$/uÅ²  | 202.38 | 220.68 | 126.41 |
| $\chi_{aa}$/MHz| 2.21  | 2.21  | -0.60 |
| $\chi_{bb}$/MHz| -2.81 | -3.11 | -0.48 |
| $\chi_{cc}$/MHz| 0.60  | 0.91  | 1.08  |
| $\chi_{ab}$/MHz| 0.00  | 0.00  | 2.74  |
| $\chi_{ac}$/MHz| 0.00  | 0.00  | 1.56  |
| $\chi_{bc}$/MHz| 2.49  | 2.29  | -1.58 |
| 1.5($\chi_{aa}$)/MHz| 3.32 | 3.31 | -0.91 |
| 0.25($\chi_{bb}$-$\chi_{cc}$)/MHz| -0.85 | -1.00 | -0.39 |
| $|\mu_a|$/$\mu$/D | 0.0 | 0.0 | 3.14 |
| $|\mu_b|$/$\mu$/D | 1.6 | 1.4 | 1.1 |
| $|\mu_c|$/$\mu$/D | 0.4 | 0.4 | 1.0 |
| $E$/h         | -859.265792 | -859.2512247 | -859.250958 |
| $\Delta E$/cm$^{-1}$ | 0.0 | 255.51 | 355.43 |
| $\Delta E$/kJmol$^{-1}$ | 0.0 | 3.06 | 4.25 |
| $C_E$(BSSE)/kJmol$^{-1}$ | -18.6 | -15.8 | -14.64 |

$^a$ $A$, $B$ and $C$ are the rotational constants; $P_{aa}$ ($\alpha = a, b$ or $c$) are the planar moments of inertia derived from the moments of inertia $I_\alpha$ as for example $P_{cc} = (I_a + I_b - I_c)/2$; $\chi_{ab}$ ($\alpha, \beta = a, b, c$) are the $^{14}$N nuclear quadrupole coupling constants. $E$ are the electronic energies; $\Delta E$ are the energies relative to the most stable conformer C1. $C_E$(BSSE) is the BSSE corrected complexation energy calculated using counterpoise procedure.
Table S3. Rotational parameters and energies predicted at MP2/6-311G++(2d,p) level for the most stable conformers of the pentafluoropyridine····formaldehyde adduct.

| Parameters<sup>a</sup> | C1     | C2     | C3     |
|------------------------|--------|--------|--------|
| \( A/\text{MHz} \)    | 804.99 | 847.20 | 905.69 |
| \( B/\text{MHz} \)    | 751.61 | 731.83 | 676.97 |
| \( C/\text{MHz} \)    | 562.29 | 592.24 | 489.77 |
| \( P_{\alpha\alpha}/\text{uÅ}^2 \) | 471.69 | 473.69 | 610.20 |
| \( P_{bb}/\text{uÅ}^2 \) | 427.10 | 379.65 | 421.67 |
| \( P_{cc}/\text{uÅ}^2 \) | 200.71 | 216.88 | 136.33 |
| \( \chi_{\alpha\alpha}/\text{MHz} \) | 1.98   | 1.98   | -0.07  |
| \( \chi_{bb}/\text{MHz} \) | -2.74  | -3.32  | -1.11  |
| \( \chi_{cc}/\text{MHz} \) | 0.75   | 1.33   | 1.18   |
| \( \chi_{ac}/\text{MHz} \) | 0.00   | 0.00   | 2.52   |
| \( \chi_{bc}/\text{MHz} \) | 0.00   | 0.00   | 1.21   |
| \( \chi_{ab}/\text{MHz} \) | 2.23   | 1.68   | -1.53  |
| \( 1.5(\chi_{aa})/\text{MHz} \) | 2.98   | 2.98   | -0.10  |
| \( 0.25(\chi_{bb}+\chi_{cc})/\text{MHz} \) | -0.87  | -1.16  | -0.57  |
| \( |\mu_\alpha|/\text{D} \)   | 0.0    | 0.0    | 3.2    |
| \( |\mu_\beta|/\text{D} \)   | 1.5    | 1.4    | 1.5    |
| \( |\mu_\gamma|/\text{D} \)   | 0.6    | 0.4    | 0.6    |
| \( E/\hbar \)         | -857.421535 | -857.420625 | -857.419654 |
| \( \Delta E/\text{cm}^{-1} \) | 0.0 | 199.7 | 412.7 |
| \( \Delta E/\text{kJmol}^{-1} \) | 0.0 | 2.39 | 1.18 |
| \( C_1(\text{BSSE})/\text{kJmol}^{-1} \) | -17.2 | -14.8 | -12.8 |

<sup>a</sup> \( A, B \) and \( C \) are the rotational constants; \( P_{\alpha\alpha} (\alpha = a, b \text{ or } c) \) are the planar moments of inertia derived from the moments of inertia \( I_\alpha \) as for example \( P_{cc} = (I_a + I_b - I_c)/2; \chi_{\alpha\beta} (\alpha, \beta = a, b, c) \) are the \(^{14}\text{N} \) nuclear quadrupole coupling constants. \( E \) are the electronic energies; \( \Delta E \) are the energies relative to the most stable conformer \( C_1 \). \( C_1(\text{BSSE}) \) is the BSSE corrected complexation energy calculated using counterpoise procedure.
Table S4. Rotational parameters and energies predicted at MP2/aug-cc-pVDZ level for the most stable conformers of the pentafluoropyridine⋯formaldehyde adduct. Form C2 corresponds to a saddle point at this level of theory.

| Parametersa | C1        | C2        | C3        |
|-------------|-----------|-----------|-----------|
| A/MHz       | 811.7     | 868.2     | 914.9     |
| B/MHz       | 749.6     | 735.5     | 680.7     |
| C/MHz       | 557.6     | 589.7     | 492.9     |
| $P_{aa}$/uÅ² | 479.0     | 481.0     | 607.59    |
| $P_{bb}$/uÅ² | 427.4     | 376.0     | 417.63    |
| $P_{cc}$/uÅ² | 195.2     | 206.1     | 134.77    |
| $\chi_{aa}$/MHz | 1.87      | 1.87      | 0.33      |
| $\chi_{bb}$/MHz | -2.59     | -3.21     | -1.30     |
| $\chi_{cc}$/MHz | 0.71      | 1.34      | 0.97      |
| $\chi_{ab}$/MHz | 0.00      | 0.00      | 2.21      |
| $\chi_{ac}$/MHz | 0.00      | 0.00      | 0.92      |
| $\chi_{bc}$/MHz | -1.84     | -1.09     | -1.42     |
| $1.5(\chi_{aa})$/MHz | 2.81      | 2.80      | -0.50     |
| $0.25(\chi_{bb}-\chi_{cc})$/MHz | -0.83     | -1.13     | -0.57     |
| $|\mu_{a}|/D$ | 0.0       | 0.0       | 3.1       |
| $|\mu_{b}|/D$ | 1.5       | 1.0       | 1.4       |
| $|\mu_{c}|/D$ | 0.7       | 0.2       | 0.6       |
| $E$/h       | -857.0655585 | -857.065195 | -857.0635155 |
| $\Delta E$/cm⁻¹ | 0.0       | 79.8      | 448.4     |
| $\Delta E$/kJmol⁻¹ | 0.0       | 1.0       | 5.4       |

a A, B and C are the rotational constants; $P_{aa}$ ($\alpha = a, b$ or $c$) are the planar moments of inertia derived from the moments of inertia $I_{\alpha}$ as for example $P_{cc} = (I_a + I_b - I_c)/2$; $\chi_{a\beta}$ ($\alpha, \beta = a, b, c$) are the $^{14}$N nuclear quadrupole coupling constants. $E$ are the electronic energies; $\Delta E$ are the energies relative to the most stable conformer C1.
Table S5. Rotational parameters and energies predicted at MP2/aug-cc-pVTZ level for the most stable conformers of the pentafluoropyridine⋯formaldehyde adduct.

| Parameters$^a$ | C1            | C2            | C3            |
|----------------|---------------|---------------|---------------|
| $A$/MHz        | 809.8         | 865.0         | 917.4         |
| $B$/MHz        | 761.1         | 741.2         | 679.9         |
| $C$/MHz        | 561.4         | 596.9         | 492.1         |
| $P_{aa}$/uÅ²   | 470.1         | 472.2         | 609.7         |
| $P_{bb}$/uÅ²   | 430.1         | 374.6         | 417.3         |
| $P_{cc}$/uÅ²   | 194.0         | 209.7         | 133.6         |
| $\chi_{aa}$/MHz| 1.83          | 1.84          | 0.21          |
| $\chi_{bb}$/MHz| -2.68         | -3.35         | -1.55         |
| $\chi_{cc}$/MHz| 0.84          | 1.51          | 1.34          |
| $\chi_{ab}$/MHz| 0.00          | 0.00          | 2.36          |
| $\chi_{ac}$/MHz| 0.00          | 0.00          | 1.03          |
| $\chi_{bc}$/MHz| 2.18          | -1.48         | -1.45         |
| $1.5(\chi_{aa})$/MHz| 2.75 | 2.76 | 0.32 |
| $0.25(\chi_{bb}-\chi_{cc})$/MHz| -0.88 | -1.21 | -0.72 |
| $|\mu_a|$| D 0.0 | 0.0 | 3.1 |
| $|\mu_b|$| D 1.4 | 1.0 | 1.6 |
| $|\mu_c|$| D 0.5 | 0.2 | 0.7 |
| $E$/ h         | -857.7717824  | -857.7711213  | -857.7698845  |
| $\Delta E$/cm$^{-1}$ | 0.0 | 145.1 | 416.5 |
| $\Delta E$/kJmol$^{-1}$ | 0.0 | 1.7 | 5.0 |

$^a$ $A$, $B$ and $C$ are the rotational constants; $P_{aa}$ ($\alpha = a, b$ or $c$) are the planar moments of inertia derived from the moments of inertia $I\alpha$ as for example $P_{cc} = (I_a + I_b - I_c)/2; \chi_{\alpha\beta}$ ($\alpha, \beta = a, b, c$) are the $^{14}$N nuclear quadrupole coupling constants. $E$ are the electronic energies; $\Delta E$ are the energies relative to the most stable conformer C1.
Table S6. Rotational parameters and energies predicted at CCSD/6-311++G(2d,p) level for the most stable conformers of the pentafluoropyridine···formaldehyde adduct.

| Parameters<sup>a</sup> | C1       | C2<sup>b</sup> |
|------------------------|----------|----------------|
| A/MHz                  | 783.9    | 750.7          |
| B/MHz                  | 748.0    | 671.3          |
| C/MHz                  | 556.5    | 585.4          |
| \(P_{aa}/\text{uÅ}^2\) | 469.5    | 471.5          |
| \(P_{bb}/\text{uÅ}^2\) | 438.6    | 391.9          |
| \(P_{cc}/\text{uÅ}^2\) | 206.1    | 281.3          |
| \(\chi_{aa}/\text{MHz}\) | 2.08     | 2.07           |
| \(\chi_{bb}/\text{MHz}\) | -2.71    | -1.77          |
| \(\chi_{cc}/\text{MHz}\) | 0.63     | -0.29          |
| \(\chi_{bc}/\text{MHz}\) | 0.0      | 0.0            |
| \(\chi_{ac}/\text{MHz}\) | 0.0      | 0.0            |
| \(\chi_{ba}/\text{MHz}\) | -2.56    | -3.03          |
| 1.5(\(\chi_{aa}\))/MHz | 3.12     | 3.10           |
| 0.25(\(\chi_{bb}-\chi_{cc}\))/MHz | -0.84 | -0.37          |
| \(|\mu_a|/\text{D}\) | 0.0      | 0.0            |
| \(|\mu_b|/\text{D}\) | 1.7      | 1.64           |
| \(|\mu_c|/\text{D}\) | 0.5      | 2.35           |
| \(E/h\)               | -857.4209832 | -857.4203509 |
| \(\Delta E/\text{cm}^{-1}\) | 0.0 | 138.8          |
| \(\Delta E/\text{kJmol}^{-1}\) | 0.0 | 1.7            |

<sup>a</sup> A, B and C are the rotational constants; \(P_{\alpha\alpha}\) (\(\alpha = a, b \text{ or } c\)) are the planar moments of inertia derived from the moments of inertia \(I_{\alpha}\) as for example \(P_{cc} = (I_a + I_b - I_c)/2\); \(\chi_{\alpha\beta}\) (\(\alpha, \beta = a, b, c\)) are the \(^{14}\text{N}\) nuclear quadrupole coupling constants. \(E\) are the electronic energies; \(\Delta E\) are the energies relative to the most stable conformer C1.
**Table S7.** Comparison of the experimental rotational constants obtained from the analysis of the spectra of pentafluoropyridine with those from the previous work and the theoretical calculations at B3LYP-D3/6-311++G(2d,p) (DFT(1)), B3LYP-D3BJ/6-311++G(2d,p) (DFT(2)), MP2/6-311++G(2d,p) (MP2(1)), MP2/aug-cc-pVDZ (MP2(2)), MP2/aug-cc-pVTZ (MP2(3)), and CCSD/6-311++G(2d,p) (CCSD) levels.

| Parametersa | parent       | Prev. workb | DFT(1)   | DFT(2)   | MP2(1)  | MP2(2)  | MP2(3)  | CCSD    |
|------------|--------------|-------------|----------|----------|---------|---------|---------|---------|
| A/MHz      | 1481.58184(19)c | 1481.539(3) | 1479.94  | 1481.35  | 1477.87 | 1452.45 | 1481.20 | 1484.36 |
| B/MHz      | 1075.37335(17) | 1075.348(4) | 1072.33  | 1073.22  | 1070.99 | 1054.43 | 1074.22 | 1075.80 |
| C/MHz      | 623.11194(16)  | 623.101(1)  | 621.79   | 622.34   | 620.98  | 610.92  | 622.65  | 623.74  |
| $P_{aa}$/μÅ² | 469.95288(16) | 469.9605(2) | 471.29   | 470.90   | 471.88  | 479.29  | 470.46  | 469.77  |
| $P_{bb}$/μÅ² | 341.10379(16) | 341.1102(2) | 341.49   | 341.16   | 341.97  | 347.95  | 341.20  | 340.47  |
| $P_{cc}$/μÅ² | 0.00399(16)   | 0.00073(2)  | 0.00     | 0.00     | 0.00    | 0.00    | 0.00    | 0.00    |
| 1.5($\chi_{aa}$)/MHz | 2.9496(31)   |           | 3.29     | 3.29     | 2.93    | 2.81    | 2.76    | 3.11    |
| 0.25($2\chi_{bb}-2\chi_{cc}$)/MHz | -1.48514(91) | -1.57     | -1.58    | -1.48    | -1.29   | -1.46   | -1.59   |         |
| $\chi_{aa}$/MHz | 1.9664(53)   | 1.94(22)   | 2.20     | 2.19     | 1.96    | 1.88    | 1.84    | 2.07    |
| $\chi_{bb}$/MHz | -3.9534(72)  | -4.08(6)   | -4.24    | -4.25    | -3.94   | -3.51   | -3.83   | -4.22   |
| $\chi_{cc}$/MHz | 1.9870(72)   | 2.14(22)   | 2.05     | 2.05     | 1.98    | 1.64    | 1.99    | 2.14    |

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*a* $A$, $B$ and $C$ are the rotational constants; $\chi_{aa}$, $\chi_{bb}$ and $\chi_{cc}$ are the $^{14}$N nuclear quadrupole coupling constants. $P_{\alpha\alpha}$ ($\alpha = a, b$ or $c$) are the planar moments of inertia derived from the moments of inertia $I_{\alpha}$ as for example $P_{c} = (I_{a} + I_{b} - I_{c})/2$. 

*b* Doraiswamy, S.; Sharma, S. D. Microwave Spectrum, Centrifugal Distortion Constants, Dipole Moment and Quadrupole Coupling Constants of Pentfluoropyridine. *Chem. Phys.* 1974, 6 (1), 76-86. 

*c* Standard errors are given in parentheses in units of the last digit.
Table S8. Rotational constants obtained from the analysis of the spectra of pentafluoropyridine and its mono-substituted $^{13}$C and $^{15}$N isotopologues.

| Parameters | parent | Parameters | $^{15}$N$_{1}$ | $^{13}$C$_{2}$ | $^{13}$C$_{3}$ | $^{13}$C$_{4}$ |
|------------|--------|------------|----------------|----------------|----------------|----------------|
| $A$/MHz    | 1481.58184(19)$^b$ | $A$/MHz | 1469.9842(12) | 1477.57710(20) |                |                |
| $B$/MHz    | 1075.37335(17) | $B$/MHz | 1075.3655(11) | 1072.48478(13) |                |                |
| $C$/MHz    | 623.11194(16) | $C$/MHz | 621.06359(46) | 621.43405(10)  |                |                |
| $\Delta_v$/kHz | 0.0290(30) | $\Delta_v$/kHz | 0.0290(30) | 0.0290(30) | 0.0290(30) | 0.0290(30) |
| $\Delta_{J}$/kHz | [0.0] | $\Delta_{J}$/kHz | 0.0290(30) | 0.0290(30) | 0.0290(30) | 0.0290(30) |
| $\Delta_K$/kHz | 0.0565(24) | $\Delta_K$/kHz | 0.0565(24) | 0.0565(24) | 0.0565(24) | 0.0565(24) |
| $\delta_v$/kHz | 0.00474(47) | $\delta_v$/kHz | 0.00474(47) | 0.00474(47) | 0.00474(47) | 0.00474(47) |
| $\delta_K$/kHz | 0.0343(18) | $\delta_K$/kHz | 0.0343(18) | 0.0343(18) | 0.0343(18) | 0.0343(18) |
| $1.5(\chi_{aa})$/MHz | 2.9496(31) | $\sigma$/kHz | 7.5 | 4.7 | 7.5 | 4.7 |
| $0.25(\chi_{bb}-\chi_{cc})$/MHz | -1.48514(91) | $\sigma$/kHz | 7.5 | 4.7 | 7.5 | 4.7 |
| $n$ | 366 | $n$ | 68 | 30 |                |                |
| $\sigma$/kHz | 5.8 | $\sigma$/kHz | 5.9 | 5.5 |                |                |

$^a$ $A$, $B$ and $C$ are the rotational constants. $\Delta_v$, $\Delta_{J}$, $\Delta_K$, $\delta_v$ and $\delta_K$ are the quartic centrifugal distortion constants and $\chi_{aa}$, $\chi_{bb}$ and $\chi_{cc}$ are the $^{14}$N nuclear quadrupole coupling constants. The quartic centrifugal distortion constants of all monosubstituted isotopologues and the $^{14}$N nuclear quadrupole coupling constants for the $^{13}$C species were fixed to the parent species values. $\sigma$ is the rms deviation of the fit. $P_{\alpha\alpha} (\alpha = a, b$ or $c)$ are the planar moments of inertia derived from the moments of inertia $I_{\alpha}$ as for example $P_{cc} = (I_{a} + I_{b} - I_{c})/2$. $^b$ Standard errors are given in parentheses in units of the last digit.
Table S9. Rotational parameters obtained from the semirigid rotor analysis of the $0^+$ and $0^-$ torsion states of the pentafluoropyridine····formaldehyde adduct and their comparison with those from theoretical calculations at B3LYP-D3/6-311++G(2d,p) (DFT), MP2/6-311++G(2d,p) (MP2(1)), MP2/aug-cc-pVDZ (MP2(2)), MP2/aug-cc-pVTZ (MP2(3)) and CCSD/6-311++G(2d,p)(CCSD) levels.

| Fitted Parameters$^a$ | $0^+$ | $0^-$ | DFT | MP2(1) | MP2(2) | MP2(3) | CCSD |
|-----------------------|-------|-------|------|--------|--------|--------|------|
| $A/\text{MHz}$        | 779.69465(13)$^b$ | 779.69184(13) | 791.1 | 805.0  | 811.7  | 809.8  | 783.89 |
| $B/\text{MHz}$        | 745.85829(10)   | 745.82527(10) | 755.0 | 751.6  | 749.6  | 761.1  | 748.01 |
| $C/\text{MHz}$        | 555.481998(67)  | 555.464049(67) | 554.6 | 562.3  | 557.6  | 561.4  | 556.48 |
| $\Delta J/\text{kHz}$ | 0.2013(11)      | 1.1527(70)    | -1.1305(73) | 0.02584(63) | 0.2491(37) |
| $\Delta K/\text{kHz}$ | 1.1527(70)      | -1.1305(73)   | 0.02584(63) | 0.2491(37) |
| $\delta J/\text{kHz}$ | 0.2013(11)      | 1.1527(70)    | -1.1305(73) | 0.02584(63) | 0.2491(37) |
| $\delta K/\text{kHz}$ | 1.1527(70)      | -1.1305(73)   | 0.02584(63) | 0.2491(37) |
| $1.5(\chi_{aa})/\text{MHz}$ | 2.9597(28)   | 3.32         | 2.98  | 2.81   | 2.75   |
| $0.25(\chi_{bb}+\chi_{cc})/\text{MHz}$ | -0.76025(79) | -0.88       | -0.87 | -0.83  | -0.88  |
| $n$                   | 261             |             |       |        |        |        |
| $\sigma/\text{kHz}$   | 3.5             |             |       |        |        |        |
| $P_{aa}/\text{uÅ}^2$  | 469.60380(15)   | 469.63233(15) | 470.92 | 471.69 | 478.96 | 470.1  | 469.55 |
| $P_{bb}/\text{uÅ}^2$  | 440.19888(15)   | 440.19975(15) | 440.37 | 427.10 | 427.38 | 430.1  | 438.62 |
| $P_{cc}/\text{uÅ}^2$  | 207.97667(15)   | 207.97814(15) | 198.45 | 200.71 | 195.21 | 194.0  | 206.08 |
| $\chi_{aa}/\text{MHz}$ | 1.9731(19)   | 2.21         | 1.98  | 1.87  | 1.84  |
| $\chi_{bb}/\text{MHz}$ | -2.5071(25)  | -2.86       | -2.74 | -2.59 | -2.68 |
| $\chi_{cc}/\text{MHz}$ | 0.5339(25)   | 0.65         | 0.75  | 0.71  | 0.84  |
| $\chi_{bc}/\text{MHz}$ | 2.44        | 2.23         | 1.84  | 2.18  |

$^a$ $A$, $B$ and $C$ are the rotational constants. $\Delta J$, $\Delta K$, $\delta J$ and $\delta K$ are the quartic centrifugal distortion constants. $\chi_{aa}$, $\chi_{bb}$ and $\chi_{cc}$ are the $^{14}$N nuclear quadrupole coupling constants. $n$ is the number of hyperfine quadrupole components fitted. $\sigma$ is the rms deviation of the fit. $P_{aa}$ ($\alpha = a$, $b$ or $c$) are the planar moments of inertia derived from the moments of inertia $I_{\alpha}$ as for example $P_{cc} = (I_a + I_b - I_c)/2$. $^b$ Standard errors are given in parentheses in units of the last digit.
Table S10. Rotational constants obtained from the analysis of the spectra of the observed
$^{13}$C and $^{15}$N isotopologues of the pentafluoropyridine⋯formaldehyde cluster.

| Parameters\(^a\) | $^{13}$C\(_2 = ^{13}$C\(_6\) | $^{13}$C\(_3 = ^{13}$C\(_5\) |
|------------------|------------------|------------------|
| $A$/MHz          | 779.06370(89)    | 779.05934(87)    |
| $B$/MHz          | 744.23775(34)    | 744.20525(33)    |
| $C$/MHz          | 554.293478(97)   | 554.275694(87)   |
| $P_{aa}$/uÅ\(^2\) | 471.05443(61)    | 471.08206(58)    |
| $P_{bb}$/uÅ\(^2\) | 440.69906(61)    | 440.70067(58)    |
| $P_{cc}$/uÅ\(^2\) | 208.00144(61)    | 208.00346(58)    |
| $n$              | 66               | 60               |
| $\sigma$/kHz     | 2.3              | 1.9              |

| Parameters\(^a\) | $^{13}$C\(_4\) | $^{13}$C\(_12\) |
|------------------|-----------------|-----------------|
| $A$/MHz          | 777.4322(10)    | 777.4322(10)    |
| $B$/MHz          | 745.822(14)     | 745.79530(45)   |
| $C$/MHz          | 554.38209(57)   | 554.363767(87)  |
| $P_{aa}$/uÅ\(^2\) | 469.5797(72)    | 469.60687(69)   |
| $P_{bb}$/uÅ\(^2\) | 442.0281(72)    | 442.03101(69)   |
| $P_{cc}$/uÅ\(^2\) | 208.0338(72)    | 208.03083(69)   |
| $n$              | 54              | 73              |
| $\sigma$/kHz     | 2.6             | 2.1             |

| Parameters\(^a\) | $^{15}$N\(_1\) |
|------------------|----------------|
| $A$/MHz          | 776.8324(30)   |
| $B$/MHz          | 744.269(14)    |
| $C$/MHz          | 554.80250(63)  |
| $P_{aa}$/uÅ\(^2\) | 469.6903(82)   |
| $P_{bb}$/uÅ\(^2\) | 441.2267(82)   |
| $P_{cc}$/uÅ\(^2\) | 209.3371(82)   |
| $n$              | 18             |
| $\sigma$/kHz     | 2.6            |

\(^a\) $A$, $B$ and $C$ are the rotational constants. The quartic centrifugal distortion constants of all
monosubstituted isotopologues and the $^{14}$N nuclear quadrupole coupling constants for the $^{13}$C
species were fixed to the parent species values. $n$ is the number of hyperfine quadrupole
components fitted. $\sigma$ is the rms deviation of the fit. $P_{\alpha\alpha}$ ($\alpha = a$, $b$ or $c$) are the planar moments
of inertia derived from the moments of inertia $I_{\alpha}$ as for example $P_{cc} = (I_a + I_b - I_c)/2$. \(^b\) Standard
errors are given in parentheses in units of the last digit.

![Diagram of the pentafluoropyridine⋯formaldehyde cluster](image-url)
**Table S11.** Comparison of the rotational constants ($A$, $B$, $C$), the moments of inertia ($I_a$, $I_b$, $I_c$), and the planar moments ($P_{aa}$, $P_{bb}$, $P_{cc}$) of pentafluoropyridine, formaldehyde, and the pentafluoropyridine···formaldehyde adduct. The constants shown for CsF3N···H2CO are the arithmetic mean of the values obtained for both tunneling states (see Tables 1 and S9).

The $P_{aa}$ value of pentafluoropyridine (469.95 uÅ²) is almost equal to that of the adduct (469.95 uÅ²). This confirms the geometry of the adduct corresponding to form C1 as illustrated in the figure below where it can be seen that $P_{aa}$ (pentafluoropyridine···formaldehyde) $\approx P_{a'a'}$ (pentafluoropyridine) + $P_{c''}$ (formaldehyde).

| Parameters$^a$ | Pentafluoropyridine$^b$ | Formaldehyde$^c$ | Pentafluoropyridine···formaldehyde$^b$ |
|----------------|------------------------|-----------------|--------------------------------------|
| $A$/MHz        | 1481.58184(19)         | 281970.5418(84) | 779.69325(13)                       |
| $B$/MHz        | 1075.37335(17)         | 38836.05020(32) | 745.84178(10)                       |
| $C$/MHz        | 623.11194(16)          | 34002.20056(30) | 555.473024(67)                      |
| $I_a$/uÅ²      | 341.107724(44)         | 1.7923117(39)   | 648.17672(11)                       |
| $I_b$/uÅ²      | 469.956791(74)         | 13.0131436(39)  | 677.595467(91)                      |
| $I_c$/uÅ²      | 811.05653(21)          | 14.863129(14)   | 909.81738(11)                       |
| $P_{aa}$/uÅ²   | 469.95280(16)          | 13.04198058(15) | 469.61806(15)                       |
| $P_{bb}$/uÅ²   | 341.10373(16)          | 1.82114862(15)  | 440.199311(15)                      |
| $P_{cc}$/uÅ²   | 0.00399(16)            | -0.02883693(15) | 207.97740(15)                       |

$^a$ $A$, $B$ and $C$ are the rotational constants. $I_a$, $I_b$ and $I_c$ are the moments of inertia. $P_{aa}$ ($\alpha = a$, $b$ or $c$) are the planar moments of inertia derived from the moments of inertia $I_\alpha$ as for example $P_{cc} = (I_a + I_b - I_c)/2$. $^b$ This work, see Tables 1 and S8-S9. $^c$ Bocquet, R.; Demaison, J.; Poteau, L.; Liedtke, M.; Belov, S.; Yamada, K. M. T.; Winnewisser, G.; Gerke, C.; Gripp, J.; Köhler, T. The Ground State Rotational Spectrum of Formaldehyde. *J. Mol. Spectrosc.* 1996, 177 (1), 154–159.
Table S12. Comparison of the $r_s$ coordinates (in Å) of pentafluoropyridine with those from $r_0$ method and $r_e$ coordinates predicted at B3LYP-D3/6-311++G(2d,p) (DFT), MP2/6-311++G(2d,p) (MP2(1)), MP2/aug-cc-pVDZ (MP2(2)), MP2/aug-cc-pVTZ (MP2(3)) and CCSD/6-311++G(2d,p) (CCSD) levels. The molecule is planar so the $c$ coordinates were assumed to be zero. The $r_s$ method gives an imaginary value for the $a$ coordinate of $C_4$ atom. The molecule exhibits a $C_{2v}$ symmetry.

|        | $a$          | $b$          |
|--------|--------------|--------------|
| $r_s$  | N1           | 0.058(26)$^b$| 1.64469(92) |
|        | $r_0$        | [0.0]$^c$    | 1.6474(19)  |
|        | DFT          | 0.0          | 1.6401      |
|        | MP2(1)       | 0.0          | 1.6474      |
|        | MP2(2)       | 0.0          | 1.6640      |
|        | MP2(3)       | 0.0          | 1.6455      |
|        | CCSD         | 0.0          | 1.6454      |
| $r_s$  | C2           | 1.1225(13)   | 0.9675(15)  |
|        | $r_0$        | 1.1239(19)   | 0.9703(12)  |
|        | DFT          | 1.1274       | 0.9738      |
|        | MP2(1)       | 1.1298       | 0.9747      |
|        | MP2(2)       | 1.1352       | 0.9818      |
|        | MP2(3)       | 1.1287       | 0.9737      |
|        | CCSD         | 1.1264       | 0.9723      |
| $r_s$  | C3           | 1.1960(13)   | 0.3980(39)  |
|        | $r_0$        | 1.1959(19)   | -0.4090(22) |
|        | DFT          | 1.1997       | -0.4122     |
|        | MP2(1)       | 1.2005       | -0.4125     |
|        | MP2(2)       | 1.2083       | -0.4156     |
|        | MP2(3)       | 1.2005       | -0.4128     |
|        | CCSD         | 1.1986       | -0.4128     |
| $r_s$  | C4           | 0.109(14)$^i$| 1.1102(13)  |
|        | $r_0$        | [0.0]$^c$    | -1.1113(26) |
|        | DFT          | 0.0          | -1.1141     |
|        | MP2(1)       | 0.0          | -1.1154     |
|        | MP2(2)       | 0.0          | -1.1255     |
|        | MP2(3)       | 0.0          | -1.1144     |
|        | CCSD         | 0.0          | -1.1141     |
| $r_s$  | F7           | 2.2598       | 1.6727      |
|        | MP2(1)       | 2.2636       | 1.6640      |
|        | MP2(2)       | 2.2809       | 1.6852      |
|        | MP2(3)       | 2.2593       | 1.6699      |
|        | CCSD         | 2.2546       | 1.6675      |
| $r_s$  | F8           | 2.3632       | -1.0605     |
|        | MP2(1)       | 2.3619       | -1.0679     |
|        | MP2(2)       | 2.3822       | -1.0681     |
|        | MP2(3)       | 2.3584       | -1.0597     |
|        | CCSD         | 2.3604       | -1.0574     |
| $r_s$  | F9           | 0.0          | -2.4391     |
|        | MP2(1)       | 0.0          | -2.4491     |
|        | MP2(2)       | 0.0          | -2.4650     |
|        | MP2(3)       | 0.0          | -2.4379     |
|        | CCSD         | 0.0          | -2.4360     |

$^a$ Absolute values. $^b$ Errors quoted calculated according to van Eijck, B. P. Influence of Molecular Vibrations on Substitution Coordinates. J. Mol. Spectrosc. 1982, 91, 348–362. $^c$ Values in square brackets were kept fixed in the $r_0$ fitting.
Table S13. \( r_s \) and \( r_0 \) structures of pentafluoropyridine (C\(_{2v}\)) calculated from the rotational constants given in Tables 1 and S8, and compared with the \( r_e \) structures predicted at B3LYP-D3/6-311++G(2d,p) (DFT), MP2/6-311++G(2d,p) (MP2(1)), MP2/aug-cc-pVDZ (MP2(2)), MP2/aug-cc-pVTZ (MP2(3)) and CCSD/6-311++G(2d,p)(CCSD) levels.

|                | \( r_N1-C2 \)/Å | \( r_s \) | \( r_e \)(DFT) | \( r_e \)(MP2(1)) | \( r_e \)(MP2(2)) | \( r_e \)(MP2(3)) | \( r_e \)(CCSD) |
|----------------|------------------|----------|---------------|-------------------|-------------------|-------------------|----------------|
| \( r(N1-C2) \)/Å | 1.3123(21)"     | 1.3125(15) | 1.3096        | 1.3149            | 1.3244            | 1.3135            | 1.3122         |
| \( r(C2-C3) \)/Å | 1.3827(21)       | 1.3675(41) | 1.3879        | 1.3890            | 1.3993            | 1.3883            | 1.3871         |
| \( r(C3-C4) \)/Å | 1.3868(24)       | 1.3929(23) | 1.3901        | 1.3911            | 1.4014            | 1.3904            | 1.3887         |
| \( r(C2-F7) \)/Å | 1.3319(24)       |          | 1.3308        | 1.3307            | 1.3445            | 1.3278            | 1.3252         |
| \( r(C3-F8) \)/Å | 1.3319(26)       |          | 1.3318        | 1.3299            | 1.3431            | 1.3264            | 1.3287         |
| \( r(C4-F9) \)/Å | 1.3283(35)       |          | 1.3249        | 1.3263            | 1.3395            | 1.3235            | 1.3219         |
| \( \angle N1-C2-C3 \)º | 124.04(17)      | 124.30(12) | 123.6         | 123.7             | 124.0             | 123.7             | 123.8          |
| \( \angle C2-C3-C4 \)º | 117.41(19)      | 117.75(16) | 117.3         | 117.4             | 117.4             | 117.3             | 117.4          |
| \( \angle C3-C4-C5 \)º | 119.21(21)      | 118.33(21) | 119.3         | 119.3             | 119.1             | 119.4             | 119.3          |
| \( \angle C2-N1-C6 \)º | 117.88(16)      | 117.56(11) | 118.8         | 118.5             | 118.0             | 118.5             | 118.3          |
| \( \angle F7-C2-N1 \)º | 117.32(11)      |          | 117.7         | 117.7             | 117.4             | 117.6             | 117.5          |
| \( \angle F8-C3-C2 \)º | 122.19(18)      |          | 122.1         | 122.1             | 122.1             | 122.2             | 122.0          |
| \( \angle F9-C4-C3 \)º | 120.40(12)      |          | 120.3         | 120.3             | 120.4             | 120.3             | 120.3          |

* Standard error in parenthesis in units of the last digit.  All C2-F7 and C3-F8 distances taken as equal.
Table S14. The \( r_s \) coordinates (in Å) of pentafluoropyridine\( \cdots \)formaldehyde and its comparison with the \( r_0 \) and \( r_e \) (CCSD/6-311++G(2d,p) (CCSD), MP2/aug-cc-pVTZ) (MP2) or B3LYP-D3/6-311++G(2d,p) (DFT)) coordinates for the most stable conformer C1. The \( r_s \) method gives imaginary values for the \( a \) coordinates of C4 and C12 atom. These imaginary coordinates have been set to cero to draw the atom positions in the figure which compares the \( r_s \) and \( r_e \) structures. The complex has \( C_s \) symmetry.

| \( r_s \) \( ^a \) | \( N_1 \) | \( a \) | \( b \) | \( c \) |
|----------------|--------|------|------|------|
| 0.00 | 1.0721(14) | 1.1219(37) |
| 0.00 | 1.0661(12) | -1.1237(14) |
| 0.00 | 1.0605 | -1.1280 |
| 0.00 | 1.0787 | -1.0952 |
| 1.1162(14) | 0.4706(32) | 0.7944(19) |
| -1.12418(1) | 0.47086(82) | -0.80103(89) |
| -1.1241 | 0.4712 | -0.8022 |
| -1.1263 | 0.5219 | -0.7638 |
| -1.1254 | 0.4864 | -0.7840 |
| 1.1949(13) | 0.7253(21) | 0.1588(96) |
| -1.19619(1) | -0.74298(5) | -1.14291(31) |
| -1.1970 | -0.7464 | -1.1455 |
| -1.1986 | -0.7278 | -0.1668 |
| -1.1982 | -0.7450 | -0.1521 |
| 1.3447(11) | | 0.174(21) |
| 0.00 | -1.35983(36) | 0.1915(15) |
| 0.00 | -1.3635 | 0.1883 |
| 0.00 | -1.3625 | 0.1325 |
| 0.00 | -1.3696 | 0.1679 |
| 2.77152(54) | 1.76847(94) |
| 0.00 | 2.7447(43) | 1.789(12) |
| 0.00 | 2.7415 | 1.8191 |
| 0.00 | 2.5871 | 1.8342 |
| 0.00 | 2.7041 | 1.7832 |

\( ^a \) Absolute values. \( ^b \) Values in square brackets were kept fixed in the \( r_0 \) fitting. \( ^c \) Errors quoted calculated according to van Eijck, B. P. Influence of Molecular Vibrations on Substitution Coordinates. \textit{J. Mol. Spectrosc.} 1982, \textit{91}, 348–362.
Table S15. $r_0$ distances and angles of pentafluoropyridine···formaldehyde calculated from the rotational constants given in Tables S1, S9, and S10, and their comparison with those from theoretical calculations at B3LYP-D3/6-311++G(2d,p) (DFT), MP2/aug-cc-pVTZ (MP2) and CCSD/6-311++G(2d,p) (CCSD) levels for the most stable form C1 of the complex.

|                  | $r_0$       | $r_s$     | $r_e$(DFT) | $r_e$(MP2) | $r_e$(CCSD) |
|------------------|-------------|-----------|------------|------------|-------------|
| $r(N_1-C_2)$ /Å  | 1.3119a     | 1.3096(22)| 1.3092     | 1.3131     | 1.3182      |
| $r(C_2-C_3)$ /Å  | 1.3812      | 1.3566(57)| 1.3859     | 1.3868     | 1.3856      |
| $r(C_3-C_4)$ /Å  | 1.3853      | 1.3865(57)| 1.3886     | 1.3889     | 1.3874      |
| $r(C_2-F_7)$ /Å  | 1.3349      | 1.3334    | 1.3308     | 1.3279     |             |
| $r(C_3-F_8)$ /Å  | 1.3325      | 1.3324    | 1.3270     | 1.3295     |             |
| $r(C_4-F_9)$ /Å  | 1.3289      | 1.3253    | 1.3241     | 1.3223     |             |
| $r(N_1-C_{12})$ /Å | 3.361(11)b  | 3.3530(34)| 3.3057     | 3.2416     | 3.3918      |
| $r(N_1-O_{13})$ /Å | 3.184(16)   | 3.1089    | 3.0572     | 3.1847     |             |
| $r(x-O_{13})$ /Å  | 3.024(14)   | 2.9580    | 2.8719     | 2.9768     |             |
| $r(x-N_1)$ /Å    | 1.3806(16)  | 1.3775    | 1.3807     | 1.3806     |             |
| $r(N_1-H_{14})$ /Å | 2.801(26)   | 2.7560    | 2.6869     | 2.8774     |             |
| $r(C_{12}-O_{13})$ /Å | 1.2091c     | 1.2031    | 1.2158     | 1.2076     |             |
| $r(C_{12}-H_{14})$ /Å | 1.1174      | 1.1065    | 1.1001     | 1.1042     |             |
| $r(C_{12}-H_{15})$ /Å | 1.1164      | 1.1065    | 1.0991     | 1.1037     |             |

|                  |            |           |            |            |            |
| $\angle N_1-C_2-C_3$ /º | 124.23     | 124.86(17)| 123.7      | 123.9      | 124.0      |
| $\angle C_2-C_3-C_4$ /º  | 117.43     | 117.15(40)| 117.3      | 117.4      | 117.4      |
| $\angle C_3-C_4-C_5$ /º  | 119.12     | 119.04(75)| 119.3      | 119.3      | 119.2      |
| $\angle C_2-N_1-C_6$ /º  | 117.55     | 116.94(23)| 118.5      | 118.1      | 117.9      |
| $\angle F_7-C_2-N_1$ /º  | 117.07     | 117.5     | 117.4      | 117.3      |            |
| $\angle F_8-C_3-C_2$ /º  | 122.06     | 122.0     | 122.1      | 121.9      |            |
| $\angle F_9-C_4-C_3$ /º  | 120.44     | 120.4     | 120.3      | 120.4      |            |
| $\angle C_{12}-N_1-C_6$ /º | 91.48(13)  | 92.25(40)| 92.2       | 91.2       | 91.2       |
| $\angle O_{13}-C_7-C_6$ /º | 71.20(89)  | 70.1      | 70.4       | 67.9       |            |
| $\angle O_{13}-N_1-C_4$ /º | 70.41(65)  | 70.8      | 69.1       | 70.3       |            |
| $\angle x-O_{13}-C_{12}$ /º | 113.3(1.1) | 114.7     | 114.3      | 117.2      |            |
| $\angle O_{13}-x-N_1$ /º  | 84.04(18)  | 80.8      | 82.5       | 82.0       |            |
| $\angle O_{13}-C_{12}-H_{14}$ /º | 122.47    | 121.6     | 121.3      | 121.5      |            |
| $\angle O_{13}-C_{12}-H_{15}$ /º | 122.59    | 121.7     | 121.4      | 121.5      |            |
| $\angle H_{14}-N_1-C_4$ /º | 109.62(52) | 110.5     | 109.7      | 109.2      |            |

a Values in square brackets were kept fixed in the $r_0$ fitting. b Standard errors in parenthesis in units of the last digit.
Table S16. Comparison of the results of the energy decomposition analysis (Electrostatic, Exchange, Induction, Dispersion, HF, and SAPT values in kJ/mol) done with the DFT-SAPT method for the C₅F₅N···CH₂O and C₅H₅N···CH₂O complexes.

| Complex       | Elect. | Exch. | Induct. | Dispers. | HF   | SAPT |
|---------------|--------|-------|---------|----------|------|------|
| C₅F₅N···CH₂O  | -17.1  | 19.6  | -2.0    | -16.8    | -1.2 | -17.5|
| C₅H₅N···CH₂O  | -24.7  | 29.4  | -3.4    | -16.0    | -3.9 | -18.5|
Table S17. Observed rotational transitions and residuals (all the values in MHz) for pentafluoropyridine molecule in the ground vibrational state.

| J' | K_{1}' | K_{1}'' | J'' | K_{1}''' | K_{1}'''' | F' | F'' | Obs.       | Obs.-Cal. |
|----|--------|---------|-----|----------|-----------|----|-----|-----------|-----------|
| 1  | 1      | 1       | 0   | 0        | 0         | 1  | 1   | 2103.7054 | -0.0003   |
| 2  | 1      |         |     |          |           |    |     | 2104.8913 | -0.0001   |
| 0  |         |         |     |          |           |    |     | 2106.6704 | -0.0003   |
| 4  | 3      | 1       | 4   | 2        | 2         | 3  | 4   | 2185.5652 | -0.0025   |
| 5  |         |         |     |          |           |    |     | 2185.7570 | -0.0031   |
| 4  |         |         |     |          |           |    |     | 2186.5119 | 0.0021    |
| 5  |         |         |     |          |           |    |     | 2187.2094 | 0.0002    |
| 3  |         |         |     |          |           |    |     | 2187.3891 | 0.0000    |
| 4  | 5      |         |     |          |           |    |     | 2187.9501 | -0.0085   |
| 3  |         |         |     |          |           |    |     | 2188.3411 | 0.0099    |
| 5  | 3      | 2       | 5   | 2        | 3         | 4  | 4   | 2358.8587 | -0.0204   |
| 6  |         |         |     |          |           |    |     | 2358.9102 | 0.0093    |
| 5  |         |         |     |          |           |    |     | 2359.0071 | 0.0001    |
| 4  | 2      | 2       | 4   | 1        | 3         | 3  | 4   | 2362.7641 | 0.0000    |
| 5  |         |         |     |          |           |    |     | 2363.1341 | -0.0025   |
| 3  |         |         |     |          |           |    |     | 2363.5151 | -0.0008   |
| 5  |         |         |     |          |           |    |     | 2363.7353 | 0.0004    |
| 4  | 4      |         |     |          |           |    |     | 2364.5851 | -0.0004   |
| 4  |         |         |     |          |           |    |     | 2365.1873 | 0.0035    |
| 3  |         |         |     |          |           |    |     | 2365.3333 | -0.0040   |
| 3  | 3      | 0       | 3   | 2        | 1         | 3  | 3   | 2461.4628 | 0.0000    |
| 4  |         |         |     |          |           |    |     | 2461.8990 | 0.0010    |
| 2  |         |         |     |          |           |    |     | 2462.0523 | 0.0015    |
| 3  | 4      |         |     |          |           |    |     | 2462.6331 | -0.0019   |
| 4  |         |         |     |          |           |    |     | 2463.0713 | 0.0010    |
| 2  | 2      |         |     |          |           |    |     | 2463.6346 | 0.0015    |
| 2  | 2      | 1       | 2   | 1        | 2         | 2  | 1   | 2574.4218 | 0.0029    |
| 2  |         |         |     |          |           |    |     | 2574.7738 | -0.0009   |
| 2  |         |         |     |          |           |    |     | 2575.4085 | 0.0005    |
| 3  | 3      |         |     |          |           |    |     | 2575.4085 | 0.0005    |
| 1  |         |         |     |          |           |    |     | 2575.4085 | 0.0005    |
| 3  | 2      |         |     |          |           |    |     | 2576.0448 | -0.0006   |
| 1  |         |         |     |          |           |    |     | 2576.3982 | 0.0011    |
| 3  | 1      | 2       | 3   | 0        | 3         | 2  | 2   | 2687.1778 | 0.0007    |
| 4  |         |         |     |          |           |    |     | 2687.7431 | 0.0005    |
| 4  |         |         |     |          |           |    |     | 2688.2551 | -0.0041   |
| 3  |         |         |     |          |           |    |     | 2688.6598 | 0.0010    |
| 3  | 4      |         |     |          |           |    |     | 2688.8448 | 0.0046    |
| 3  |         |         |     |          |           |    |     | 2689.3568 | 0.0000    |
| 3  |         |         |     |          |           |    |     | 2689.3568 | 0.0000    |
| 2  | 0      | 2       | 1   | 1        | 1         | 1  | 0   | 2765.8686 | -0.0013   |
| 3  |         |         |     |          |           |    |     | 2767.6213 | -0.0039   |
| 2  |         |         |     |          |           |    |     | 2768.7665 | -0.0011   |
| 1  |         |         |     |          |           |    |     | 2768.8363 | 0.0011    |
| J'  | K_{J-1}' | K_{J+1}' | J'' | K_{J-1}'' | K_{J+1}'' | F'   | F''   | Obs.     | Obs.-Cal. |
|-----|----------|----------|-----|-----------|-----------|------|-------|----------|-----------|
| 6   | 4        | 2        | 6   | 3         | 3         | 6    | 6     | 2881.6016 | 0.0015    |
| 7   | 4        | 3        | 7   | 3         | 4         | 8    | 8     | 3058.3174 | 0.0094    |
| 6   | 3        | 3        | 6   | 2         | 4         | 5    | 6     | 3160.4495 | -0.0018   |
| 6   | 5        | 1        | 5   | 3         | 2         | 5    | 5     | 3241.9377 | 0.0000    |
| 4   | 2        | 3        | 3   | 3         | 3         | 3    | 2     | 3250.9850 | 0.0015    |
| 3   | 3        | 1        | 3   | 2         | 2         | 3    | 3     | 3278.6178 | 0.0001    |
| 2   | 1        | 2        | 1   | 0         | 1         | 2    | 1     | 3349.9291 | 0.0000    |
| 3   | 2        | 2        | 3   | 1         | 3         | 3    | 2     | 3370.8059 | 0.0003    |
| 5   | 3        | 8        | 4   | 4         | 4         | 8    | 8     | 3543.6615 | 0.0030    |
| 5   | 2        | 3        | 5   | 1         | 4         | 4    | 5     | 3616.9719 | 0.0066    |

Table S17 (Continued).
| J' | K_{J1} | K_{K1} | J'' | K_{J2} | K_{K2} | F'   | F'' | Obs.  | Obs.-Cal. |
|---|---|---|---|---|---|---|---|---|---|
| 9 | 5 | 4 | 9 | 4 | 5 | 8 | 8 | 3741.2299 | 0.0123 |
| 4 | 4 | 0 | 4 | 3 | 1 | 4 | 4 | 3755.8963 | -0.0002 |
| 10 | 10 | 3741.2299 | 0.0123 |
| 5 | 4 | 3756.6046 | 0.0111 |
| 4 | 5 | 3756.6476 | 0.0015 |
| 3 | 4 | 3756.7751 | 0.0012 |
| 4 | 3 | 3756.8388 | 0.0002 |
| 5 | 5 | 3757.3436 | 0.0005 |
| 3 | 3 | 3757.7165 | 0.0005 |
| 4 | 3 | 2 | 4 | 2 | 3 | 3 | 4 | 3762.1930 | -0.0066 |
| 5 | 4 | 3762.2186 | -0.0087 |
| 3 | 3 | 3762.3018 | -0.0016 |
| 5 | 5 | 3762.3018 | -0.0016 |
| 5 | 2 | 4 | 4 | 3 | 1 | 5 | 4 | 3784.5189 | -0.0020 |
| 6 | 5 | 3785.3018 | 0.0045 |
| 4 | 3 | 3785.5072 | 0.0094 |
| 8 | 4 | 4 | 8 | 3 | 5 | 7 | 7 | 3941.5947 | 0.0065 |
| 9 | 9 | 3941.6752 | 0.0098 |
| 8 | 8 | 3942.2783 | 0.0006 |
| 7 | 5 | 2 | 7 | 4 | 3 | 7 | 7 | 3967.2265 | 0.0034 |
| 8 | 8 | 3968.0822 | -0.0005 |
| 6 | 6 | 3968.2108 | 0.0040 |
| 4 | 1 | 3 | 4 | 0 | 4 | 3 | 3 | 4074.9907 | 0.0013 |
| 5 | 5 | 4075.3384 | 0.0013 |
| 4 | 3 | 4075.7420 | 0.0008 |
| 3 | 4 | 4075.9369 | 0.0013 |
| 4 | 5 | 4075.9369 | 0.0013 |
| 5 | 4 | 4076.0937 | 0.0042 |
| 4 | 4 | 4076.6873 | -0.0004 |
| 10 | 6 | 4 | 10 | 5 | 5 | 10 | 10 | 4182.2183 | 0.0044 |
| 11 | 11 | 4182.5429 | 0.0033 |
| 9 | 9 | 4182.5429 | 0.0033 |
| 4 | 4 | 1 | 4 | 3 | 2 | 4 | 4 | 4193.5444 | 0.0002 |
| 4 | 5 | 4193.6695 | 0.0030 |
| 4 | 3 | 4193.6695 | 0.0030 |
| 5 | 4 | 4194.2923 | -0.0011 |
| 5 | 5 | 4194.4044 | 0.0022 |
| 3 | 4 | 4194.4798 | -0.0065 |
| 3 | 3 | 4194.6233 | 0.0006 |
| 3 | 0 | 3 | 2 | 1 | 2 | 3 | 3 | 4245.2121 | 0.0000 |
| 2 | 1 | 4245.5539 | -0.0002 |
| 4 | 3 | 4245.7281 | -0.0005 |
| 3 | 2 | 4245.8502 | -0.0002 |
| 2 | 2 | 4246.5475 | -0.0010 |
Table S17 (Continued).

| J′  | K_{1}′ | K_{1}′ | J′′ | K_{0}′′ | K_{0}′′ | F′  | F′′  | Obs.       | Obs.-Cal. |
|-----|--------|--------|-----|---------|---------|-----|------|------------|-----------|
| 3   | 1      | 2      | 2   | 2       | 1       | 2   | 1    | 4357.3277  | -0.0008   |
|     | 4      | 3      | 2   | 2       | 2       | 3   | 3    | 4358.0638  | -0.0005   |
|     | 2      | 2      | 3   | 3       | 3       | 4   | 4    | 4358.3107  | -0.0017   |
|     | 3      | 3      | 2   | 2       | 4       | 5   | 5    | 4359.1634  | 0.0015    |
|     | 3      | 2      | 3   | 3       | 1       | 4   | 4    | 4359.7949  | 0.0008    |
| 4   | 2      | 3      | 4   | 1       | 4       | 3   | 3    | 4390.0597  | 0.0004    |
|     | 4      | 3      | 3   | 1       | 3       | 4   | 4    | 4390.1581  | 0.0000    |
|     | 5      | 5      | 5   | 3       | 1       | 4   | 4    | 4390.2827  | 0.0009    |
|     | 4      | 4      | 4   | 3       | 3       | 5   | 5    | 4391.1462  | -0.0004   |
| 5   | 4      | 2      | 5   | 3       | 3       | 5   | 5    | 4399.8660  | 0.0015    |
|     | 6      | 6      | 6   | 3       | 3       | 5   | 5    | 4400.2100  | 0.0010    |
|     | 4      | 4      | 4   | 3       | 3       | 5   | 5    | 4400.2818  | 0.0027    |
| 3   | 1      | 3      | 2   | 0       | 2       | 3   | 2    | 4476.0760  | -0.0009   |
|     | 4      | 3      | 3   | 1       | 3       | 4   | 4    | 4476.7063  | 0.0005    |
|     | 2      | 1      | 2   | 2       | 2       | 5   | 5    | 4476.9172  | -0.0005   |
|     | 2      | 2      | 4   | 4       | 3       | 6   | 6    | 4476.9896  | 0.0044    |
| 7   | 3      | 4      | 7   | 2       | 5       | 6   | 6    | 4518.4606  | 0.0097    |
|     | 8      | 8      | 8   | 4       | 4       | 7   | 7    | 4518.5905  | 0.0076    |
|     | 7      | 7      | 7   | 5       | 5       | 7   | 7    | 4519.4991  | 0.0017    |
| 5   | 3      | 3      | 5   | 2       | 4       | 4   | 4    | 4525.4309  | 0.0018    |
|     | 6      | 6      | 6   | 4       | 4       | 5   | 5    | 4525.5152  | 0.0026    |
|     | 5      | 5      | 5   | 3       | 3       | 5   | 5    | 4525.9129  | 0.0010    |
|     | 4      | 3      | 3   | 2       | 4       | 6   | 6    | 4535.2108  | 0.0000    |
|     | 6      | 5      | 5   | 4       | 4       | 6   | 6    | 4553.4704  | 0.0036    |
|     | 5      | 4      | 4   | 3       | 3       | 6   | 6    | 4554.5646  | 0.0101    |
| 6   | 5      | 1      | 6   | 4       | 2       | 6   | 6    | 4610.0565  | 0.0006    |
|     | 7      | 7      | 7   | 5       | 5       | 7   | 7    | 4611.1342  | 0.0024    |
|     | 5      | 5      | 5   | 4       | 4       | 8   | 8    | 4611.3146  | 0.0011    |
| 9   | 6      | 3      | 9   | 5       | 4       | 9   | 9    | 4651.7023  | 0.0069    |
|     | 10     | 10     | 10  | 6       | 6       | 10  | 10   | 4652.4267  | 0.0096    |
|     | 8      | 8      | 8   | 5       | 5       | 11  | 11   | 4652.5021  | 0.0042    |
| 10  | 5      | 5      | 10  | 4       | 6       | 11  | 11   | 4711.6119  | -0.0043   |
|     | 10     | 10     | 10  | 6       | 6       | 11  | 11   | 4712.1710  | -0.0078   |
| 6   | 4      | 3      | 6   | 3       | 4       | 5   | 5    | 4865.9668  | -0.0008   |
|     | 7      | 7      | 7   | 6       | 6       | 5   | 5    | 4865.9668  | -0.0008   |
|     | 6      | 6      | 6   | 5       | 5       | 5   | 5    | 4865.9668  | -0.0008   |
| 2   | 2      | 1      | 1   | 1       | 0       | 2   | 1    | 5066.8679  | 0.0000    |
|     | 2      | 2      | 2   | 1       | 1       | 2   | 2    | 5067.4623  | -0.0012   |
|     | 1      | 1      | 1   | 1       | 0       | 3   | 2    | 5067.8525  | 0.0006    |
|     | 1      | 2      | 2   | 1       | 0       | 4   | 4    | 5068.4503  | 0.0028    |
|     | 0      | 0      | 0   | 5       | 5       | 5   | 5    | 5069.3398  | -0.0014   |
| 5   | 5      | 0      | 5   | 4       | 1       | 5   | 5    | 5076.9153  | 0.0002    |
|     | 6      | 6      | 6   | 4       | 4       | 6   | 6    | 5078.0428  | -0.0007   |
|     | 4      | 4      | 4   | 3       | 3       | 4   | 4    | 5078.2752  | 0.0020    |
Table S17 (Continued).

| J' | K_{j1}' | K_{i1}' | J'' | K_{i1}'' | K_{i1}''' | F' | F'' | Obs.  | Obs.-Cal. |
|----|---------|---------|-----|-----------|-----------|----|-----|-------|-----------|
| 6  | 2       | 4       | 6   | 1         | 5         | 5  | 5   | 5092.4221 | 0.0006    |
| 5  | 5       | 1       | 5   | 4         | 2         | 5  | 5   | 5092.5899 | 0.0111    |
| 6  | 6       | 1       | 5   | 4         | 2         | 5  | 5   | 5093.5772 | 0.0000    |
| 5  | 5       | 1       | 5   | 4         | 2         | 5  | 5   | 5254.1489 | -0.0002   |
| 6  | 6       | 1       | 5   | 4         | 2         | 5  | 5   | 5255.0308 | 0.0021    |
| 4  | 4       | 4       | 4   | 3         | 3         | 3  | 2   | 5265.2841 | 0.0047    |
| 7  | 7       | 7       | 7   | 7         | 7         | 7  | 7   | 5265.8217 | 0.0027    |
| 5  | 5       | 1       | 5   | 4         | 2         | 5  | 5   | 5265.9146 | 0.0045    |
| 4  | 2       | 2       | 3   | 3         | 1         | 3  | 2   | 5365.1460 | 0.0007    |
| 5  | 4       | 4       | 4   | 3         | 3         | 3  | 2   | 5365.7451 | 0.0011    |
| 3  | 3       | 3       | 3   | 3         | 3         | 3  | 2   | 5366.0075 | -0.0092   |
| 4  | 3       | 3       | 3   | 3         | 3         | 3  | 2   | 5367.8403 | 0.0021    |
| 9  | 4       | 5       | 9   | 3         | 6         | 8  | 8   | 5402.0646 | -0.0010   |
| 10 | 10      | 10      | 10  | 10        | 10        | 8  | 8   | 5402.1649 | 0.0108    |
| 9  | 9       | 9       | 9   | 9         | 9         | 8  | 8   | 5402.9448 | -0.0005   |
| 8  | 6       | 2       | 8   | 5         | 3         | 8  | 8   | 5407.6821 | 0.0034    |
| 9  | 9       | 9       | 9   | 9         | 9         | 8  | 8   | 5408.5809 | 0.0095    |
| 7  | 7       | 7       | 7   | 7         | 7         | 8  | 8   | 5408.6858 | 0.0019    |
| 5  | 1       | 4       | 5   | 0         | 5         | 4  | 4   | 5439.8626 | 0.0000    |
| 6  | 6       | 6       | 6   | 6         | 6         | 4  | 4   | 5440.0735 | 0.0009    |
| 5  | 6       | 6       | 6   | 6         | 6         | 4  | 4   | 5440.2309 | 0.0116    |
| 5  | 5       | 5       | 5   | 5         | 5         | 4  | 4   | 5441.1009 | -0.0009   |
| 7  | 5       | 3       | 7   | 4         | 4         | 7  | 7   | 5456.4011 | 0.0070    |
| 8  | 8       | 8       | 8   | 8         | 8         | 7  | 7   | 5456.6240 | 0.0040    |
| 6  | 3       | 4       | 6   | 2         | 5         | 5  | 5   | 5523.9982 | 0.0011    |
| 7  | 7       | 7       | 7   | 7         | 7         | 5  | 5   | 5524.0953 | 0.0019    |
| 5  | 2       | 4       | 5   | 1         | 5         | 4  | 4   | 5547.4041 | 0.0012    |
| 6  | 6       | 6       | 6   | 6         | 6         | 4  | 4   | 5547.5775 | 0.0011    |
| 5  | 5       | 5       | 5   | 5         | 5         | 4  | 4   | 5548.4368 | -0.0019   |
| 4  | 0       | 4       | 3   | 1         | 3         | 4  | 4   | 5576.2260 | 0.0023    |
| 5  | 4       | 4       | 4   | 4         | 4         | 4  | 4   | 5576.9090 | 0.0130    |
| 3  | 3       | 3       | 3   | 3         | 3         | 4  | 4   | 5576.9693 | -0.0068   |
| 7  | 7       | 7       | 7   | 7         | 7         | 4  | 4   | 5618.2365 | 0.0063    |
| 6  | 6       | 6       | 6   | 6         | 6         | 4  | 4   | 5618.5511 | 0.0050    |
| 4  | 1       | 4       | 3   | 0         | 3         | 4  | 4   | 5643.6225 | 0.0021    |
| 5  | 4       | 4       | 4   | 4         | 4         | 4  | 4   | 5644.1391 | 0.0020    |
| 3  | 3       | 3       | 3   | 3         | 3         | 4  | 4   | 5644.4002 | -0.0060   |
| 7  | 7       | 7       | 7   | 7         | 7         | 3  | 3   | 5645.1251 | -0.0003   |
Table S17 (Continued).

| $J'$ | $K_{1'}$ | $K_{3'}$ | $J''$ | $K_{3''}$ | $K_{4''}$ | $F'$ | $F''$ | Obs.  | Obs.-Cal. |
|------|----------|----------|-------|-----------|-----------|------|-------|-------|-----------|
| 2    | 2        | 0        | 1     | 1         | 1         | 1    | 0     | 5741.0556 | 0.0005    |
|      | 3        | 2        | 5742.8598 | 0.0021  |
|      | 1        | 1        | 5744.0198 | -0.0002  |
|      | 2        | 1        | 5744.0859 | -0.0010  |
| 8    | 5        | 4        | 8     | 4         | 5         | 7    | 7     | 5915.9931 | 0.0016    |
|      | 9        | 9        | 5915.9931 | 0.0016  |
|      | 8        | 8        | 5915.9931 | 0.0016  |
| 5    | 3        | 2        | 4     | 4         | 1         | 4    | 3     | 5916.3701 | -0.0050   |
|      | 6        | 5        | 5916.8521 | 0.0028   |
|      | 5        | 4        | 5918.9790 | -0.0002  |
| 7    | 6        | 1        | 7     | 5         | 2         | 7    | 7     | 6010.0545 | 0.0038    |
|      | 8        | 8        | 6010.9255 | 0.0011   |
|      | 6        | 6        | 6011.0486 | -0.0018  |
| 8    | 3        | 5        | 8     | 2         | 6         | 7    | 7     | 6080.2263 | -0.0051   |
|      | 9        | 9        | 6080.3386 | 0.0052   |
|      | 8        | 8        | 6081.1497 | 0.0082   |
| 10   | 7        | 3        | 10    | 6         | 4         | 10   | 10    | 6160.1627 | -0.0087   |
|      | 11       | 11       | 6160.9387 | -0.0137  |
|      | 9        | 9        | 6161.0337 | 0.0029   |
| 4    | 1        | 3        | 3     | 2         | 2         | 3    | 2     | 6281.1189 | 0.0008    |
|      | 3        | 3        | 6281.1189 | 0.0008   |
|      | 4        | 4        | 6281.2732 | 0.0010   |
|      | 4        | 3        | 6281.8717 | 0.0013   |
|      | 4        | 4        | 6281.8717 | 0.0013   |
| 8    | 6        | 3        | 8     | 5         | 4         | 8    | 8     | 6286.4161 | -0.0037   |
| 7    | 6        | 2        | 7     | 5         | 3         | 7    | 7     | 6297.7760 | -0.0003   |
|      | 8        | 8        | 6298.3919 | 0.0063   |
|      | 6        | 6        | 6298.4867 | -0.0037   |
| 3    | 2        | 2        | 2     | 1         | 1         | 3    | 2     | 6313.0904 | 0.0008    |
|      | 2        | 2        | 6313.0904 | 0.0008   |
|      | 3        | 3        | 6314.3608 | 0.0007   |
|      | 4        | 4        | 6314.3608 | 0.0007   |
|      | 2        | 3        | 6314.3608 | 0.0007   |
| 6    | 6        | 0        | 6     | 5         | 1         | 6    | 6     | 6333.5726 | -0.0035   |
|      | 7        | 7        | 6334.4751 | -0.0034   |
|      | 5        | 5        | 6334.6325 | 0.0017   |
| 6    | 6        | 1        | 6     | 5         | 2         | 6    | 6     | 6392.6635 | -0.0040   |
|      | 7        | 7        | 6393.4937 | 0.0044   |
|      | 5        | 5        | 6393.6268 | -0.0011  |
| 9    | 6        | 4        | 9     | 5         | 5         | 9    | 9     | 6467.8294 | 0.0029    |
|      | 10       | 10       | 6468.0127 | 0.0154   |
|      | 8        | 8        | 6468.0127 | 0.0154   |
Table S17 (Continued).

| $J'$ | $K_{l1}'$ | $K_{s1}'$ | $J''$ | $K_{l1}''$ | $K_{s1}''$ | $F'$ | $F''$ | Obs. | Obs.-Cal. |
|------|----------|----------|------|----------|----------|-----|-----|------|----------|
| 7    | 2        | 5        | 7    | 1        | 6        | 6   | 6   | 6516.1600 | 0.0036    |
|      | 8        | 8        |      | 6516.2702 | 0.0024   |
|      | 7        | 7        |      | 6517.0401 | 0.0012   |
| 8    | 4        | 5        | 8    | 3        | 6        | 9   | 9   | 6612.5900 | -0.0072   |
|      | 8        | 8        |      | 6613.0379 | 0.0073   |
| 9    | 5        | 5        | 9    | 4        | 6        | 9   | 9   | 6668.5997 | -0.0072   |
|      | 8        | 8        |      | 6668.3198 | -0.0153  |
| 7    | 3        | 5        | 7    | 2        | 6        | 6   | 6   | 6673.2133 | 0.0001    |
|      | 8        | 8        |      | 6673.2993 | -0.0013  |
| 6    | 1        | 5        | 6    | 0        | 6        | 5   | 5   | 6737.8340 | -0.0007   |
|      | 7        | 7        |      | 6737.9747 | -0.0010  |
|      | 6        | 6        |      | 6738.8079 | -0.0023  |
| 6    | 2        | 5        | 6    | 1        | 6        | 5   | 5   | 6768.2279 | -0.0007   |
|      | 7        | 7        |      | 6768.3597 | -0.0019  |
|      | 6        | 6        |      | 6769.1496 | -0.0015  |
| 5    | 0        | 5        | 4    | 1        | 4        | 5   | 5   | 6846.6134 | 0.0014    |
|      | 5        | 4        |      | 6847.4020 | 0.0042   |
|      | 6        | 5        |      | 6847.5117 | 0.0171   |
|      | 4        | 4        |      | 6848.4679 | 0.0072   |
| 5    | 1        | 5        | 4    | 0        | 4        | 5   | 5   | 6863.1171 | 0.0044    |
|      | 5        | 4        |      | 6863.8705 | 0.0052   |
|      | 4        | 3        |      | 6864.0036 | 0.0067   |
|      | 6        | 5        |      | 6864.0036 | 0.0067   |
|      | 4        | 4        |      | 6864.9393 | 0.0034   |
| 9    | 7        | 2        | 9    | 6        | 3        | 9   | 9   | 6890.2391 | -0.0147   |
|      | 10       | 10       |      | 6890.9883 | -0.0075  |
|      | 8        | 8        |      | 6891.0621 | -0.0166  |
| 10   | 6        | 5        | 10   | 5        | 6        | 9   | 9   | 6927.7325 | 0.0004    |
|      | 11       | 11       |      | 6927.7325 | 0.0004   |
| 10   | 4        | 6        | 10   | 3        | 7        | 9   | 9   | 7047.1035 | -0.0063   |
|      | 11       | 11       |      | 7047.1681 | -0.0118  |
|      | 10       | 10       |      | 7047.8970 | 0.0195   |
| 9    | 7        | 3        | 9    | 6        | 4        | 10  | 10  | 7300.0196 | 0.0104    |
|      | 8        | 8        |      | 7300.0196 | 0.0104   |
| 8    | 7        | 1        | 8    | 6        | 2        | 8   | 8   | 7321.9013 | 0.0016    |
|      | 9        | 9        |      | 7322.5983 | -0.0055  |
|      | 7        | 7        |      | 7322.6974 | 0.0048   |
| 4    | 2        | 3        | 3    | 1        | 2        | 3   | 3   | 7345.8263 | -0.0015   |
|      | 4        | 3        |      | 7345.9285 | 0.0017   |
|      | 5        | 4        |      | 7346.9470 | 0.0017   |
|      | 4        | 4        |      | 7347.0322 | 0.0077   |
|      | 3        | 2        |      | 7347.3114 | 0.0019   |
| $J^\prime$ | $K_{s1}^\prime$ | $K_{s1}^\prime\prime$ | $J^\prime\prime$ | $K_{s1}^\prime\prime\prime$ | $K_{s1}^\prime\prime\prime\prime$ | $F^\prime$ | $F^\prime\prime$ | Obs.       | Obs.-Cal. |
|----------|----------------|-----------------|---------------|----------------|----------------|-------------|-------------|------------|-----------|
| 8        | 7              | 2               | 8             | 6              | 3              | 8           | 8           | 7426.5922  | -0.0102   |
|          | 9              |                 |               |                |                | 7           | 7           | 7427.2156  | 0.0077    |
|          | 7              |                 |               |                |                | 7           | 7           | 7427.2846  | 0.0004    |
| 11       | 7              | 5               | 11            | 6              | 6              | 11          | 11          | 7445.4378  | -0.0156   |
|          | 12             |                 |               |                |                | 12          | 12          | 7445.5789  | -0.0027   |
| 9        | 3              | 6               | 9             | 2              | 7              | 9           | 9           | 7562.6644  | 0.0099    |
| 7        | 7              | 1               | 7             | 6              | 2              | 7           | 7           | 7563.6979  | 0.0217    |
| 5        | 2              | 3               | 4             | 3              | 2              | 4           | 3           | 7752.1220  | 0.0033    |
|          | 6              |                 |               |                |                | 6           | 5           | 7752.3534  | 0.0028    |
|          | 5              |                 |               |                |                | 5           | 4           | 7753.5214  | 0.0050    |
| 9        | 4              | 6               | 9             | 3              | 7              | 10          | 10          | 7763.9996  | -0.0125   |
| 8        | 2              | 6               | 8             | 1              | 7              | 7           | 7           | 7847.1356  | -0.0029   |
| 8        | 3              | 6               | 8             | 2              | 7              | 7           | 7           | 7895.0730  | -0.0129   |
|          | 9              |                 |               |                |                | 9           | 9           | 7895.1644  | 0.0048    |
|          | 8              |                 |               |                |                | 8           | 8           | 7895.7396  | -0.0037   |
| 5        | 1              | 4               | 4             | 2              | 3              | 4           | 3           | 7897.2853  | 0.0037    |
|          | 6              |                 |               |                |                | 5           | 5           | 7897.2853  | 0.0037    |
| 6        | 0              | 6               | 5             | 1              | 5              | 6           | 5           | 8099.4284  | 0.0016    |
|          | 5              |                 |               |                |                | 5           | 4           | 8099.5148  | 0.0156    |
| 6        | 1              | 6               | 5             | 0              | 5              | 6           | 5           | 8103.0840  | 0.0017    |
|          | 6              |                 |               |                |                | 5           | 4           | 8103.1731  | 0.0100    |
|          | 7              |                 |               |                |                | 7           | 6           | 8103.1731  | 0.0100    |
| 3        | 3              | 1               | 2             | 2              | 0              | 3           | 2           | 8151.0870  | -0.0017   |
|          | 4              |                 |               |                |                | 4           | 3           | 8151.7745  | -0.0029   |
|          | 2              |                 |               |                |                | 2           | 1           | 8152.0233  | -0.0037   |
| 5        | 2              | 4               | 4             | 1              | 3              | 5           | 4           | 8335.6130  | -0.0032   |
|          | 6              |                 |               |                |                | 6           | 5           | 8336.2406  | -0.0006   |
|          | 4              |                 |               |                |                | 4           | 3           | 8336.3947  | -0.0081   |
| 3        | 3              | 0               | 2             | 2              | 1              | 2           | 1           | 8453.6491  | -0.0054   |
|          | 4              |                 |               |                |                | 4           | 3           | 8453.8494  | -0.0041   |
|          | 3              |                 |               |                |                | 3           | 2           | 8454.0455  | -0.0049   |
|          | 2              |                 |               |                |                | 2           | 2           | 8454.6342  | -0.0042   |
| 3        | 2              | 1               | 2             | 1              | 2              | 2           | 1           | 8565.4128  | -0.0115   |
|          | 4              |                 |               |                |                | 4           | 3           | 8566.1842  | -0.0060   |
|          | 3              |                 |               |                |                | 3           | 2           | 8567.9943  | -0.0066   |
| 6        | 1              | 5               | 5             | 2              | 4              | 6           | 5           | 9289.7962  | -0.0020   |
|          | 7              |                 |               |                |                | 7           | 6           | 9289.9078  | -0.0042   |
|          | 5              |                 |               |                |                | 5           | 4           | 9289.9078  | -0.0042   |
Table S17 (Continued).

| $J'$ | $K_{1}'$ | $K_{1}''$ | $J''$ | $K_{1}''$ | $K_{2}''$ | $F'$   | $F''$   | Obs.     | Obs.-Cal. |
|------|----------|-----------|-------|-----------|-----------|--------|--------|----------|-----------|
| 7    | 0        | 7         | 6     | 1         | 6         | 6      | 5      | 9346.8536 | 0.0003    |
|      |          |           |       |           |           |        |        | 9346.8536 | 0.0003    |
| 7    | 1        | 7         | 6     | 0         | 6         | 6      | 5      | 9347.6198 | 0.0018    |
|      |          |           |       |           |           |        |        | 9347.6198 | 0.0018    |
| 6    | 2        | 5         | 5     | 1         | 4         | 6      | 5      | 9431.1216 | -0.0099   |
|      |          |           |       |           |           |        |        | 9431.4506 | -0.0081   |
|      |          |           |       |           |           |        |        | 9431.5004 | -0.0190   |
| 4    | 3        | 2         | 3     | 2         | 1         | 4      | 3      | 9475.4592 | -0.0098   |
|      |          |           |       |           |           |        |        | 9476.5255 | -0.0071   |
|      |          |           |       |           |           |        |        | 9476.9102 | -0.0049   |
| 6    | 2        | 4         | 5     | 3         | 3         | 5      | 4      | 9856.9043 | -0.0089   |
|      |          |           |       |           |           |        |        | 9856.9686 | -0.0131   |
|      |          |           |       |           |           |        |        | 9857.4552 | -0.0084   |
Table S18. Observed rotational transitions and residuals (all the values in MHz) for the $^{15}$N$_1$ isotopologue of pentafluoropyridine molecule in the ground vibrational state.

| J' | K$_{1}'$ | K$_{2}'$ | J'' | K$_{1}''$ | K$_{2}''$ | Obs.     | Obs.-Cal. |
|----|---------|---------|-----|---------|---------|---------|-----------|
| 2  | 1       | 2       | 1   | 0       | 1       | 3333.1717| -0.0026   |
| 3  | 1       | 2       | 2   | 2       | 1       | 4383.9699| 0.0066    |
| 3  | 1       | 3       | 2   | 0       | 2       | 4456.3183| -0.0103   |
| 2  | 2       | 1       | 1   | 1       | 0       | 5031.0221| 0.0077    |
| 4  | 0       | 4       | 3   | 1       | 3       | 5560.9503| 0.0152    |
| 4  | 1       | 4       | 3   | 0       | 3       | 5623.1719| -0.0067   |
| 5  | 0       | 5       | 4   | 1       | 4       | 6825.6323| 0.0061    |
| 5  | 1       | 5       | 4   | 0       | 4       | 6840.4967| 0.0003    |
| 4  | 2       | 3       | 3   | 1       | 2       | 7302.1683| -0.0108   |
| 1  | 1       | 1       | 0   | 0       | 0       | 2091.0427| -0.0049   |
| 3  | 2       | 2       | 3   | 1       | 3       | 3348.0742| -0.0035   |
| 5  | 3       | 3       | 4   | 4       | 0       | 4619.1145| -0.0057   |
| 3  | 2       | 2       | 2   | 1       | 1       | 6273.1434| 0.0037    |
Table S19. Observed rotational transitions and residuals (all the values in MHz) for the $^{13}$C$_2$ isotopologue of pentafluoropyridine molecule in the ground vibrational state. (see Table S13 for atom labelling).

| J' | K'$_1$' | K'$_2$' | J'' | K'$_1$'' | K'$_2$'' | F' | F'' | Obs.  | Obs.-Cal. |
|----|---------|---------|-----|----------|----------|----|-----|-------|-----------|
| 2  | 1       | 2       | 1   | 0        | 1        | 2  | 1   | 3340.8908 | 0.0000     |
|    | 2       | 2       |     | 3341.4789 | -0.0016  |
|    | 1       | 1       |     | 3341.8810 | -0.0041  |
|    | 3       | 2       |     | 3342.1191 | 0.0001   |
|    | 1       | 0       |     | 3343.3547 | -0.0047  |
| 3  | 2       | 2       | 3   | 1        | 3        | 2  | 2   | 3361.6991 | 0.0003     |
|    | 4       | 4       |     | 3361.9282 | -0.0059  |
|    | 3       | 3       |     | 3362.6068 | 0.0002   |
| 4  | 3       | 2       | 4   | 2        | 3        | 3  | 3   | 3752.1085 | 0.0007     |
|    | 5       | 5       |     | 3752.1085 | 0.0007   |
| 4  | 1       | 3       | 4   | 0        | 4        | 3  | 3   | 4064.0536 | 0.0102     |
|    | 5       | 5       |     | 4064.3904 | -0.0005  |
|    | 4       | 4       |     | 4065.7415 | -0.0002  |
| 3  | 0       | 3       | 2   | 1        | 2        | 3  | 3   | 4233.7881 | -0.0040    |
|    | 2       | 1       |     | 4234.1339 | -0.0004  |
|    | 4       | 3       |     | 4234.3072 | -0.0015  |
|    | 3       | 2       |     | 4234.4286 | -0.0019  |
|    | 2       | 2       |     | 4235.1271 | -0.0015  |
| 3  | 1       | 2       | 2   | 2        | 1        | 2  | 1   | 4345.6692 | -0.0079    |
|    | 4       | 3       |     | 4346.4074 | -0.0056  |
|    | 3       | 2       |     | 4348.1398 | -0.0029  |
| 4  | 2       | 3       | 4   | 1        | 4        | 3  | 3   | 4378.2231 | -0.0003    |
|    | 5       | 5       |     | 4378.4480 | 0.0020   |
|    | 4       | 4       |     | 4379.3077 | -0.0031  |
| 5  | 4       | 2       | 5   | 3        | 3        | 5  | 5   | 4387.9016 | 0.0019     |
|    | 6       | 6       |     | 4388.2356 | -0.0085  |
|    | 4       | 4       |     | 4388.3173 | 0.0029   |
| 3  | 1       | 3       | 2   | 0        | 2        | 3  | 2   | 4464.0080 | -0.0021    |
|    | 4       | 3       |     | 4464.6379 | -0.0011  |
|    | 2       | 1       |     | 4464.8486 | -0.0023  |
|    | 2       | 2       |     | 4464.9215 | 0.0030   |
| 5  | 3       | 3       | 5   | 2        | 4        | 6  | 6   | 4513.2956 | 0.0055     |
|    | 5       | 5       |     | 4513.6865 | -0.0028  |
| 6  | 4       | 3       | 6   | 3        | 4        | 5  | 5   | 4852.7887 | 0.0044     |
|    | 7       | 7       |     | 4852.7887 | 0.0044   |
| 2  | 2       | 1       | 1   | 1        | 0        | 2  | 1   | 5053.1754 | -0.0004    |
|    | 2       | 2       |     | 5053.7743 | 0.0029   |
|    | 1       | 1       |     | 5054.1579 | -0.0018  |
|    | 3       | 2       |     | 5054.4033 | -0.0002  |
|    | 1       | 0       |     | 5055.6503 | 0.0011   |
Table S19 (Continued).

| J'  | K_{1}' | K_{1+1}' | J'' | K_{1}' | K_{1+1}' | F'   | F''   | Obs.   | Obs._Cal. |
|-----|--------|----------|-----|--------|----------|------|-------|--------|-----------|
| 5   | 1      | 4        | 5   | 0      | 5        | 4    | 4     | 5425.2332 | 0.0026    |
|     |        |          |     |        |          |      |       | 5425.4385 | -0.0018   |
|     |        |          |     |        |          |      |       | 5426.4649 | -0.0046   |
| 6   | 3      | 4        | 6   | 2      | 5        | 7    | 7     | 5509.1941 | -0.0127   |
|     |        |          |     |        |          |      |       | 5509.7805 | 0.0056    |
| 5   | 2      | 4        | 5   | 1      | 5        | 4    | 4     | 5532.4577 | -0.0030   |
|     |        |          |     |        |          |      |       | 5532.6362 | 0.0018    |
|     |        |          |     |        |          |      |       | 5533.4979 | 0.0012    |
| 4   | 0      | 4        | 3   | 1      | 3        | 4    | 3     | 5561.8941 | 0.0109    |
|     |        |          |     |        |          |      |       | 5561.9540 | 0.0061    |
|     |        |          |     |        |          |      |       | 5561.9540 | 0.0061    |
| 4   | 1      | 4        | 3   | 0      | 3        | 4    | 4     | 5628.4051 | -0.0102   |
|     |        |          |     |        |          |      |       | 5628.9311 | -0.0008   |
|     |        |          |     |        |          |      |       | 5629.1934 | -0.0156   |
|     |        |          |     |        |          |      |       | 5629.1934 | -0.0156   |
| 2   | 2      | 0        | 1   | 1      | 1        | 1    | 0     | 5725.5661 | 0.0021    |
|     |        |          |     |        |          |      |       | 5727.3680 | 0.0013    |
|     |        |          |     |        |          |      |       | 5728.5257 | -0.0033   |
|     |        |          |     |        |          |      |       | 5728.5955 | -0.0004   |
| 4   | 1      | 3        | 3   | 2      | 2        | 3    | 2     | 6264.2657 | -0.0004   |
|     |        |          |     |        |          |      |       | 6264.2657 | -0.0004   |
|     |        |          |     |        |          |      |       | 6264.4214 | 0.0011    |
|     |        |          |     |        |          |      |       | 6265.0176 | -0.0008   |
|     |        |          |     |        |          |      |       | 6265.0176 | -0.0008   |
| 3   | 2      | 2        | 2   | 1      | 1        | 3    | 2     | 6296.0432 | 0.0014    |
|     |        |          |     |        |          |      |       | 6296.0432 | 0.0014    |
|     |        |          |     |        |          |      |       | 6297.3127 | 0.0005    |
|     |        |          |     |        |          |      |       | 6297.3127 | 0.0005    |
|     |        |          |     |        |          |      |       | 6298.0180 | -0.0005   |
| 7   | 2      | 5        | 7   | 1      | 6        | 6    | 6     | 6498.6583 | 0.0087    |
|     |        |          |     |        |          |      |       | 6498.7667 | 0.0058    |
|     |        |          |     |        |          |      |       | 6499.5263 | -0.0058   |
| 5   | 0      | 5        | 4   | 1      | 4        | 5    | 4     | 6828.9615 | 0.0012    |
|     |        |          |     |        |          |      |       | 6829.0694 | 0.0124    |
| 5   | 1      | 5        | 4   | 0      | 4        | 5    | 4     | 6845.3838 | 0.0041    |
|     |        |          |     |        |          |      |       | 6845.5170 | 0.0057    |
|     |        |          |     |        |          |      |       | 6845.5170 | 0.0057    |
| 4   | 2      | 3        | 3   | 1      | 2        | 4    | 3     | 7326.0986 | 0.0005    |
|     |        |          |     |        |          |      |       | 7327.1174 | 0.0008    |
|     |        |          |     |        |          |      |       | 7327.4838 | 0.0031    |
| 5   | 2      | 3        | 4   | 3      | 2        | 4    | 3     | 7731.4038 | 0.0044    |
|     |        |          |     |        |          |      |       | 7731.6292 | -0.0020   |
|     |        |          |     |        |          |      |       | 7732.7949 | -0.0019   |
Table S19 (Continued).

| J'  | K_{i1}' | K_{i2}' | J'' | K_{i1}'' | K_{i2}'' | F'  | F''  | Obs.     | Obs.-Cal. |
|-----|---------|---------|-----|----------|----------|-----|-------|----------|-----------|
| 5   | 1       | 4       | 4   | 2        | 3        | 4   | 3     | 7876.0538 | 0.0062    |
|     |         |         |     |          |          | 6   | 5     | 7876.0538 | 0.0062    |
|     |         |         |     |          |          | 5   | 4     | 7876.1138 | -0.0051   |
| 3   | 3       | 1       | 2   | 2        | 0        | 4   | 3     | 8129.7496 | 0.0011    |
|     |         |         |     |          |          | 2   | 1     | 8129.9951 | -0.0030   |
|     |         |         |     |          |          | 3   | 2     | 8129.0535 | -0.0062   |
Table S20. Observed rotational transitions and residuals (all the values in MHz) for the $^{13}$C$_3$ isotopologue of pentafluoropyridine molecule in the ground vibrational state. (see Table S13 for atom labelling).

| J' | K$_{1}'$ | K$_{1}''$ | J'' | K$_{1}''$ | F' | F'' | Obs.   | Obs.-Cal. |
|----|----------|-----------|------|-----------|----|------|--------|-----------|
| 2  | 1        | 2         | 1    | 0         | 1  |      | 3345.6039 | -0.0036   |
|    | 2        | 2         |      |           |    |      | 3346.1969 | -0.0004   |
|    | 1        | 1         |      |           |    |      | 3346.5936 | -0.0082   |
|    | 3        | 2         |      |           |    |      | 3346.8354 | -0.0003   |
|    | 1        | 0         |      |           |    |      | 3348.0742 | -0.0021   |
| 3  | 2        | 2         | 3    | 1         | 3  |      | 3368.1897 | -0.0066   |
|    | 4        | 4         |      |           |    |      | 3368.4323 | 0.0008    |
|    | 3        | 3         |      |           |    |      | 3369.1013 | -0.0015   |
| 4  | 1        | 3         | 4    | 0         | 4  |      | 4061.9855 | -0.0032   |
|    | 5        | 5         |      |           |    |      | 4062.3393 | 0.0014    |
|    | 4        | 4         |      |           |    |      | 4063.7027 | 0.0088    |
| 3  | 0        | 3         | 2    | 1         | 2  |      | 4235.2075 | -0.0003   |
|    | 4        | 3         |      |           |    |      | 4235.3826 | -0.0009   |
|    | 3        | 2         |      |           |    |      | 4235.5086 | 0.0000    |
| 3  | 1        | 2         | 2    | 2         | 1  |      | 4335.6529 | -0.0197   |
|    | 4        | 3         |      |           |    |      | 4336.4127 | 0.0028    |
|    | 3        | 2         |      |           |    |      | 4338.1459 | 0.0023    |
| 4  | 2        | 3         | 4    | 1         | 4  |      | 4383.1148 | 0.0077    |
|    | 4        | 4         |      |           |    |      | 4383.9699 | -0.0020   |
| 3  | 1        | 3         | 2    | 0         | 2  |      | 4469.1710 | -0.0022   |
|    | 4        | 3         |      |           |    |      | 4469.8052 | 0.0000    |
|    | 2        | 1         |      |           |    |      | 4470.0190 | -0.0001   |
|    | 2        | 2         |      |           |    |      | 4470.0862 | 0.0057    |
| 5  | 3        | 3         | 5    | 2         | 4  |      | 4521.5258 | -0.0080   |
|    | 6        | 6         |      |           |    |      | 4521.5978 | 0.0024    |
|    | 5        | 4         |      |           |    |      | 4522.0129 | 0.0118    |
|    | 5        | 5         |      |           |    |      | 4522.0129 | 0.0118    |
| 6  | 4        | 3         | 6    | 3         | 4  |      | 4868.1816 | 0.0151    |
|    | 7        | 7         |      |           |    |      | 4868.1816 | 0.0151    |
|    | 6        | 6         |      |           |    |      | 4868.1816 | 0.0151    |
| 2  | 2        | 1         | 1    | 1         | 0  |      | 5063.6175 | -0.0007   |
|    | 2        | 2         |      |           |    |      | 5064.2130 | -0.0007   |
|    | 1        | 1         |      |           |    |      | 5064.6025 | 0.0003    |
|    | 3        | 2         |      |           |    |      | 5064.8448 | -0.0011   |
|    | 1        | 0         |      |           |    |      | 5066.0928 | 0.0012    |
| 6  | 4        | 3         | 6    | 2         | 5  |      | 5514.2254 | -0.0031   |
|    | 6        | 6         |      |           |    |      | 5514.7962 | 0.0005    |
| 5  | 2        | 4         | 5    | 1         | 5  |      | 5536.2350 | -0.0044   |
|    | 6        | 6         |      |           |    |      | 5536.4331 | -0.0017   |
| 4  | 0        | 4         | 3    | 1         | 3  |      | 5565.2331 | 0.0086    |
|    | 5        | 4         |      |           |    |      | 5565.2963 | -0.0071   |
Table S20 (Continued).

| J' | K_{i1}' | K_{i1}'' | J'' | K_{i1}''' | K_{i1}'''' | F' | F'' | Obs. | Obs.-Cal. |
|----|---------|---------|-----|-----------|-----------|----|-----|------|-----------|
| 4  | 1       | 4       | 3   | 0         | 3         | 4  | 3   | 5634.0043 | 0.0015    |
| 5  | 4       |         |     |           |           | 5  | 4   | 5634.2663 | -0.0159   |
| 3  | 2       |         |     |           |           | 3  | 2   | 5634.2663 | -0.0159   |
| 2  | 2       | 0       | 1   | 1         | 1         | 1  | 1   | 5733.4373 | -0.0025   |
| 3  | 2       |         |     |           |           | 3  | 2   | 5735.2425 | 0.0020    |
| 2  | 1       |         |     |           |           | 2  | 1   | 5736.4659 | 0.0003    |
| 4  | 1       | 3       | 3   | 2         | 2         | 3  | 2   | 6259.0601 | 0.0063    |
| 3  | 3       |         |     |           |           | 3  | 3   | 6259.0601 | 0.0063    |
| 5  | 4       |         |     |           |           | 5  | 4   | 6259.2102 | 0.0003    |
| 4  | 3       |         |     |           |           | 4  | 3   | 6259.8203 | 0.0049    |
| 4  | 4       |         |     |           |           | 4  | 4   | 6259.8203 | 0.0049    |
| 3  | 2       | 2       | 2   | 1         | 1         | 3  | 2   | 6307.4117 | 0.0005    |
| 2  | 2       |         |     |           |           | 2  | 2   | 6307.4117 | 0.0005    |
| 3  | 3       |         |     |           |           | 3  | 3   | 6308.6809 | -0.0007   |
| 4  | 3       |         |     |           |           | 4  | 3   | 6308.6809 | -0.0007   |
| 2  | 1       |         |     |           |           | 2  | 1   | 6309.3855 | -0.0024   |
| 5  | 0       | 5       | 4   | 1         | 4         | 5  | 4   | 6833.8083 | 0.0020    |
| 6  | 5       |         |     |           |           | 6  | 5   | 6833.9173 | 0.0144    |
| 5  | 1       | 5       | 4   | 0         | 4         | 5  | 4   | 6850.7887 | 0.0049    |
| 4  | 3       |         |     |           |           | 4  | 3   | 6850.9212 | 0.0048    |
| 6  | 5       |         |     |           |           | 6  | 5   | 6850.9212 | 0.0048    |
| 4  | 2       | 3       | 3   | 1         | 2         | 4  | 3   | 7338.3190 | 0.0001    |
| 5  | 4       |         |     |           |           | 5  | 4   | 7339.3393 | -0.0006   |
| 3  | 2       |         |     |           |           | 3  | 2   | 7339.7040 | -0.0011   |
| 3  | 3       | 1       | 2   | 2         | 0         | 4  | 3   | 8147.3185 | -0.0025   |
| 3  | 2       |         |     |           |           | 3  | 2   | 8146.6246 | -0.0108   |
| J' | K_{J'} | K_{J+1'} | J'' | K_{J''} | K_{J+1''} | F' | F'' | Obs.     | Obs.-Cal. |
|----|--------|----------|-----|---------|-----------|----|------|----------|-----------|
| 2  | 1      | 2        | 1   | 0       | 1         | 2  | 1    | 3341.7957 | -0.0028   |
|    | 3      | 2        |     |         |            |    | 3    | 3343.0229 | -0.0038   |
| 3  | 0      | 3        | 2   | 1       | 2         | 2  | 1    | 4242.0947 | 0.0091    |
|    | 4      | 3        |     |         |            |    | 3    | 4242.2660 | 0.0077    |
|    | 3      | 2        |     |         |            |    | 2    | 4242.3825 | 0.0070    |
| 3  | 1      | 3        | 2   | 0       | 2         | 3  | 2    | 4466.8207 | -0.0063   |
|    | 4      | 3        |     |         |            |    | 4    | 4467.4453 | -0.0063   |
|    | 3      | 1        |     |         |            | 2  | 1    | 4467.6545 | -0.0064   |
| 4  | 0      | 3        | 4   | 3       | 1         | 5  | 5    | 5098.9030 | -0.0044   |
|    | 4      | 3        |     |         |            | 4  | 2    | 5099.0737 | 0.0003    |
| 4  | 1      | 4        | 3   | 0       | 3         | 4  | 4    | 5569.6725 | 0.0140    |
|    | 5      | 4        |     |         |            | 4  | 5    | 5569.7347 | -0.0056   |
|    | 5      | 4        |     |         |            | 4  | 5    | 5634.7505 | -0.0066   |
| 3  | 2      | 2        | 2   | 1       | 1         | 3  | 2    | 6294.2833 | -0.0002   |
|    | 2      | 2        |     |         |            | 2  | 3    | 6294.2833 | -0.0002   |
|    | 3      | 3        |     |         |            | 3  | 3    | 6295.5548 | 0.0008    |
|    | 4      | 3        |     |         |            | 4  | 4    | 6295.5548 | 0.0008    |
|    | 2      | 3        |     |         |            | 2  | 1    | 6296.2571 | -0.0032   |
| 5  | 1      | 5        | 4   | 0       | 4         | 5  | 4    | 6853.1902 | 0.0000    |
|    | 4      | 3        |     |         |            | 4  | 3    | 6853.3184 | -0.0022   |
|    | 6      | 5        |     |         |            | 6  | 5    | 6853.3184 | -0.0022   |
| 4  | 2      | 3        | 3   | 1       | 2         | 4  | 3    | 7325.4767 | -0.0071   |
|    | 5      | 4        |     |         |            | 5  | 4    | 7326.4962 | -0.0025   |
|    | 3      | 2        |     |         |            | 3  | 2    | 7326.8642 | 0.0028    |
Table S22. Observed rotational transitions and residuals in increasing order of frequency (all the values in MHz) for pentafluoropyridine–formaldehyde adduct in the 0° (ν=0) and 0° (ν=1) torsion states.

| J’  | K’ | K’’ | J’’ | K’’ | ν | F’ | F’’ | Obs.   | Obs.-Cal. |
|-----|----|-----|-----|-----|---|----|-----|--------|-----------|
| 2   | 0  | 2   | 1   | 1   | 0 | 1  | 0   | 2406.9517 | -0.0144   |
| 3   | 2  | 2408.0715     | 0.0066  |
| 2   | 1  | 2408.7670     | 0.0039  |
| 1   | 1  | 2406.8766     | 0.0046  |
| 3   | 2  | 2407.9693     | -0.0013 |
| 2   | 1  | 2408.6606     | -0.0083 |
| 2   | 1  | 2408.5073     | 0.0029  |
| 3   | 2  | 2446.2717     | 0.0040  |
| 1   | 0  | 2447.2652     | 0.0137  |
| 1   | 2  | 2445.4466     | -0.0010 |
| 3   | 2  | 2446.2087     | -0.0023 |
| 1   | 0  | 2447.1968     | 0.0020  |
| 2   | 2  | 2893.8910     | -0.0080 |
| 3   | 2  | 2894.6879     | -0.0051 |
| 1   | 0  | 2895.2699     | -0.0158 |
| 2   | 2  | 3245.4512     | 0.0015  |
| 3   | 2  | 3245.3772     | 0.0069  |
| 1   | 3  | 3246.1758     | -0.0002 |
| 3   | 0  | 3537.4203     | 0.0023  |
| 2   | 3  | 3537.4203     | 0.0023  |
| 1   | 4  | 3537.3076     | 0.0024  |
| 3   | 2  | 3537.3076     | 0.0024  |
| 1   | 3  | 3541.8814     | 0.0000  |
| 2   | 1  | 3541.9328     | 0.0152  |
| 3   | 2  | 3541.7836     | 0.0081  |
| 1   | 4  | 3541.7836     | 0.0081  |
| 3   | 2  | 3541.6428     | -0.0006 |
| 2   | 3  | 3883.1054     | -0.0018 |
| 3   | 2  | 3883.5605     | -0.0026 |
| 2   | 1  | 3884.4901     | -0.0015 |
| 4   | 3  | 3882.9183     | -0.0006 |
| 3   | 2  | 3883.3741     | -0.0008 |
| 3   | 2  | 3884.3035     | -0.0001 |
| 3   | 2  | 4004.8519     | -0.0007 |
| 4   | 3  | 4005.6628     | 0.0045  |
| 2   | 1  | 4006.1034     | -0.0027 |
| 1   | 3  | 4004.7875     | -0.0028 |
| 4   | 3  | 4005.5935     | -0.0024 |
| 2   | 1  | 4006.0427     | -0.0011 |
| 3   | 3  | 4468.6124     | 0.0000  |
| 1   | 3  | 4469.3163     | 0.0015  |
| 2   | 1  | 4469.5741     | 0.0030  |

43
| $J'$ | $K_{i1}'$ | $K_{i1}''$ | $J''$ | $K_{i1}''$ | $v$ | $F'$ | $F''$ | Obs. | Obs.-Cal. |
|---|---|---|---|---|---|---|---|---|---|
| 3  | 3  | 1  | 2  | 2  | 0  | 1  | 3  | 2  | 4468.5914 | -0.0010 |
| 4  | 3  | 4  | 4  | 4  | 4  | 3  | 4  | 4  | 4469.2936 | -0.0011 |
| 2  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 4469.5496 | -0.0013 |
| 4  | 0  | 4  | 3  | 1  | 3  | 0  | 4  | 3  | 4650.2743 | 0.0000 |
| 3  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 4650.3032 | -0.0012 |
| 5  | 4  | 5  | 5  | 5  | 5  | 5  | 5  | 5  | 4650.3119 | -0.0003 |
| 1  | 4  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 4650.1290 | -0.0002 |
| 3  | 2  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 4650.1578 | -0.0015 |
| 5  | 4  | 5  | 5  | 5  | 5  | 5  | 5  | 5  | 4650.1671 | 0.0000 |
| 4  | 1  | 4  | 3  | 0  | 3  | 0  | 4  | 3  | 4650.6040 | 0.0002 |
| 3  | 2  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 4650.6433 | -0.0007 |
| 5  | 4  | 5  | 5  | 5  | 5  | 5  | 5  | 5  | 4650.6488 | -0.0002 |
| 1  | 4  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 4650.2811 | 0.0015 |
| 4  | 3  | 4  | 4  | 4  | 4  | 4  | 4  | 4  | 4650.4604 | 0.0008 |
| 3  | 2  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 4650.4970 | -0.0027 |
| 5  | 4  | 5  | 5  | 5  | 5  | 5  | 5  | 5  | 4650.5048 | 0.0000 |
| 3  | 3  | 0  | 2  | 2  | 0  | 2  | 2  | 2  | 4752.9403 | -0.0017 |
| 4  | 3  | 4  | 4  | 4  | 4  | 4  | 4  | 4  | 4753.2523 | -0.0010 |
| 3  | 2  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 4753.7705 | -0.0009 |
| 1  | 2  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 4752.8227 | -0.0019 |
| 4  | 3  | 4  | 4  | 4  | 4  | 4  | 4  | 4  | 4753.1349 | -0.0011 |
| 3  | 2  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 4753.6527 | -0.0010 |
| 4  | 1  | 3  | 3  | 2  | 2  | 0  | 3  | 2  | 5053.6385 | -0.0008 |
| 5  | 4  | 5  | 5  | 5  | 5  | 5  | 5  | 5  | 5053.6543 | 0.0014 |
| 4  | 3  | 4  | 4  | 4  | 4  | 4  | 4  | 4  | 5053.7024 | -0.0019 |
| 1  | 3  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 5053.4730 | -0.0003 |
| 5  | 4  | 5  | 5  | 5  | 5  | 5  | 5  | 5  | 5053.4861 | -0.0007 |
| 4  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 5053.5365 | -0.0019 |
| 4  | 2  | 3  | 3  | 1  | 2  | 0  | 4  | 3  | 5075.8434 | 0.0008 |
| 3  | 2  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 5076.2182 | 0.0049 |
| 1  | 4  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 5075.7176 | 0.0000 |
| 5  | 4  | 5  | 5  | 5  | 5  | 5  | 5  | 5  | 5075.9876 | -0.0028 |
| 3  | 2  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 5076.0820 | -0.0064 |
| 4  | 2  | 2  | 3  | 3  | 1  | 0  | 5  | 4  | 5321.0325 | -0.0018 |
| 4  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 5322.2301 | 0.0035 |
| 1  | 3  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 5320.3329 | -0.0037 |
| 5  | 4  | 5  | 5  | 5  | 5  | 5  | 5  | 5  | 5320.7033 | -0.0006 |
| 4  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 5321.8949 | -0.0015 |
| 4  | 3  | 2  | 3  | 2  | 1  | 0  | 4  | 3  | 5581.5699 | 0.0009 |
| 5  | 4  | 5  | 5  | 5  | 5  | 5  | 5  | 5  | 5582.3616 | -0.0018 |
| 3  | 2  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 5582.6477 | 0.0021 |
| 1  | 4  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 5581.5152 | -0.0016 |
| 5  | 4  | 5  | 5  | 5  | 5  | 5  | 5  | 5  | 5582.3177 | 0.0064 |
| 3  | 2  | 3  | 3  | 2  | 2  | 1  | 0  | 4  | 5582.5876 | -0.0058 |
Table S22 (Continued).

| J  | K_{i1} | J'' | K_{i1}'' | ν | F' | F'' | Obs.  | Obs.-Cal. |
|----|--------|-----|-----------|---|----|-----|-------|----------|
| 5  | 0      | 5   | 4         | 1 | 4  | 0   | 5    | 4       | 5761.3293 | 0.0013   |
|    |        |     |           |   |    |     | 6    | 5       | 5761.3568 | 0.0010   |
| 0  |        | 4   | 3         |   |    |     | 6    | 5       | 5761.1505 | 0.0031   |
| 1  |        | 5   | 4         |   |    |     | 6    | 5       | 5761.1769 | 0.0018   |
| 6  | 4      | 3   | 3         |   |    |     | 0    | 4       | 5761.3470 | -0.0020  |
| 5  | 1      | 5   | 4         | 0 | 4  | 0   | 5    | 4       | 5761.3470 | -0.0020  |
| 5  | 0      | 5   | 4         | 1 | 4  | 1   | 4    | 3       | 5761.1666 | -0.0018  |
| 5  | 1      | 5   | 4         | 0 | 4  | 1   | 5    | 4       | 5761.1666 | -0.0018  |
|    |        |     |           |   |    |     | 1    | 4       | 5761.3789 | 0.0046   |
| 4  | 4      | 1   | 3         | 3 | 0  | 0   | 4    | 4       | 6053.0397 | -0.0034  |
| 0  |        |     |           |   |    |     | 1    | 4       | 6053.0397 | -0.0034  |
| 0  |        |     |           |   |    |     | 0    | 4       | 6053.1515 | -0.0080  |
| 1  |        |     |           |   |    |     | 1    | 4       | 6053.1515 | -0.0080  |
| 0  |        |     |           |   |    |     | 0    | 5       | 6053.7314 | -0.0059  |
| 6  | 5      |     |           |   |    |     | 1    | 5       | 6053.7314 | -0.0059  |
| 0  | 3      | 2   | 3         |   |    |     | 0    | 3       | 6053.8682 | -0.0064  |
| 1  | 3      | 2   | 3         |   |    |     | 1    | 3       | 6053.8682 | -0.0064  |
| 4  | 4      | 0   | 3         | 3 | 0  | 0   | 4    | 3       | 6139.9469 | 0.0004   |
| 5  | 4      |     |           |   |    |     | 5    | 4       | 6140.1482 | -0.0008  |
| 3  | 2      |     |           |   |    |     | 3    | 2       | 6140.1897 | -0.0004  |
| 1  | 4      | 3   |           |   |    |     | 1    | 4       | 6139.8663 | 0.0006   |
| 5  | 4      |     |           |   |    |     | 5    | 4       | 6140.0677 | -0.0006  |
| 3  | 2      |     |           |   |    |     | 3    | 2       | 6140.1110 | 0.0016   |
| 5  | 1      | 4   | 4         | 2 | 3  | 0   | 5    | 4       | 6173.8002 | 0.0030   |
| 6  | 5      |     |           |   |    |     | 6    | 5       | 6173.8530 | -0.0028  |
| 4  | 3      |     |           |   |    |     | 4    | 3       | 6173.8530 | -0.0028  |
| 1  | 5      | 4   |           |   |    |     | 1    | 5       | 6173.6083 | -0.0034  |
| 6  | 5      |     |           |   |    |     | 6    | 5       | 6173.6680 | -0.0024  |
| 4  | 3      |     |           |   |    |     | 4    | 3       | 6173.6680 | -0.0024  |
| 5  | 2      | 4   | 4         | 1 | 3  | 0   | 5    | 4       | 6176.1382 | -0.0005  |
| 6  | 5      |     |           |   |    |     | 6    | 5       | 6176.2249 | 0.0000   |
| 4  | 3      |     |           |   |    |     | 4    | 3       | 6176.2445 | -0.0007  |
| 1  | 5      | 4   |           |   |    |     | 1    | 5       | 6175.9599 | 0.0000   |
| 6  | 5      |     |           |   |    |     | 6    | 5       | 6176.0460 | 0.0000   |
| 4  | 3      |     |           |   |    |     | 4    | 3       | 6176.0644 | -0.0019  |
| 4  | 4      | 1   | 3         | 3 | 1  | 0   | 3    | 2       | 6177.1275 | 0.0003   |
| 4  | 3      |     |           |   |    |     | 4    | 3       | 6177.1275 | 0.0003   |
| 5  | 4      |     |           |   |    |     | 5    | 4       | 6177.1745 | 0.0002   |
| 1  | 3      | 2   |           |   |    |     | 1    | 3       | 6177.0575 | 0.0008   |
| 4  | 3      |     |           |   |    |     | 4    | 3       | 6177.0575 | 0.0008   |
| 5  | 4      |     |           |   |    |     | 5    | 4       | 6177.1041 | 0.0003   |
Table S22 (Continued).

| $J$ | $K_{1}$ | $K_{a1}$ | $J''$ | $K_{1}'$ | $K_{a1}'$ | $v$ | $F'$ | $F''$ | Obs. | Obs.-Cal. |
|-----|--------|----------|-------|----------|----------|-----|-------|-------|------|----------|
| 4   | 4      | 0        | 3     | 3        | 1        | 0   | 5     | 4     | 6263.5757 | -0.0048 |
|     | 4      | 3        |       |          |          |     |       |       | 6263.9093 | -0.0009 |
|     | 3      | 2        |       |          |          |     |       |       | 6263.4379 | -0.0008 |
|     | 1      | 5        | 4     | 6263.4379 | -0.0008 |
|     | 4      | 3        |       |          |          |     |       |       | 6263.2885 | -0.0070 |
|     | 3      | 2        |       |          |          |     |       |       | 6263.7696 | 0.0000  |
| 5   | 2      | 3        | 4     | 3        | 2        | 0   | 6     | 5     | 6558.3171 | 0.0171  |
|     | 5      | 4        |       |          |          |     |       |       | 6558.4772 | 0.0051  |
|     | 1      | 4        | 3     | 6558.0183 | -0.0067 |
|     | 6      | 5        |       |          |          |     |       |       | 6558.0533 | -0.0047 |
|     | 5      | 4        |       |          |          |     |       |       | 6558.2302 | -0.0002 |
| 4   | 3      | 1        | 3     | 2        | 2        | 0   | 3     | 2     | 6566.3822 | -0.0014 |
|     | 5      | 4        |       |          |          |     |       |       | 6566.5907 | 0.0003  |
|     | 4      | 3        |       |          |          |     |       |       | 6567.3940 | 0.0005  |
|     | 1      | 3        | 2     | 6566.1133 | 0.0013  |
|     | 5      | 4        |       |          |          |     |       |       | 6566.3212 | 0.0026  |
|     | 4      | 3        |       |          |          |     |       |       | 6567.1231 | 0.0015  |
| 5   | 3      | 3        | 4     | 2        | 2        | 0   | 4     | 3     | 6625.2888 | -0.0027 |
|     | 6      | 5        |       |          |          |     |       |       | 6625.1684 | -0.0073 |
|     | 1      | 4        | 3     | 6625.1684 | -0.0073 |
|     | 5      | 4        |       |          |          |     |       |       | 6624.6440 | -0.0064 |
|     | 6      | 5        |       |          |          |     |       |       | 6625.0571 | -0.0007 |
| 5   | 3      | 2        | 4     | 4        | 1        | 0   | 4     | 3     | 6711.6507 | -0.0002 |
|     | 6      | 5        |       |          |          |     |       |       | 6711.9805 | 0.0018  |
|     | 5      | 4        |       |          |          |     |       |       | 6713.4039 | -0.0001 |
|     | 1      | 4        | 3     | 6711.1237 | -0.0009 |
|     | 6      | 5        |       |          |          |     |       |       | 6711.4517 | -0.0008 |
|     | 5      | 4        |       |          |          |     |       |       | 6712.8751 | -0.0031 |
| 6   | 0      | 6        | 5     | 1        | 5        | 0   | 7     | 6     | 6872.2508 | 0.0006  |
|     | 6      | 5        |       |          |          |     |       |       | 6872.2309 | 0.0002  |
| 6   | 1      | 6        | 5     | 0        | 5        | 0   | 6     | 5     | 6872.2309 | 0.0002  |
| 6   | 0      | 6        | 5     | 1        | 5        | 0   | 5     | 4     | 6872.2444 | -0.0009 |
| 6   | 1      | 6        | 5     | 0        | 5        | 0   | 5     | 4     | 6872.2444 | -0.0009 |
| 6   | 0      | 6        | 5     | 1        | 5        | 1   | 6     | 5     | 6872.0145 | 0.0004  |
| 6   | 1      | 6        | 5     | 0        | 5        | 1   | 6     | 5     | 6872.0145 | 0.0004  |
| 6   | 0      | 6        | 5     | 1        | 5        | 4   | 6     | 5     | 6872.0269 | -0.0018 |
| 6   | 1      | 6        | 5     | 0        | 5        | 1   | 5     | 4     | 6872.0269 | -0.0018 |
| 6   | 0      | 6        | 5     | 1        | 5        | 1   | 7     | 6     | 6872.0346 | 0.0004  |
| 6   | 1      | 6        | 5     | 0        | 5        | 1   | 7     | 6     | 6872.0346 | 0.0004  |
|     | 0      | 7        | 6     | 6872.2524 | 0.0010  |
| 5   | 4      | 2        | 5     | 3        | 1        | 0   | 5     | 4     | 7174.5688 | 0.0000  |
|     | 6      | 5        |       |          |          |     |       |       | 7175.3362 | -0.0010 |
|     | 4      | 3        |       |          |          |     |       |       | 7175.5360 | -0.0006 |
Table S22 (Continued).

| J' | K_{i1}' | K_{i2}' | J'' | K_{i1}'' | K_{i2}'' | ν  | F'  | F'' | Obs.  | Obs.-Cal. |
|----|---------|---------|-----|-----------|-----------|----|-----|-----|-------|-----------|
| 5  | 4       | 2       | 4   | 3         | 1         | 1  | 5   | 4   | 7174.5409 | 0.0008    |
| 6  | 5       | 7175.3082 | | 4         | 3         | 7175.5074 | | -0.0004 |       |           |
| 6  | 1       | 5       | 5   | 2         | 4         | 0  | 6   | 5   | 7285.4906 | -0.0062   |
| 7  | 6       | 7285.5442 | | 5         | 4         | 7285.5546 | | 0.0026  |       |           |
| 1  | 6       | 5       | 7285.2773 | | 7         | 6         | 7285.3249 | | -0.0012 |       |           |
| 6  | 2       | 5       | 5   | 1         | 4         | 0  | 6   | 5   | 7285.6858 | 0.0001    |
| 7  | 6       | 7285.7368 | | 5         | 4         | 7285.7448 | | 0.0012  |       |           |
| 1  | 6       | 5       | 7285.4674 | | 7         | 6         | 7285.5188 | | 0.0008  |       |           |
| 5  | 4       | 7285.5266 | | 0         | 6         | 5       | 0   | 0   | 7640.8695 | -0.0072   |
| 5  | 5       | 1       | 4   | 4         | 0         | 0  | 4   | 3   | 7640.3647 | -0.0042   |
| 1  | 5       | 4       | 7640.3647 | | 0         | 6         | 5       | 0   | 0   | 7640.8018 | 0.0006    |
| 1  | 6       | 5       | 7640.8018 | | 4         | 3         | 7640.8018 | | 0.0006  |       |           |
| 6  | 2       | 4       | 5   | 5         | 3         | 3  | 0   | 6   | 7695.8842 | -0.0003   |
| 7  | 6       | 7695.6935 | | 5         | 4         | 7695.9369 | | 0.0011  |       |           |
| 1  | 6       | 5       | 7695.6542 | | 7         | 6         | 7695.7068 | | 0.0014  |       |           |
| 5  | 5       | 0       | 4   | 4         | 0         | 0  | 5   | 4   | 7696.1260 | 0.0008    |
| 6  | 5       | 7696.3203 | | 4         | 3         | 7696.3415 | | -0.0015 |       |           |
| 1  | 5       | 4       | 7696.0502 | | 6         | 5       | 7696.2454 | | 0.0001  |       |           |
| 4  | 3       | 7696.2668 | | 0         | 6         | 5       | 0   | 0   | 7705.3081 | 0.0031    |
| 6  | 3       | 4       | 5   | 2         | 3         | 0  | 6   | 5   | 7705.4316 | -0.0001   |
| 5  | 4       | 7705.4605 | | 1         | 6         | 5       | 0   | 0   | 7705.1013 | 0.0009    |
| 5  | 5       | 1       | 4   | 4         | 1         | 0  | 5   | 4   | 7727.1578 | 0.0027    |
| 4  | 3       | 7727.1875 | | 6         | 5       | 7727.2123 | | 0.0000  |       |           |
| 1  | 5       | 4       | 7727.0764 | | 4         | 3       | 7727.1058 | | -0.0016 |       |           |
| 6  | 5       | 7727.1325 | | 0         | 6         | 5       | 0   | 0   | 7727.1325 | -0.0005   |
| $J'$ | $K_{1}'$ | $K_{3}'$ | $J''$ | $K_{1}''$ | $K_{3}''$ | $\nu$ | $F'$ | $F''$ | Obs.     | Obs.-Cal. |
|------|----------|----------|-------|----------|----------|------|-----|-------|----------|-----------|
| 7    | 0        | 7        | 6     | 1        | 6        | 0    | 7   | 6    | 7983.1007 | -0.0021   |
| 7    | 1        | 7        | 6     | 0        | 6        | 0    | 7   | 6    | 7983.1007 | -0.0021   |
| 7    | 0        | 7        | 6     | 1        | 6        | 0    | 6   | 5    | 7983.1132 | -0.0003   |
| 7    | 1        | 7        | 6     | 0        | 6        | 0    | 6   | 5    | 7983.1132 | -0.0003   |
| 7    | 0        | 7        | 6     | 1        | 6        | 0    | 8   | 7    | 7983.1185 | 0.0004    |
| 7    | 1        | 7        | 6     | 0        | 6        | 0    | 8   | 7    | 7983.1185 | 0.0004    |
| 7    | 0        | 7        | 6     | 1        | 6        | 1    | 7   | 6    | 7982.8492 | -0.0011   |
| 7    | 1        | 7        | 6     | 0        | 6        | 1    | 7   | 6    | 7982.8492 | -0.0011   |
| 7    | 0        | 7        | 6     | 1        | 6        | 1    | 6   | 5    | 7982.8609 | -0.0002   |
| 7    | 1        | 7        | 6     | 0        | 6        | 1    | 6   | 5    | 7982.8609 | -0.0002   |
| 7    | 0        | 7        | 6     | 1        | 6        | 1    | 8   | 7    | 7982.8668 | 0.0012    |
| 7    | 1        | 7        | 6     | 0        | 6        | 1    | 8   | 7    | 7982.8668 | 0.0012    |
| 7    | 1        | 6        | 6     | 2        | 5        | 0    | 7   | 6    | 8396.3311 | -0.0045   |
|      |          |          |       |           |          |      |     |       | 8396.3745 | 0.0002    |
|      |          |          |       |           |          |      |     |       | 8396.3745 | 0.0002    |
|      |          |          |       |           |          |      |     |       | 8396.0780 | -0.0030   |
|      |          |          |       |           |          |      |     |       | 8396.1201 | 0.0004    |
|      |          |          |       |           |          |      |     |       | 8396.1201 | 0.0004    |
| 7    | 2        | 6        | 6     | 1        | 5        | 0    | 7   | 6    | 8396.3469 | -0.0017   |
|      |          |          |       |           |          |      |     |       | 8396.3921 | 0.0047    |
|      |          |          |       |           |          |      |     |       | 8396.0947 | 0.0005    |
|      |          |          |       |           |          |      |     |       | 8396.1378 | 0.0049    |
|      |          |          |       |           |          |      |     |       | 8396.1378 | 0.0049    |
| 8    | 0        | 8        | 7     | 1        | 7        | 0    | 8   | 7    | 9093.9473 | -0.0017   |
| 8    | 1        | 8        | 7     | 0        | 7        | 0    | 8   | 7    | 9093.9473 | -0.0017   |
| 8    | 0        | 8        | 7     | 1        | 7        | 0    | 7   | 6    | 9093.9567 | -0.0004   |
| 8    | 1        | 8        | 7     | 0        | 7        | 0    | 7   | 6    | 9093.9567 | -0.0004   |
| 8    | 0        | 8        | 7     | 1        | 7        | 0    | 9   | 8    | 9093.9613 | 0.0004    |
| 8    | 1        | 8        | 7     | 0        | 7        | 0    | 9   | 8    | 9093.9613 | 0.0004    |
| 8    | 0        | 8        | 7     | 1        | 7        | 1    | 8   | 7    | 9093.6601 | -0.0005   |
| 8    | 1        | 8        | 7     | 0        | 7        | 1    | 8   | 7    | 9093.6601 | -0.0005   |
| 8    | 0        | 8        | 7     | 1        | 7        | 1    | 6   | 5    | 9093.6690 | 0.0002    |
| 8    | 1        | 8        | 7     | 0        | 7        | 1    | 6   | 5    | 9093.6690 | 0.0002    |
| 8    | 0        | 8        | 7     | 1        | 7        | 1    | 9   | 8    | 9093.6735 | 0.0010    |
| 8    | 1        | 8        | 7     | 0        | 7        | 1    | 9   | 8    | 9093.6735 | 0.0010    |
| 6    | 4        | 2        | 5     | 3        | 3        | 0    | 5   | 4    | 10010.3151| 0.0000    |
|      |          |          |       |           |           |      |     |       | 10010.4305| -0.0005   |
|      |          |          |       |           |           |      |     |       | 10011.1450| -0.0009   |
|      |          |          |       |           |           |      |     |       | 10009.8470| 0.0000    |
|      |          |          |       |           |           |      |     |       | 10009.9639| 0.0009    |
|      |          |          |       |           |           |      |     |       | 10010.6789| 0.0009    |
Table S23. Observed rotational transitions and residuals (all the values in MHz) for the $^{15}\text{N}_1$ isotopologue of pentafluoropyridine·formaldehyde adduct in the $0^+$ ($\nu=0$) and $0^-$ ($\nu=1$) torsion states. (see Table S15 for atom labelling).

| $J'$ | $K_{1}'$ | $K_{1}''$ | $J''$ | $K_{1}''$ | Residual | \(v\) | Obs. | Obs.-Cal. |
|-----|---------|---------|------|---------|----------|-----|------|----------|
| 5   | 0       | 5       | 4    | 1       | 4        | 1   | 5752.9050 | -0.0007  |
| 5   | 1       | 5       | 4    | 0       | 4        | 1   | 5752.9218 | -0.0019  |
| 5   | 0       | 5       | 4    | 1       | 4        | 0   | 5753.0504 | 0.0006   |
| 5   | 1       | 5       | 4    | 0       | 4        | 0   | 5753.0699 | 0.0017   |
| 6   | 0       | 6       | 5    | 1       | 5        | 1   | 6862.3865 | -0.0003  |
| 6   | 1       | 6       | 5    | 0       | 5        | 1   | 6862.3865 | -0.0003  |
| 7   | 0       | 7       | 6    | 1       | 6        | 1   | 7971.8407 | 0.0003   |
| 7   | 1       | 7       | 6    | 0       | 6        | 1   | 7971.8407 | 0.0003   |
| 7   | 0       | 7       | 6    | 1       | 6        | 0   | 7972.0911 | -0.0072  |
| 7   | 1       | 7       | 6    | 0       | 6        | 0   | 7972.0911 | -0.0072  |
| 7   | 1       | 6       | 6    | 2       | 5        | 1   | 8382.3612 | 0.0003   |
| 7   | 2       | 6       | 6    | 1       | 5        | 1   | 8382.3719 | 0.0002   |
| 6   | 2       | 4       | 5    | 3       | 3        | 1   | 7680.9958 | 0.0000   |
| 6   | 3       | 4       | 5    | 2       | 3        | 1   | 7689.3851 | 0.0000   |
| 8   | 0       | 8       | 7    | 1       | 7        | 1   | 9081.2700 | 0.0012   |
| 8   | 1       | 8       | 7    | 0       | 7        | 1   | 9081.2700 | 0.0012   |
| 8   | 0       | 8       | 7    | 1       | 7        | 0   | 9081.5886 | 0.0048   |
| 8   | 1       | 8       | 7    | 0       | 7        | 0   | 9081.5886 | 0.0048   |
Table S24. Observed rotational transitions and residuals (all the values in MHz) for the $^{13}$C$_2$ isotopologue of pentafluoropyridine::formaldehyde adduct in the $0^+$ ($\nu=0$) and $0^-$ ($\nu=1$) torsion states. (see Table S15 for atom labelling).

| J' | K'$_1$ | K'$_2$ | J'' | K''$_1$ | K''$_2$ | v | F' | F'' | Obs.       | Obs.-Cal. |
|----|--------|--------|-----|--------|---------|---|----|-----|------------|------------|
| 5  | 0      | 5      | 4   | 1      | 4       | 1 | 5  | 4   | 5749.2863  | 0.0009     |
| 6  | 5      | 5749.3104 |    | -0.0028 |
| 4  | 3      | 5749.3059 |    | -0.0020 |
| 5  | 1      | 5      | 4   | 0      | 4       | 1 | 5  | 4   | 5749.3059  | 0.0011     |
| 6  | 5      | 5749.3356 |    | 0.0011  |
| 4  | 3      | 5749.3356 |    | 0.0011  |
| 5  | 2      | 3      | 4   | 3      | 2       | 0 | 4  | 3   | 6544.6213  | -0.0002    |
| 6  | 5      | 6544.6542 |    | -0.0019 |
| 5  | 4      | 6544.8389 |    | 0.0028  |
| 1  | 4      | 6544.3828 |    | 0.0028  |
| 6  | 5      | 6544.4133 |    | -0.0013 |
| 5  | 4      | 6544.5941 |    | -0.0007 |
| 6  | 0      | 6      | 5   | 1      | 5       | 0 | 6  | 5   | 6857.9904  | -0.0009     |
| 6  | 1      | 6     | 5   | 0      | 5       | 0 | 6  | 5   | 6857.9904  | -0.0009     |
| 6  | 0      | 6     | 5   | 1      | 5       | 0 | 5  | 4   | 6858.0066  | 0.0005      |
| 6  | 1      | 6     | 5   | 0      | 5       | 0 | 5  | 4   | 6858.0066  | 0.0005      |
| 6  | 0      | 6     | 5   | 1      | 5       | 0 | 7  | 6   | 6858.0129  | 0.0014      |
| 6  | 1      | 6     | 5   | 0      | 5       | 0 | 7  | 6   | 6858.0129  | 0.0014      |
| 6  | 0      | 6     | 5   | 1      | 5       | 1 | 6  | 5   | 6857.7747  | -0.0014     |
| 6  | 1      | 6     | 5   | 0      | 5       | 1 | 6  | 5   | 6857.7747  | -0.0014     |
| 6  | 0      | 6     | 5   | 1      | 5       | 1 | 5  | 4   | 6857.7896  | -0.0012     |
| 6  | 1      | 6     | 5   | 0      | 5       | 1 | 5  | 4   | 6857.7896  | -0.0012     |
| 6  | 0      | 6     | 5   | 1      | 5       | 1 | 7  | 6   | 6857.7956  | -0.0007     |
| 6  | 1      | 6     | 5   | 0      | 5       | 1 | 7  | 6   | 6857.7956  | -0.0007     |
| 6  | 1      | 5     | 5   | 2      | 4       | 0 | 6  | 5   | 7271.3040  | -0.0001     |
|    | 7      | 6     | 7271.3040 | 0.0074 |
|    | 5      | 4     | 7271.3665 | 0.0068 |
|    | 1      | 6     | 7271.0836 | -0.0017 |
|    | 7      | 6     | 7271.1336 | -0.0001 |
|    | 5      | 4     | 7271.1426 | 0.0017  |
| 6  | 2      | 5     | 5   | 1      | 4       | 0 | 6  | 5   | 7271.5155  | -0.0008     |
|    | 7      | 6     | 7271.5155 | -0.0008 |
|    | 5      | 4     | 7271.5648 | -0.0025 |
|    | 1      | 6     | 7271.2963 | -0.0020 |
|    | 7      | 6     | 7271.3481 | -0.0012 |
|    | 5      | 4     | 7271.3584 | 0.0014  |
| 6  | 2      | 4     | 5   | 3      | 3       | 0 | 6  | 5   | 7681.4267  | -0.0028     |
|    | 7      | 6     | 7681.4267 | -0.0028 |
|    | 5      | 4     | 7681.4667 | -0.0011 |
|    | 1      | 6     | 7681.1942 | -0.0037 |
|    | 7      | 6     | 7681.2355 | -0.0007 |
|    | 5      | 4     | 7681.2480 | 0.0005  |
| $J'$ | $K_{1}'$ | $K_{01}'$ | $J''$ | $K_{1}''$ | $K_{01}''$ | v | $F'$ | $F''$ | Obs. | Obs.-Cal. |
|------|---------|----------|------|----------|----------|---|------|------|------|-----------|
| 7    | 0       | 7        | 6    | 1        | 6        | 0 | 7    | 6    | 7966.4860 | -0.0002   |
| 7    | 1       | 7        | 6    | 0        | 6        | 0 | 7    | 6    | 7966.4860 | -0.0002   |
| 7    | 0       | 7        | 6    | 1        | 6        | 0 | 6    | 5    | 7966.4954 | -0.0015   |
| 7    | 1       | 7        | 6    | 0        | 6        | 0 | 6    | 5    | 7966.4954 | -0.0015   |
| 7    | 0       | 7        | 6    | 1        | 6        | 0 | 8    | 7    | 7966.5000 | -0.0015   |
| 7    | 1       | 7        | 6    | 0        | 6        | 0 | 8    | 7    | 7966.5000 | -0.0015   |
| 7    | 0       | 7        | 6    | 1        | 6        | 1 | 7    | 6    | 7966.2358 | 0.0005    |
| 7    | 1       | 7        | 6    | 0        | 6        | 1 | 7    | 6    | 7966.2358 | 0.0005    |
| 7    | 0       | 7        | 6    | 1        | 6        | 1 | 6    | 5    | 7966.2444 | -0.0017   |
| 7    | 1       | 7        | 6    | 0        | 6        | 1 | 6    | 5    | 7966.2444 | -0.0017   |
| 7    | 0       | 7        | 6    | 1        | 6        | 1 | 8    | 7    | 7966.2517 | 0.0011    |
| 7    | 1       | 7        | 6    | 0        | 6        | 1 | 8    | 7    | 7966.2517 | 0.0011    |
| 7    | 1       | 6        | 6    | 2        | 5        | 0 | 7    | 6    | 8379.7700 | -0.0003   |
|       | 6        | 5        | 8379.8072 | -0.0020   | 8    | 7    | 8379.8072 | -0.0020   |
|       | 1        | 7        | 6    | 8379.5202 | 0.0041   |
|       | 6        | 5        | 8379.5536 | -0.0014   | 8    | 7    | 8379.5536 | -0.0014   |
| 7    | 2       | 6        | 6    | 1        | 5        | 0 | 7    | 6    | 8379.7831 | -0.0023   |
|       | 6        | 5        | 8379.8269 | 0.0023    | 8    | 7    | 8379.8269 | 0.0023    |
|       | 1        | 7        | 6    | 8379.5345 | 0.0032   |
|       | 6        | 5        | 8379.5752 | 0.0028    | 8    | 7    | 8379.5697 | 0.0007    |
Table S25. Observed rotational transitions and residuals (all the values in MHz) for the $^{13}$C$_3$ isotopologue of pentafluoropyridine--formaldehyde adduct in the 0$^+$ (v=0) and 0$^-$ (v=1) torsion states. (see Table S15 for atom labelling).

| $J'$ | $K_1'$ | $K_2'$ | $J''$ | $K_1''$ | $K_2''$ | $v$ | $F'$ | $F''$ | Obs.   | Obs.-Cal. |
|------|--------|--------|-------|---------|---------|-----|------|-------|--------|-----------|
| 5    | 0      | 5      | 4     | 1       | 4       | 1   | 5    | 4     | 5751.5082| 0.0023    |
|      | 4      | 3      |       |         |         |     |      | 4     | 5751.5267| -0.0006   |
|      | 6      | 5      |       |         |         |     |      | 6     | 5751.5336| 0.0000    |
|      | 0      | 5      | 4     |         |         |     |      | 0     | 5751.6897| -0.0014   |
|      | 6      | 5      |       |         |         |     |      | 6     | 5751.7179| -0.0010   |
|      | 4      | 3      |       |         |         |     |      | 4     | 5751.7142| 0.0003    |
| 5    | 1      | 5      | 4     | 0       | 4       | 0   | 5    | 4     | 5751.7142| 0.0003    |
|      | 4      | 3      |       |         |         |     |      | 4     | 5751.7390| 0.0021    |
|      | 6      | 5      |       |         |         |     |      | 6     | 5751.7427| -0.0004   |
|      | 1      | 5      | 4     |         |         |     |      | 1     | 5751.5295| -0.0002   |
|      | 4      | 3      |       |         |         |     |      | 4     | 5751.5513| -0.0005   |
|      | 6      | 5      |       |         |         |     |      | 6     | 5751.5589| 0.0008    |
| 5    | 2      | 3      | 4     | 3       | 2       | 1   | 4    | 3     | 6543.4063| -0.0008   |
|      | 6      | 5      |       |         |         |     |      | 6     | 6543.4407| -0.0013   |
|      | 5      | 4      |       |         |         |     |      | 5     | 6543.6259| 0.0019    |
| 6    | 0      | 6      | 5     | 1       | 5       | 0   | 6    | 5     | 6860.7982| -0.0041   |
| 6    | 1      | 6      | 5     | 0       | 5       | 0   | 6    | 5     | 6860.7982| -0.0041   |
| 6    | 0      | 6      | 5     | 1       | 5       | 0   | 5    | 4     | 6860.8142| -0.0030   |
| 6    | 1      | 6      | 5     | 0       | 5       | 0   | 5    | 4     | 6860.8142| -0.0030   |
| 6    | 0      | 6      | 5     | 1       | 5       | 0   | 7    | 6     | 6860.8220| -0.0006   |
| 6    | 1      | 6      | 5     | 0       | 5       | 0   | 7    | 6     | 6860.8220| -0.0006   |
| 6    | 0      | 6      | 5     | 1       | 5       | 1   | 6    | 5     | 6860.5855| 0.0004    |
| 6    | 1      | 6      | 5     | 0       | 5       | 1   | 6    | 5     | 6860.5855| 0.0004    |
| 6    | 0      | 6      | 5     | 1       | 5       | 1   | 5    | 4     | 6860.5980| -0.0019   |
| 6    | 1      | 6      | 5     | 0       | 5       | 1   | 5    | 4     | 6860.5980| -0.0019   |
| 6    | 0      | 6      | 5     | 1       | 5       | 1   | 7    | 6     | 6860.6065| 0.0011    |
| 6    | 1      | 6      | 5     | 0       | 5       | 1   | 7    | 6     | 6860.6065| 0.0011    |
| 6    | 1      | 5      | 5     | 2       | 4       | 1   | 6    | 5     | 7272.4491| -0.0020   |
|      | 7      | 6      |       |         |         |     |      | 7     | 7272.4991| -0.0006   |
|      | 5      | 4      |       |         |         |     |      | 5     | 7272.5071| 0.0003    |
| 6    | 2      | 5      | 5     | 1       | 4       | 1   | 6    | 5     | 7272.6676| -0.0011   |
|      | 7      | 6      |       |         |         |     |      | 7     | 7272.7165| -0.0033   |
|      | 5      | 4      |       |         |         |     |      | 5     | 7272.7310| 0.0035    |
| 6    | 2      | 4      | 5     | 3       | 3       | 1   | 6    | 5     | 7681.0606| -0.0013   |
|      | 7      | 6      |       |         |         |     |      | 7     | 7681.1002| 0.0003    |
|      | 5      | 4      |       |         |         |     |      | 5     | 7681.1139| 0.0027    |
| 7    | 0      | 7      | 6     | 1       | 6       | 0   | 7    | 6     | 7969.8857| 0.0037    |
| 7    | 1      | 7      | 6     | 0       | 6       | 0   | 7    | 6     | 7969.8857| 0.0037    |
| 7    | 0      | 7      | 6     | 1       | 6       | 0   | 6    | 5     | 7969.8925| -0.0004   |
| 7    | 1      | 7      | 6     | 0       | 6       | 0   | 6    | 5     | 7969.8925| -0.0004   |
| 7    | 0      | 7      | 6     | 1       | 6       | 0   | 8    | 7     | 7969.9003| 0.0030    |
| 7    | 1      | 7      | 6     | 0       | 6       | 0   | 8    | 7     | 7969.9003| 0.0030    |
Table S25 (Continued).

| J'  | K_{1'} | K_{1''} | J'' | K_{1''} | v | F'   | F''   | Obs.      | Obs.-Cal. |
|-----|--------|---------|-----|---------|---|------|-------|-----------|-----------|
| 7   | 0      | 7       | 6   | 1       | 6 | 1    | 7     | 6         | 7969.6321 | -0.0006   |
| 7   | 1      | 7       | 6   | 0       | 6 | 1    | 7     | 6         | 7969.6321 | -0.0006   |
| 7   | 0      | 7       | 6   | 1       | 6 | 1    | 6     | 5         | 7969.6427 | -0.0008   |
| 7   | 1      | 7       | 6   | 0       | 6 | 1    | 6     | 5         | 7969.6427 | -0.0008   |
| 7   | 0      | 7       | 6   | 1       | 6 | 1    | 8     | 7         | 7969.6498 | 0.0018    |
| 7   | 1      | 7       | 6   | 0       | 6 | 1    | 8     | 7         | 7969.6498 | 0.0018    |
| 7   | 1      | 6       | 6   | 2       | 5 | 0    | 7     | 6         | 8381.7735 | 0.0029    |
|     |        |         |     |          |   |      | 8     | 7         | 8381.8057 | -0.0023   |
|     |        |         |     |          |   |      | 6     | 5         | 8381.8116 | 0.0000    |
| 1   | 7      | 6       | 8   | 3       | 8 | 7    | 3     | 8         | 8381.4710 | -0.0004   |
|     | 6       | 5       |     |          |   |      | 8     | 7         | 8381.5071 | -0.0019   |
| 6   | 5       | 8381.5100 |     |          |   |      | 6     | 5         | 8381.5100 | -0.0023   |
| 1   | 2      | 6       | 6   | 1       | 5 | 0    | 7     | 6         | 8381.7833 | -0.0027   |
|     | 2       | 6       |     |          |   |      | 6     | 5         | 8381.8279 | 0.0028    |
|     | 8       | 7       |     |          |   |      | 8     | 7         | 8381.8279 | 0.0028    |
|     | 1       | 7       |     |          |   |      | 8     | 7         | 8381.4867 | -0.0003   |
|     | 6       | 5       |     |          |   |      | 8     | 7         | 8381.5266 | 0.0018    |
|     |         |         |     |          |   |      | 6     | 5         | 8381.5317 | 0.0034    |
Table S26. Observed rotational transitions and residuals (all the values in MHz) for the $^{13}$C$_4$ isotopologue of pentafluoropyridine···formaldehyde adduct in the $0^+$ (ν=0) and $0^-$ (ν=1) torsion states. (see Table S15 for atom labelling).

| $J'$ | $K_{t1}'$ | $K_{t1}''$ | $J''$ | $K_{t1}''$ | $K_{t1}''$ | ν | F' | F'' | Obs.  | Obs.-Cal. |
|------|-----------|-------------|------|-------------|-------------|---|----|------|------|---------|
| 5    | 2         | 3           | 4    | 3           | 2           | 1 | 4  | 3    | 6551.2377 | -0.0025 |
| 6    | 0         | 6           | 5    | 1           | 5           | 0  | 6  | 5    | 6551.2731 | 0.0036  |
|      | 5         | 4           |      |             |             |    |    |      | 6551.4253 | 0.0009  |
| 6    | 0         | 6           | 5    | 1           | 5           | 0  | 5  | 4    | 6859.0804 | -0.0017 |
| 6    | 0         | 6           | 5    | 0           | 5           | 0  | 5  | 4    | 6859.0804 | -0.0017 |
| 6    | 0         | 6           | 5    | 1           | 5           | 0  | 6  | 5    | 6859.0893 | 0.0017  |
| 6    | 0         | 6           | 5    | 0           | 5           | 0  | 7  | 6    | 6859.0893 | 0.0017  |
| 6    | 0         | 6           | 5    | 1           | 5           | 0  | 7  | 6    | 6859.0893 | 0.0017  |
| 6    | 0         | 6           | 5    | 0           | 5           | 0  | 7  | 6    | 7272.1935 | -0.0015 |
| 6    | 0         | 6           | 5    | 1           | 5           | 1  | 6  | 5    | 7272.2427 | 0.0002  |
| 6    | 0         | 6           | 5    | 0           | 5           | 1  | 6  | 5    | 7272.2526 | 0.0034  |
| 6    | 2         | 5           | 5    | 1           | 4           | 1  | 6  | 5    | 7272.3409 | 0.0023  |
| 6    | 2         | 4           | 5    | 3           | 3           | 1  | 6  | 5    | 7683.2742 | -0.0043 |
| 7    | 7         | 6           | 1    | 6           | 0           | 7  | 6  | 7967.7389 | -0.0019 |
| 7    | 1         | 7           | 6    | 0           | 6           | 0  | 7  | 6    | 7967.7389 | -0.0019 |
| 7    | 0         | 7           | 6    | 1           | 6           | 0  | 6  | 5    | 7967.7519 | -0.0019 |
| 7    | 1         | 7           | 6    | 0           | 6           | 0  | 6  | 5    | 7967.7519 | 0.0007  |
| 7    | 0         | 7           | 6    | 1           | 6           | 0  | 8  | 7    | 7967.7577 | 0.0007  |
| 7    | 1         | 7           | 6    | 0           | 6           | 0  | 8  | 7    | 7967.7577 | 0.0019  |
| 7    | 0         | 7           | 6    | 1           | 6           | 1  | 7  | 6    | 7967.4878 | 0.0019  |
| 7    | 1         | 7           | 6    | 0           | 6           | 1  | 7  | 6    | 7967.4878 | -0.0008 |
| 7    | 0         | 7           | 6    | 1           | 6           | 1  | 6  | 5    | 7967.4971 | -0.0008 |
| 7    | 1         | 7           | 6    | 0           | 6           | 1  | 6  | 5    | 7967.4971 | -0.0020 |
| 7    | 0         | 7           | 6    | 1           | 6           | 1  | 8  | 7    | 7967.5042 | -0.0020 |
| 7    | 1         | 7           | 6    | 0           | 6           | 1  | 8  | 7    | 7967.5042 | 0.0005  |
| 7    | 1         | 6           | 6    | 2           | 5           | 0  | 7  | 6    | 8380.7912 | 0.0013  |
|      | 6         | 5           |      |             |             |    |    |      | 8380.8349 | 0.0041  |
|      | 6         | 5           |      |             |             |    |    |      | 8380.8427 | 0.0036  |
| 7    | 2         | 6           | 6    | 1           | 5           | 0  | 8  | 7    | 8380.8026 | 0.0034  |
Table S26 (Continued).

| $J'$ | $K_{1}'$ | $K_{1}''$ | $J''$ | $K_{1}''$ | $\nu$ | $F'$ | $F''$ | Obs.     | Obs.-Cal. |
|------|----------|-----------|-------|-----------|------|------|-------|----------|-----------|
| 8    | 0        | 8         | 7     | 1         | 7    | 0    | 8     | 7        | 9076.3838 | -0.0037   |
| 8    | 1        | 8         | 7     | 0         | 7    | 0    | 8     | 7        | 9076.3838 | -0.0037   |
| 8    | 0        | 8         | 7     | 1         | 7    | 0    | 7     | 6        | 9076.3937 | -0.0017   |
| 8    | 1        | 8         | 7     | 0         | 7    | 0    | 7     | 6        | 9076.3937 | -0.0017   |
| 8    | 0        | 8         | 7     | 1         | 7    | 0    | 9     | 8        | 9076.4043 | 0.0050    |
| 8    | 1        | 8         | 7     | 0         | 7    | 0    | 9     | 8        | 9076.4043 | 0.0050    |
| 8    | 0        | 8         | 7     | 1         | 7    | 1    | 8     | 7        | 9076.0975 | -0.0011   |
| 8    | 1        | 8         | 7     | 0         | 7    | 1    | 8     | 7        | 9076.0975 | -0.0011   |
| 8    | 0        | 8         | 7     | 1         | 7    | 1    | 7     | 6        | 9076.1040 | -0.0026   |
| 8    | 1        | 8         | 7     | 0         | 7    | 1    | 7     | 6        | 9076.1040 | -0.0026   |
| 8    | 0        | 8         | 7     | 1         | 9    | 7    | 8     | 9        | 9076.1100 | -0.0005   |
| 8    | 1        | 8         | 7     | 0         | 7    | 1    | 9     | 8        | 9076.1100 | -0.0005   |
Table S27. Observed rotational transitions and residuals (all the values in MHz) for the $^{13}\text{C}_{12}$ isotopologue of Pentafluoropyridine–formaldehyde adduct in the $0^+$ ($\nu=0$) and $0^-$ ($\nu=1$) torsion states. (see Table S15 for atom labelling).

| $J'$ | $K_{\text{J}1}'$ | $K_{\text{J}2}'$ | $J''$ | $K_{\text{J}1}''$ | $K_{\text{J}2}''$ | $\nu$ | $F'$ | $F''$ | Obs.  | Obs.-Cal. |
|------|----------------|----------------|------|----------------|----------------|-----|-----|-----|-------|----------|
| 5    | 0              | 5              | 4    | 1              | 4              | 0   | 4   | 3   | 5711.2898 | -0.0037 |
|      | 6              | 5              | 5    | 4              | 4              | 0   | 4   | 3   | 5711.3012 | 0.0005  |
|      | 1              | 5              | 4    | 4              | 3              | 0   | 4   | 3   | 5711.1141 | -0.0005 |
|      | 6              | 5              | 1    | 4              | 3              | 0   | 4   | 3   | 5711.1222 | 0.0009  |
| 5    | 1              | 5              | 4    | 0              | 4              | 1   | 4   | 3   | 5711.1222 | 0.0009  |
|      | 6              | 5              | 1    | 4              | 3              | 0   | 4   | 3   | 5711.1268 | 0.0009  |
|      | 5              | 4              | 1    | 4              | 3              | 0   | 4   | 3   | 5711.1004 | -0.0008 |
|      | 0              | 4              | 3    | 5711.2993      | 0.0000  |
|      | 6              | 5              | 1    | 4              | 3              | 0   | 4   | 3   | 5711.3078 | 0.0013  |
| 5    | 2              | 3              | 4    | 3              | 2              | 1   | 6   | 5   | 6510.5153 | -0.0014 |
|      | 5              | 4              | 2    | 4              | 3              | 2   | 1   | 6   | 6510.6229 | 0.0030  |
| 6    | 0              | 6              | 5    | 1              | 5              | 0   | 6   | 5   | 6812.7700 | 0.0017  |
| 6    | 1              | 6              | 5    | 0              | 5              | 0   | 6   | 5   | 6812.7700 | 0.0017  |
| 6    | 0              | 6              | 5    | 1              | 5              | 0   | 5   | 4   | 6812.7831 | 0.0016  |
| 6    | 1              | 6              | 5    | 0              | 5              | 0   | 5   | 4   | 6812.7831 | 0.0016  |
| 6    | 0              | 6              | 5    | 1              | 5              | 0   | 7   | 6   | 6812.7892 | 0.0019  |
| 6    | 1              | 6              | 5    | 0              | 5              | 0   | 7   | 6   | 6812.7892 | 0.0019  |
| 6    | 0              | 6              | 5    | 1              | 5              | 1   | 6   | 5   | 6812.5572 | 0.0047  |
| 6    | 1              | 6              | 5    | 0              | 5              | 1   | 6   | 5   | 6812.5572 | 0.0047  |
| 6    | 0              | 6              | 5    | 1              | 5              | 1   | 5   | 4   | 6812.5673 | 0.0016  |
| 6    | 1              | 6              | 5    | 0              | 5              | 1   | 5   | 4   | 6812.5673 | 0.0016  |
| 6    | 0              | 6              | 5    | 1              | 5              | 1   | 7   | 6   | 6812.5738 | 0.0022  |
| 6    | 1              | 6              | 5    | 0              | 5              | 1   | 7   | 6   | 6812.5738 | 0.0022  |
| 6    | 1              | 5              | 5    | 2              | 4              | 1   | 6   | 5   | 7219.7485 | -0.0001 |
|      | 7              | 6              | 7219.7918 | -0.0021 |
|      | 5              | 4              | 7219.7985 | -0.0011 |
| 6    | 2              | 5              | 5    | 1              | 4              | 1   | 6   | 5   | 7219.8030 | 0.0023  |
|      | 7              | 6              | 7219.8436 | -0.0031 |
|      | 5              | 4              | 7219.8555 | 0.0028 |
| 7    | 0              | 7              | 6    | 1              | 6              | 0   | 8   | 7   | 7914.2482 | -0.0030 |
| 7    | 1              | 7              | 6    | 0              | 6              | 0   | 8   | 7   | 7914.2482 | -0.0030 |
| 7    | 0              | 7              | 6    | 1              | 6              | 1   | 7   | 6   | 7913.9844 | 0.0004  |
| 7    | 1              | 7              | 6    | 0              | 6              | 1   | 7   | 6   | 7913.9844 | 0.0004  |
| 7    | 0              | 7              | 6    | 1              | 6              | 1   | 6   | 5   | 7913.9908 | -0.0029 |
| 7    | 1              | 7              | 6    | 0              | 6              | 1   | 6   | 5   | 7913.9908 | -0.0029 |
| 7    | 0              | 7              | 6    | 1              | 6              | 1   | 8   | 7   | 7913.9982 | -0.0002 |
| 7    | 1              | 7              | 6    | 0              | 6              | 1   | 8   | 7   | 7913.9982 | -0.0002 |
Table S27 (Continued).

| J′ | K_1′ | K_1′′ | J′′ | K_1′′ | v  | F′  | F′′ | Obs.      | Obs.-Cal. |
|----|------|-------|-----|-------|----|-----|-----|----------|-----------|
| 7  | 2    | 6     | 6   | 1     | 5  | 0   | 7   | 6        | 8321.3728 | -0.0001   |
| 7  | 1    | 6     | 6   | 2     | 5  | 0   | 7   | 6        | 8321.3728 | -0.0001   |
| 7  | 2    | 6     | 6   | 1     | 5  | 1   | 8   | 7        | 8321.1704 | 0.0029    |
| 7  | 1    | 6     | 6   | 2     | 5  | 1   | 8   | 7        | 8321.1704 | 0.0029    |
| 7  | 2    | 6     | 6   | 1     | 5  | 1   | 6   | 5        | 8321.1704 | 0.0029    |
| 7  | 1    | 6     | 6   | 2     | 5  | 1   | 7   | 6        | 8321.1298 | -0.0019   |
| 7  | 2    | 6     | 6   | 1     | 5  | 1   | 7   | 6        | 8321.1298 | -0.0019   |
| 8  | 0    | 8     | 7   | 1     | 7  | 1   | 8   | 7        | 9015.3850 | -0.0033   |
| 8  | 1    | 8     | 7   | 0     | 7  | 1   | 8   | 7        | 9015.3850 | -0.0033   |
| 8  | 0    | 8     | 7   | 1     | 7  | 1   | 7   | 6        | 9015.3956 | -0.0002   |
| 8  | 1    | 8     | 7   | 0     | 7  | 1   | 7   | 6        | 9015.3956 | -0.0002   |
| 8  | 0    | 8     | 7   | 1     | 7  | 1   | 9   | 8        | 9015.4003 | 0.0006    |
| 8  | 1    | 8     | 7   | 0     | 7  | 1   | 9   | 8        | 9015.4003 | 0.0006    |