

# Chemistry–A European Journal

Supporting Information

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

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## Flexible model analysis

Meyer's flexible model<sup>[1]</sup> 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<sub>2</sub>CO torsion pathway, the periodic two-fold double minimum function:

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

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:

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

where the  $\alpha$  values of  $0^\circ$ ,  $180^\circ$ , and  $360^\circ$  correspond to the equilibrium configuration C1 with H<sub>2</sub>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  $90^\circ$  and  $270^\circ$  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  $r(\text{C}_{12}\text{N}_1)$  distance ( $r(\alpha)$ ) and the  $\angle\text{C}_{12}\text{N}_1\text{C}_4$  ( $\beta(\alpha)$ ) and  $\angle\text{O}_{13}\text{C}_{12}\text{N}_1$  ( $\gamma(\alpha)$ ) angles (see Figure 5 for labeling) with the following equations to model the structural relaxations:

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

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

$$\gamma(\alpha) = \gamma(0) + \gamma_2(1 - \cos(2\alpha))/2 + \gamma_4(1 - \cos(4\alpha))/2 \quad (5)$$

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) *ab initio* constrained calculations ( $V_2 = 218 \text{ cm}^{-1}$  and  $V_4 = 30 \text{ cm}^{-1}$ ), while the *ab initio* structural relaxation parameters ( $r_2 = 0.15 \text{ \AA}$ ,  $r_4 = 0.006 \text{ \AA}$ ,  $\beta_2 = -4.43^\circ$ ,  $\beta_4 = -0.35^\circ$ ,  $\gamma_2 = -1.88^\circ$ , and  $\gamma_4 = -0.03^\circ$ ) were used together with the  $r_0$  results ( $r(0) = 3.361 \text{ \AA}$ ,  $\beta(0) = 91.48^\circ$  and  $\gamma(0) = 71.20^\circ$ ). A reasonable agreement ( $\Delta P_{aa} = 0.028 \text{ u\AA}^2$ ,  $\Delta P_{bb} = -0.001 \text{ u\AA}^2$  and  $\Delta P_{cc} = 0.001 \text{ u\AA}^2$ ) with the experimental planar moments of inertia was reached using a scale factor for both potential parameters to give  $V_2 = 155 \text{ cm}^{-1}$  and  $V_4 = 21 \text{ cm}^{-1}$  with slight modifications of the relaxation parameters ( $r_2 = 0.14 \text{ \AA}$ ,  $r_4 = 0.006 \text{ \AA}$ ,  $\beta_2 = -3.7^\circ$ ,  $\beta_4 = -0.35^\circ$ ,  $\gamma_2 = -2.40^\circ$ , and  $\gamma_4 = -0.03^\circ$ ). The potential energy function is shown in Figure 3 (black continuous, trace 4).

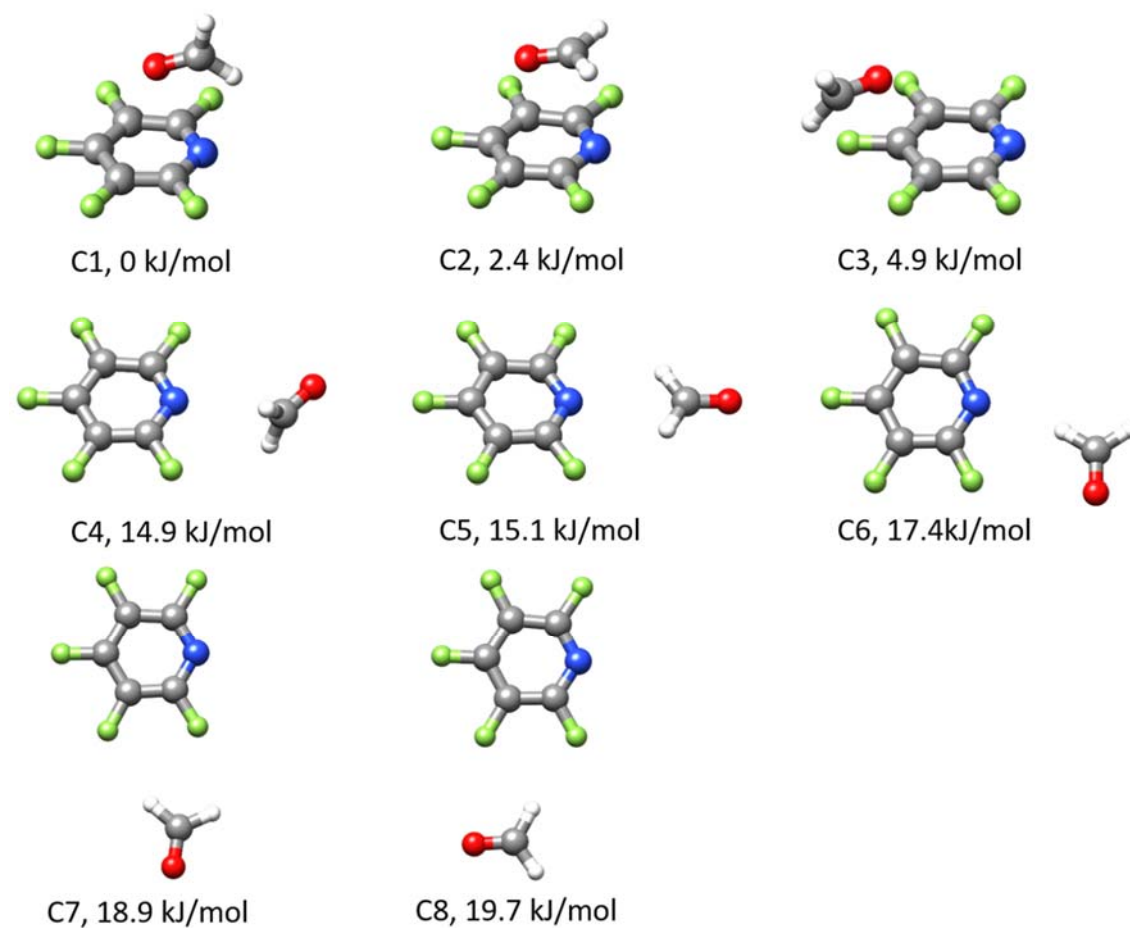
When using the potential function (2) we started from the MP2/aug-cc-pVTZ parameters ( $V_2 = 166 \text{ cm}^{-1}$ ,  $V_4 = 77 \text{ cm}^{-1}$ , and  $V_6 = -18 \text{ cm}^{-1}$ ) and proceeded in the same way as before using a common scale factor for the potential energy parameters. Assuming the same relaxation parameters determined before, the same degree of agreement between experimental and predicted parameters was obtained for values of the potential energy parameters of  $V_2 = 132.8 \text{ cm}^{-1}$ ,  $V_4 = 32.7 \text{ cm}^{-1}$ , and  $V_6 = 14.4 \text{ cm}^{-1}$ , with C2 structure being  $118.4 \text{ cm}^{-1}$  higher than C1 and barriers of  $145.8 \text{ cm}^{-1}$  (Figure 3, black dashed, trace 5). The C2 energies calculated at CCSD/6-311++G(2d,p) ( $138 \text{ cm}^{-1}$ ) is between the values of the energy of C2 estimated for potential function (1) of  $155.0 \text{ cm}^{-1}$  or (2) of  $118.0 \text{ cm}^{-1}$ . 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, *J. Mol. Spectrosc.* **1979**, 76, 266–300.

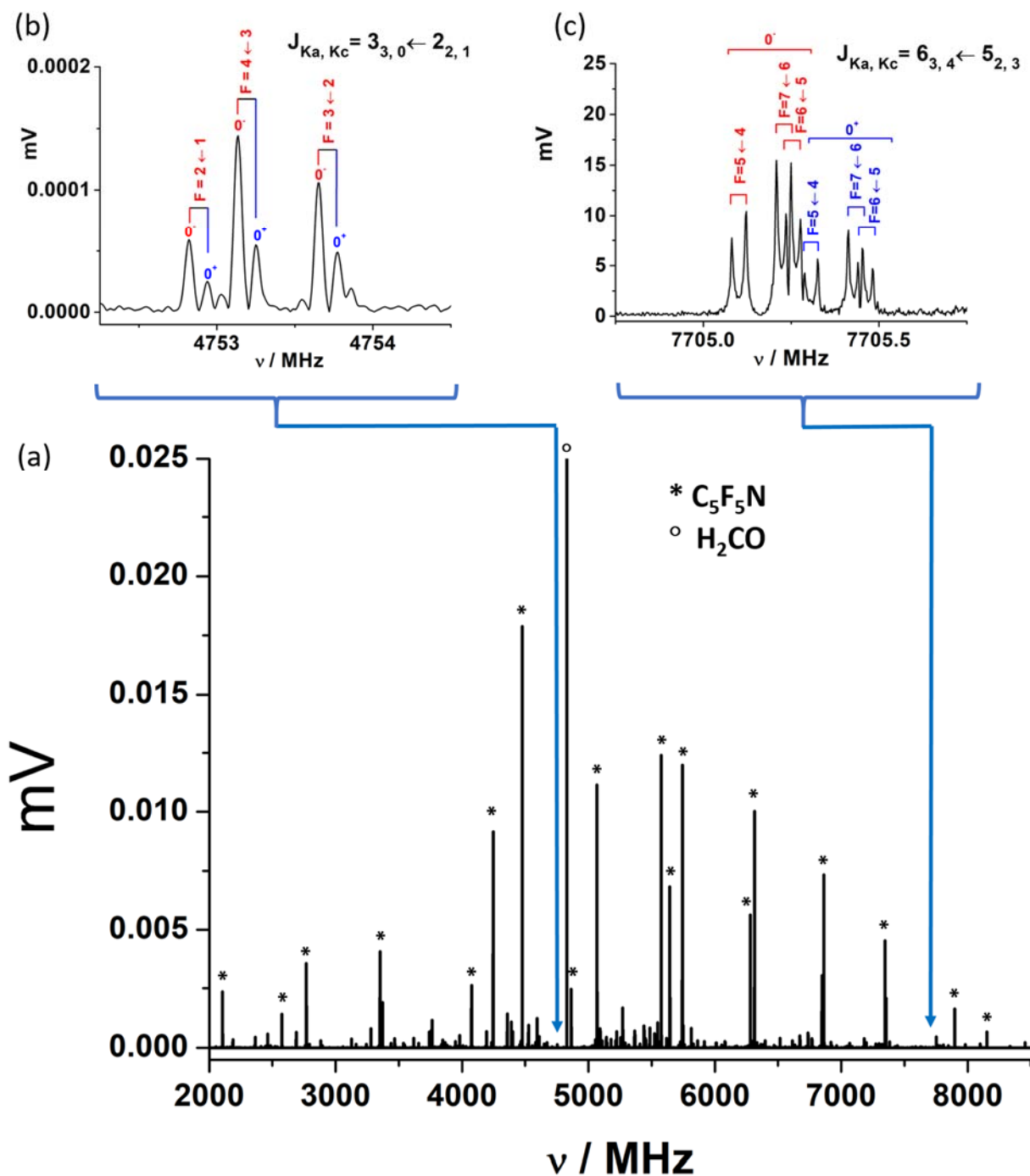
### **Complete reference 33**

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.

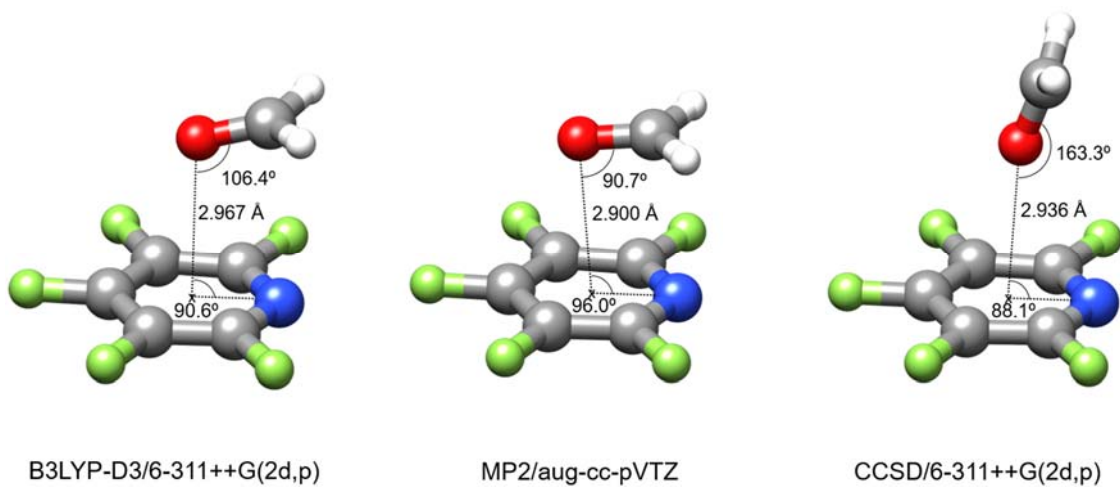


**Figure S2.** (a) Observed broadband FTMW spectrum (2-8 GHz) dominated by the spectra of  $C_5F_5N$  (\*) and  $CH_2CO$  (°). (b) The  $3_{3,0} \leftarrow 2_{2,1}$  transition assigned to  $C_5F_5N \cdots H_2CO$  showing the  $F+1 \leftarrow F$  quadrupole coupling hyperfine components and the  $0^+/0^-$  doublets with an intensity ratio 1/3. (c) The  $6_{3,4} \leftarrow 5_{2,3}$  transition recorded with the narrow band FP-FTMW spectrometer shows an additional Doppler doubling.

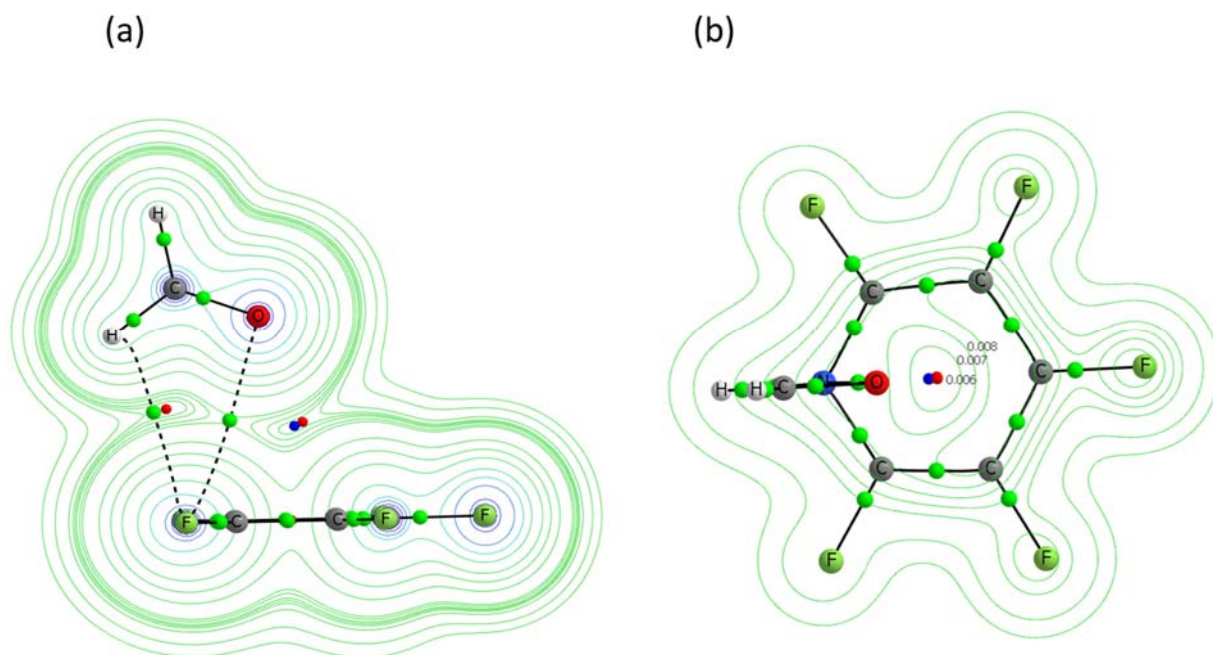




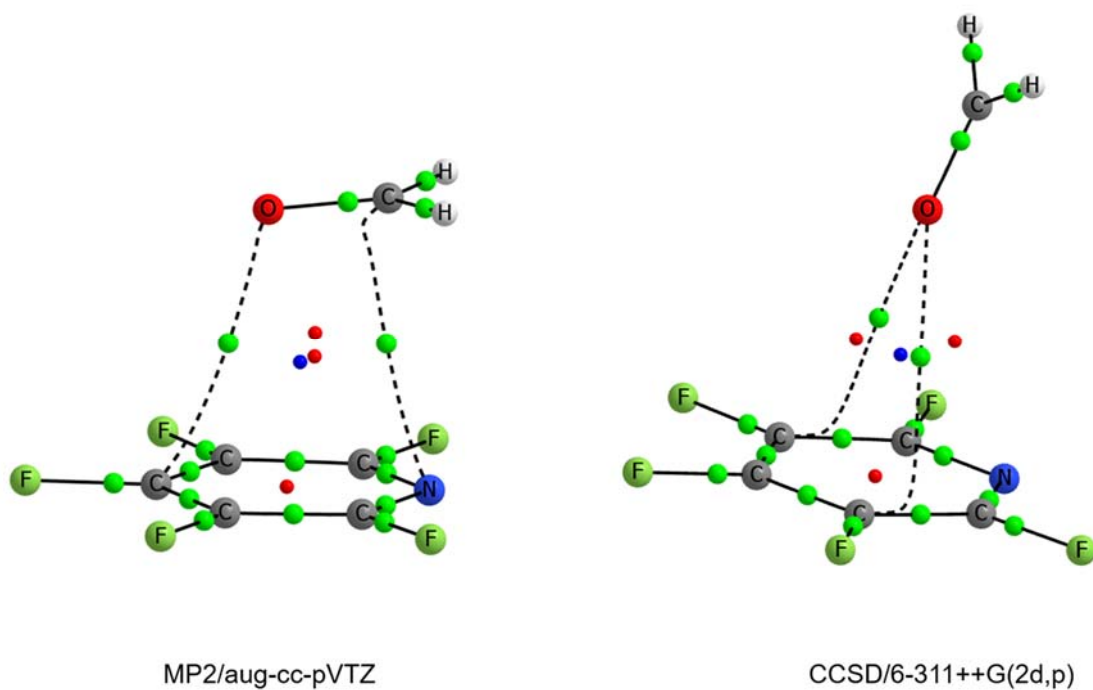
**Figure S3.** Comparison of the structures calculated for configuration C2 of the adduct pentafluoropyridine···formaldehyde at B3LYP-D3/6-311++G(2d,p), MP2/aug-cc-pVTZ, and CCSD/6-311++G(2d,p).



**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.

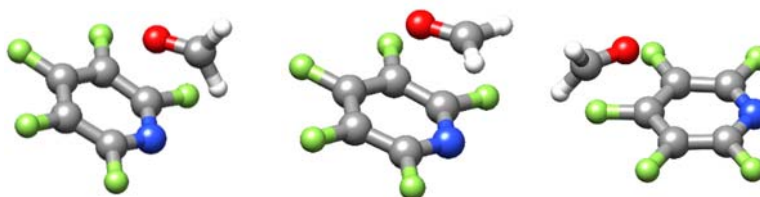


**Figure S5.** Comparison of the molecular graphs of the predicted configuration of form C2 of the complex pentafluoropyridine...formaldehyde calculated at MP2/aug-cc-pVTZ, and CCSD/6-311++G(2d,p). The green, red and blue dots represent the location of the bond, ring, and cage critical points.



**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.

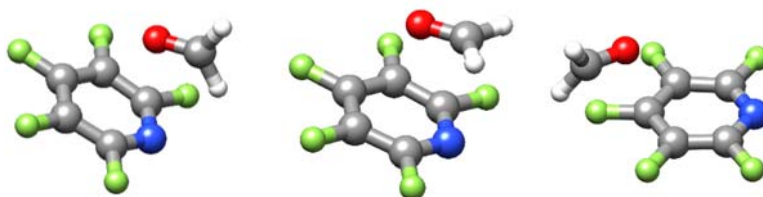
Parameters <sup>a</sup>	C1	C2	C3
$A/\text{MHz}$	791.12	813.25	909.03
$B/\text{MHz}$	755.01	728.65	668.36
$C/\text{MHz}$	554.58	578.47	477.10
$P_{aa}/\text{u}\text{\AA}^2$	470.92	472.90	629.74
$P_{bb}/\text{u}\text{\AA}^2$	440.37	400.75	429.54
$P_{cc}/\text{u}\text{\AA}^2$	198.45	220.68	126.41
$\chi_{aa}/\text{MHz}$	2.21	2.21	-0.60
$\chi_{bb}/\text{MHz}$	-2.86	-3.11	-0.48
$\chi_{cc}/\text{MHz}$	0.65	0.91	1.08
$\chi_{ab}/\text{MHz}$	0.00	0.00	2.74
$\chi_{ac}/\text{MHz}$	0.00	0.00	1.56
$\chi_{bc}/\text{MHz}$	2.44	2.29	-1.58
$1.5(\chi_{aa})/\text{MHz}$	3.32	3.31	-0.91
$0.25(\chi_{bb}-\chi_{cc})/\text{MHz}$	-0.88	-1.00	-0.39
$ \mu_a /\text{D}$	0.0	0.0	3.14
$ \mu_b /\text{D}$	1.6	1.4	1.1
$ \mu_c /\text{D}$	0.4	0.4	1.0
$E/h$	-859.252389	-859.251225	-859.250958
$\Delta E/\text{cm}^{-1}$	0.0	255.5	314.13
$\Delta E/\text{kJmol}^{-1}$	0.0	3.06	3.76
$C_E(\text{BSSE})/\text{kJmol}^{-1}$	-19.0	-15.8	-15.5



<sup>a</sup>  $A$ ,  $B$  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  $^{14}\text{N}$  nuclear quadrupole coupling constants.  $E$  are the electronic energies;  $\Delta E$  are the energies relative to the most stable conformer C1.  $C_E(\text{BSSE})$  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.

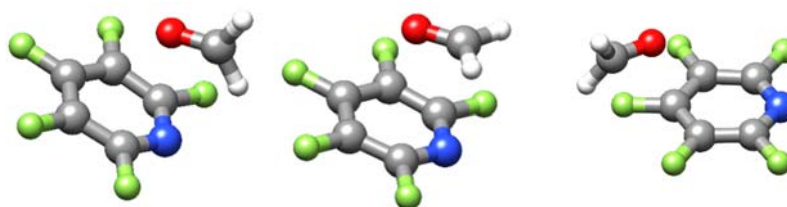
Parameters <sup>a</sup>	C1	C2	C3
<i>A</i> /MHz	785.77	813.25	909.03
<i>B</i> /MHz	750.98	728.65	668.36
<i>C</i> /MHz	554.53	578.47	477.10
<i>P</i> <sub>aa</sub> /uÅ <sup>2</sup>	470.58	472.90	629.74
<i>P</i> <sub>bb</sub> /uÅ <sup>2</sup>	440.79	400.75	429.54
<i>P</i> <sub>cc</sub> /uÅ <sup>2</sup>	202.38	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 $ /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
<i>E</i> /h	-859.265792	-859.2512247	-859.250958
$\Delta E$ /cm <sup>-1</sup>	0.0	255.51	355.43
$\Delta E$ /kJmol <sup>-1</sup>	0.0	3.06	4.25
<i>C</i> <sub>E</sub> (BSSE)/ kJmol <sup>-1</sup>	-18.6	-15.8	-14.64



<sup>a</sup> *A*, *B* and *C* are the rotational constants; *P*<sub>αα</sub> (α = *a*, *b* or *c*) are the planar moments of inertia derived from the moments of inertia *I*<sub>α</sub> as for example *P*<sub>cc</sub> = (*I*<sub>a</sub> + *I*<sub>b</sub> - *I*<sub>c</sub>)/2;  $\chi_{\alpha\beta}$  (α,β = *a*, *b*, *c*) are the <sup>14</sup>N nuclear quadrupole coupling constants. *E* are the electronic energies;  $\Delta E$  are the energies relative to the most stable conformer C1. *C*<sub>E</sub>(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.

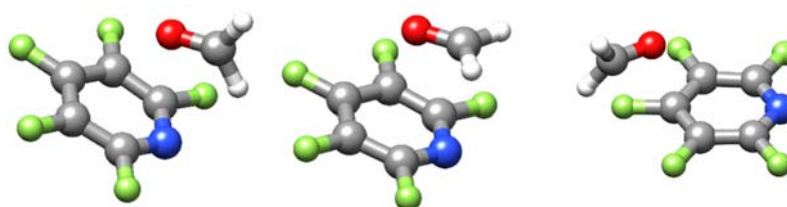
Parameters <sup>a</sup>	C1	C2	C3
<i>A</i> /MHz	804.99	847.20	905.69
<i>B</i> /MHz	751.61	731.83	676.97
<i>C</i> /MHz	562.29	592.24	489.77
<i>P</i> <sub>aa</sub> /uÅ <sup>2</sup>	471.69	473.69	610.20
<i>P</i> <sub>bb</sub> /uÅ <sup>2</sup>	427.10	379.65	421.67
<i>P</i> <sub>cc</sub> /uÅ <sup>2</sup>	200.71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



<sup>a</sup> *A*, *B* and *C* are the rotational constants; *P*<sub>αα</sub> (α = *a*, *b* or *c*) are the planar moments of inertia derived from the moments of inertia *I*<sub>α</sub> as for example *P*<sub>cc</sub> = (*I*<sub>a</sub> + *I*<sub>b</sub> - *I*<sub>c</sub>)/2;  $\chi_{\alpha\beta}$  (α,β = *a*, *b*, *c*) are the <sup>14</sup>N nuclear quadrupole coupling constants. *E* are the electronic energies;  $\Delta E$  are the energies relative to the most stable conformer C1. *C*<sub>E</sub>(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.

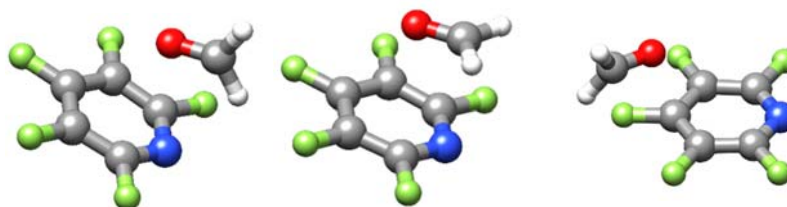
Parameters <sup>a</sup>	C1	C2	C3
<i>A</i> /MHz	811.7	868.2	914.9
<i>B</i> /MHz	749.6	735.5	680.7
<i>C</i> /MHz	557.6	589.7	492.9
<i>P</i> <sub>aa</sub> /uÅ <sup>2</sup>	479.0	481.0	607.59
<i>P</i> <sub>bb</sub> /uÅ <sup>2</sup>	427.4	376.0	417.63
<i>P</i> <sub>cc</sub> /uÅ <sup>2</sup>	195.2	206.1	134.77
$\chi_{aa}$ /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
<i>E</i> /h	-857.0655585	-857.065195	-857.0635155
$\Delta E$ /cm <sup>-1</sup>	0.0	79.8	448.4
$\Delta E$ /kJmol <sup>-1</sup>	0.0	1.0	5.4



<sup>a</sup> *A*, *B* and *C* are the rotational constants; *P*<sub>αα</sub> (α = *a*, *b* or *c*) are the planar moments of inertia derived from the moments of inertia *I*<sub>α</sub> as for example *P*<sub>cc</sub> = (*I*<sub>a</sub> + *I*<sub>b</sub> - *I*<sub>c</sub>)/2;  $\chi_{\alpha\beta}$  (α,β = *a*, *b*, *c*) are the <sup>14</sup>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 <sup>a</sup>	C1	C2	C3
$A/\text{MHz}$	809.8	865.0	917.4
$B/\text{MHz}$	761.1	741.2	679.9
$C/\text{MHz}$	561.4	596.9	492.1
$P_{aa}/\text{u}\text{\AA}^2$	470.1	472.2	609.7
$P_{bb}/\text{u}\text{\AA}^2$	430.1	374.6	417.3
$P_{cc}/\text{u}\text{\AA}^2$	194.0	209.7	133.6
$\chi_{aa}/\text{MHz}$	1.83	1.84	0.21
$\chi_{bb}/\text{MHz}$	-2.68	-3.35	-1.55
$\chi_{cc}/\text{MHz}$	0.84	1.51	1.34
$\chi_{ab}/\text{MHz}$	0.00	0.00	2.36
$\chi_{ac}/\text{MHz}$	0.00	0.00	1.03
$\chi_{bc}/\text{MHz}$	2.18	-1.48	-1.45
$1.5(\chi_{aa})/\text{MHz}$	2.75	2.76	0.32
$0.25(\chi_{bb}-\chi_{cc})/\text{MHz}$	-0.88	-1.21	-0.72
$ \mu_a /\text{D}$	0.0	0.0	3.1
$ \mu_b /\text{D}$	1.4	1.0	1.6
$ \mu_c /\text{D}$	0.5	0.2	0.7
$E/h$	-857.7717824	-857.7711213	-857.7698845
$\Delta E/\text{cm}^{-1}$	0.0	145.1	416.5
$\Delta E/\text{kJmol}^{-1}$	0.0	1.7	5.0

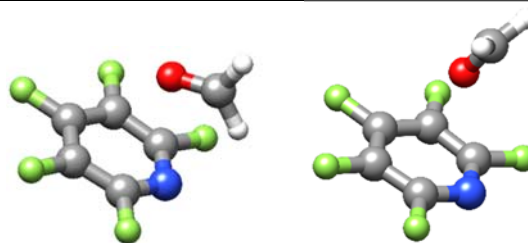


<sup>a</sup>  $A$ ,  $B$  and  $C$  are the rotational constants;  $P_{\alpha\alpha}$  ( $\alpha = a, b$  or  $c$ ) are the planar moments of inertia derived from the moments of inertia  $I_\alpha$  as for example  $P_{cc} = (I_a + I_b - I_c)/2$ ;  $\chi_{\alpha\beta}$  ( $\alpha, \beta = a, b, c$ ) are the  $^{14}\text{N}$  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>
<i>A</i> /MHz	783.9	750.7
<i>B</i> /MHz	748.0	671.3
<i>C</i> /MHz	556.5	585.4
<i>P</i> <sub>aa</sub> /uÅ <sup>2</sup>	469.5	471.5
<i>P</i> <sub>bb</sub> /uÅ <sup>2</sup>	438.6	391.9
<i>P</i> <sub>cc</sub> /uÅ <sup>2</sup>	206.1	281.3
$\chi_{aa}$ /MHz	2.08	2.07
$\chi_{bb}$ /MHz	-2.71	-1.77
$\chi_{cc}$ /MHz	0.63	-0.29
$\chi_{ab}$ /MHz	0.00	0.00
$\chi_{ac}$ /MHz	0.00	0.00
$\chi_{bc}$ /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 $ /D	0.0	0.0
$ \mu_b $ /D	1.7	1.64
$ \mu_c $ /D	0.5	2.35
<i>E</i> /h	-857.4209832	-857.4203509
$\Delta E$ /cm <sup>-1</sup>	0.0	138.8
$\Delta E$ /kJmol <sup>-1</sup>	0.0	1.7



<sup>a</sup> *A*, *B* and *C* are the rotational constants; *P*<sub>αα</sub> (α = *a*, *b* or *c*) are the planar moments of inertia derived from the moments of inertia *I*<sub>α</sub> as for example *P*<sub>cc</sub> = (*I*<sub>a</sub> + *I*<sub>b</sub> - *I*<sub>c</sub>)/2;  $\chi_{\alpha\beta}$  (α,β = *a*, *b*, *c*) are the <sup>14</sup>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.

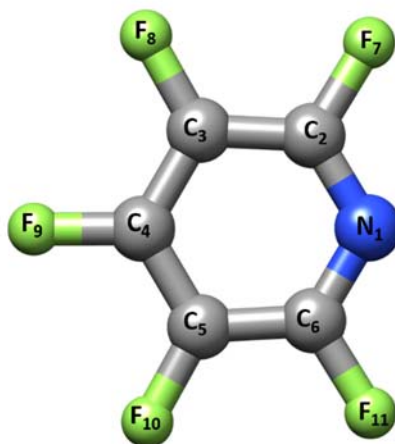
Parameters <sup>a</sup>	parent	Prev. work <sup>b</sup>	DFT(1)	DFT(2)	MP2(1)	MP2(2)	MP2(3)	CCSD
<i>A</i> /MHz	1481.58184(19) <sup>c</sup>	1481.539(3)	1479.94	1481.35	1477.87	1452.45	1481.20	1484.36
<i>B</i> /MHz	1075.37335(17)	1075.348(4)	1072.33	1073.22	1070.99	1054.43	1074.22	1075.80
<i>C</i> /MHz	623.11194(16)	623.101(1)	621.79	622.34	620.98	610.92	622.65	623.74
<i>P</i> <sub>aa</sub> /uÅ <sup>2</sup>	469.95288(16)	469.9605(2)	471.29	470.90	471.88	479.29	470.46	469.77
<i>P</i> <sub>bb</sub> /uÅ <sup>2</sup>	341.10379(16)	341.1102(2)	341.49	341.16	341.97	347.95	341.20	340.47
<i>P</i> <sub>cc</sub> /uÅ <sup>2</sup>	0.00399(16)	0.0073(2)	0.00	0.00	0.00	0.00	0.00	0.00
1.5( $\chi$ <sub>aa</sub> )/MHz	2.9496(31)		3.29	3.29	2.93	2.81	2.76	3.11
0.25( $\chi$ <sub>bb</sub> - $\chi$ <sub>cc</sub> )/MHz	-1.48514(91)		-1.57	-1.58	-1.48	-1.29	-1.46	-1.59
$\chi$ <sub>aa</sub> /MHz	1.9664(53)	1.94(22)	2.20	2.19	1.96	1.88	1.84	2.07
$\chi$ <sub>bb</sub> /MHz	-3.9534(72)	-4.08(6)	-4.24	-4.25	-3.94	-3.51	-3.83	-4.22
$\chi$ <sub>cc</sub> /MHz	1.9870(72)	2.14(22)	2.05	2.05	1.98	1.64	1.99	2.14

<sup>a</sup> *A*, *B* and *C* are the rotational constants;  $\chi$ <sub>aa</sub>,  $\chi$ <sub>bb</sub> and  $\chi$ <sub>cc</sub> are the <sup>14</sup>N nuclear quadrupole coupling constants. *P* <sub>$\alpha\alpha$</sub>  ( $\alpha = a, b$  or *c*) are the planar moments of inertia derived from the moments of inertia *I* <sub>$\alpha$</sub>  as for example *P*<sub>*c*</sub> = (*I*<sub>*a*</sub>+*I*<sub>*b*</sub>-*I*<sub>*c*</sub>)/2. <sup>b</sup> Doraiswamy, S.; Sharma, S. D. Microwave Spectrum, Centrifugal Distortion Constants, Dipole Moment and Quadrupole Coupling Constants of Pentafluoropyridine. *Chem. Phys.* **1974**, *6* (1), 76-86. <sup>c</sup> 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  $^{13}\text{C}$  and  $^{15}\text{N}$  isotopologues.

Parameters <sup>a</sup>	parent	Parameters	$^{15}\text{N}_1$	$^{13}\text{C}_2$
$A/\text{MHz}$	1481.58184(19) <sup>b</sup>	$A/\text{MHz}$	1469.9842(12)	1477.57710(20)
$B/\text{MHz}$	1075.37335(17)	$B/\text{MHz}$	1075.3655(11)	1072.48478(13)
$C/\text{MHz}$	623.11194(16)	$C/\text{MHz}$	621.06359(46)	621.43405(10)
$\Delta_J/\text{kHz}$	0.0290(30)			
$\Delta_{JK}/\text{kHz}$	[0.0]	$P_{aa}/\text{u}\text{\AA}^2$	469.94639(68)	471.21836(12)
$\Delta_K/\text{kHz}$	0.0565(24)	$P_{bb}/\text{u}\text{\AA}^2$	343.78511(68)	342.02805(12)
$\delta_J/\text{kHz}$	0.00474(47)	$P_{cc}/\text{u}\text{\AA}^2$	0.01383(68)	0.00419(12)
$\delta_K/\text{kHz}$	0.0343(18)	n	13	91
$1.5(\chi_{aa})/\text{MHz}$	2.9496(31)	$\sigma/\text{kHz}$	7.5	4.7
$0.25(\chi_{bb}-\chi_{cc})/\text{MHz}$	-1.48514(91)			
			$^{13}\text{C}_3$	$^{13}\text{C}_4$
n	366	$A/\text{MHz}$	1480.90341(33)	1476.24411(63)
$\sigma/\text{kHz}$	5.8	$B/\text{MHz}$	1072.11470(26)	1075.40090(45)
		$C/\text{MHz}$	621.89756(15)	622.18098(23)
$P_{aa}/\text{u}\text{\AA}^2$	469.95280(16)	$P_{aa}/\text{u}\text{\AA}^2$	471.38075(19)	469.93689(32)
$P_{bb}/\text{u}\text{\AA}^2$	341.10373(16)	$P_{bb}/\text{u}\text{\AA}^2$	341.25953(19)	342.33322(32)
$P_{cc}/\text{u}\text{\AA}^2$	0.00399(16)	$P_{cc}/\text{u}\text{\AA}^2$	0.00446(19)	0.00787(32)
$\chi_{aa}/\text{MHz}$	1.9664(53)	n	68	30
$\chi_{bb}/\text{MHz}$	-3.9534(72)	$\sigma/\text{kHz}$	5.9	5.5
$\chi_{cc}/\text{MHz}$	1.9870(72)			

<sup>a</sup>  $A$ ,  $B$  and  $C$  are the rotational constants.  $\Delta_J$ ,  $\Delta_{JK}$ ,  $\Delta_K$ ,  $\delta_J$  and  $\delta_K$  are the quartic centrifugal distortion constants and  $\chi_{aa}$ ,  $\chi_{bb}$  and  $\chi_{cc}$  are the  $^{14}\text{N}$  nuclear quadrupole coupling constants. The quartic centrifugal distortion constants of all monosubstituted isotopologues and the  $^{14}\text{N}$  nuclear quadrupole coupling constants for the  $^{13}\text{C}$  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  $P_{cc} = (I_a + I_b - I_c)/2$ . <sup>b</sup> 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.

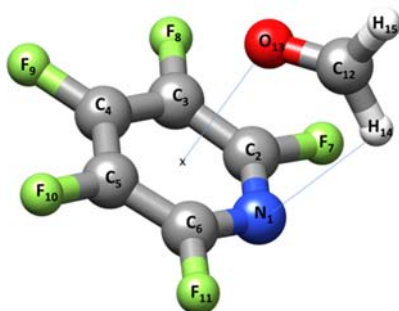
Fitted Parameters <sup>a</sup>	$0^+$	$0^-$	DFT	MP2(1)	MP2(2)	MP2(3)	CCSD
$A/\text{MHz}$	779.69465(13) <sup>b</sup>	779.69184(13)	791.1	805.0	811.7	809.8	783.89
$B/\text{MHz}$	745.85829(10)	745.82527(10)	755.0	751.6	749.6	761.1	748.01
$C/\text{MHz}$	555.481998(67)	555.464049(67)	554.6	562.3	557.6	561.4	556.48
$\Delta_J/\text{kHz}$	0.2013(11)						
$\Delta_{JK}/\text{kHz}$	1.1527(70)						
$\Delta_K/\text{kHz}$	-1.1305(73)						
$\delta_J/\text{kHz}$	0.02584(63)						
$\delta_K/\text{kHz}$	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						
$P_{aa}/\text{u}\text{\AA}^2$	469.60380(15)	469.63233(15)	470.92	471.69	478.96	470.1	469.55
$P_{bb}/\text{u}\text{\AA}^2$	440.19888(15)	440.19975(15)	440.37	427.10	427.38	430.1	438.62
$P_{cc}/\text{u}\text{\AA}^2$	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	

<sup>a</sup>  $A$ ,  $B$  and  $C$  are the rotational constants.  $\Delta_J$ ,  $\Delta_{JK}$ ,  $\Delta_K$ ,  $\delta_J$  and  $\delta_K$  are the quartic centrifugal distortion constants.  $\chi_{aa}$ ,  $\chi_{bb}$  and  $\chi_{cc}$  are the  $^{14}\text{N}$  nuclear quadrupole coupling constants.  $n$  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  $P_{cc} = (I_a + I_b - I_c)/2$ . <sup>b</sup> 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  $^{13}\text{C}$  and  $^{15}\text{N}$  isotopologues of the pentafluoropyridine...formaldehyde cluster.

Parameters <sup>a</sup>	$^{13}\text{C}_2 = ^{13}\text{C}_6$		$^{13}\text{C}_3 = ^{13}\text{C}_5$	
	0 <sup>+</sup>	0 <sup>-</sup>	0 <sup>+</sup>	0 <sup>-</sup>
<i>A</i> /MHz	779.06370(89) <sup>b</sup>	779.05934(87)	778.68523(72)	778.68523(72)
<i>B</i> /MHz	744.23775(34)	744.20525(33)	743.8135(12)	743.73763(28)
<i>C</i> /MHz	554.293478(97)	554.275694(87)	554.585907(96)	554.569896(71)
<i>P</i> <sub>aa</sub> /uÅ <sup>2</sup>	471.05443(61)	471.08206(58)	470.85006(93)	470.89787(49)
<i>P</i> <sub>bb</sub> /uÅ <sup>2</sup>	440.69906(61)	440.70067(58)	440.42267(93)	440.40117(49)
<i>P</i> <sub>cc</sub> /uÅ <sup>2</sup>	208.00144(61)	208.00346(58)	208.59312(93)	208.61462(49)
<i>n</i>		66		60
$\sigma$ /kHz		2.3		1.9
Parameters <sup>a</sup>	$^{13}\text{C}_4$		$^{13}\text{C}_{12}$	
	0 <sup>+</sup>	0 <sup>-</sup>	0 <sup>+</sup>	0 <sup>-</sup>
<i>A</i> /MHz	777.4322(10)	777.4322(10)	766.9150(12)	766.9150(12)
<i>B</i> /MHz	745.822(14)	745.79530(45)	742.5431(25)	742.51905(53)
<i>C</i> /MHz	554.38209(57)	554.363767(87)	550.77887(16)	550.760409(74)
<i>P</i> <sub>aa</sub> /uÅ <sup>2</sup>	469.5797(72)	469.60687(69)	469.6003(18)	469.62670(82)
<i>P</i> <sub>bb</sub> /uÅ <sup>2</sup>	442.0281(72)	442.03101(69)	447.9712(18)	447.97559(82)
<i>P</i> <sub>cc</sub> /uÅ <sup>2</sup>	208.0338(72)	208.03083(69)	211.0053(18)	211.00097(82)
<i>n</i>		54		73
$\sigma$ /kHz		2.6		2.1
Parameters <sup>a</sup>	$^{15}\text{N}_1$			
	0 <sup>+</sup>	0 <sup>-</sup>		
<i>A</i> /MHz	776.8324(30)	776.8324(30)		
<i>B</i> /MHz	744.269(14)	744.4765(28)		
<i>C</i> /MHz	554.80250(63)	554.77401(14)		
<i>P</i> <sub>aa</sub> /uÅ <sup>2</sup>	469.6903(82)	469.6190(26)		
<i>P</i> <sub>bb</sub> /uÅ <sup>2</sup>	441.2267(82)	441.3447(26)		
<i>P</i> <sub>cc</sub> /uÅ <sup>2</sup>	209.3371(82)	209.2191(26)		
<i>n</i>		18		
$\sigma$ /kHz		2.6		

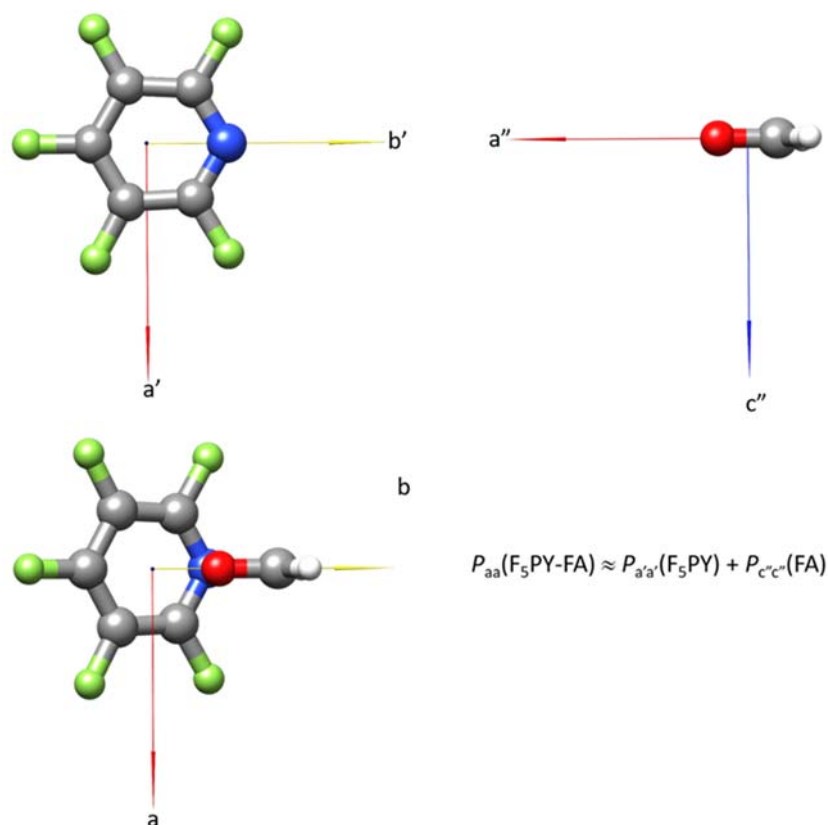
<sup>a</sup> *A*, *B* and *C* are the rotational constants. The quartic centrifugal distortion constants of all monosubstituted isotopologues and the  $^{14}\text{N}$  nuclear quadrupole coupling constants for the  $^{13}\text{C}$  species were fixed to the parent species values. *n* is the number of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



**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 $\cdots$ formaldehyde adduct. The constants shown for  $C_5F_5N\cdots H_2CO$  are the arithmetic mean of the values obtained for both tunneling states (see Tables 1 and S9). The  $P_{aa}$  value of pentafluoropyridine ( $469.95 \text{ u}\text{\AA}^2$ ) is almost equal to that of the adduct ( $469.95 \text{ u}\text{\AA}^2$ ). 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 $\cdots$ formaldehyde)  $\approx P_{a'a'}$  (pentafluoropyridine) +  $P_{c''c''}$  (formaldehyde).

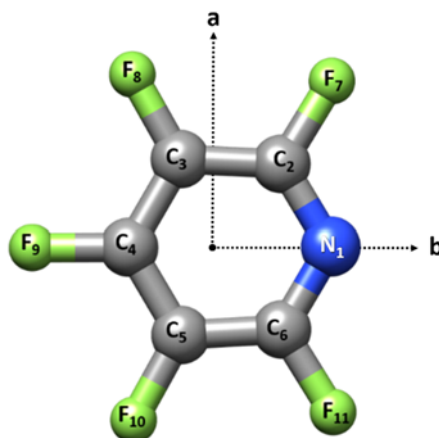
Parameters <sup>a</sup>	Pentafluoropyridine <sup>b</sup>	Formaldehyde <sup>c</sup>	Pentafluoropyridine $\cdots$ formaldehyde <sup>b</sup>
$A/\text{MHz}$	1481.58184(19)	281970.5418(84)	779.69325(13)
$B/\text{MHz}$	1075.37335(17)	38836.05020(32)	745.84178(10)
$C/\text{MHz}$	623.11194(16)	34002.20056(30)	555.473024(67)
$I_a/\text{u}\text{\AA}^2$	341.107724(44)	1.7923117(39)	648.17672(11)
$I_b/\text{u}\text{\AA}^2$	469.956791(74)	13.0131436(39)	677.595467(91)
$I_c/\text{u}\text{\AA}^2$	811.05653(21)	14.863129(14)	909.81738(11)
$P_{aa}/\text{u}\text{\AA}^2$	469.95280(16)	13.04198058(15)	469.61806(15)
$P_{bb}/\text{u}\text{\AA}^2$	341.10373(16)	1.82114862(15)	440.199311(15)
$P_{cc}/\text{u}\text{\AA}^2$	0.00399(16)	-0.02883693(15)	207.97740(15)

<sup>a</sup>  $A$ ,  $B$  and  $C$  are the rotational constants.  $I_a$ ,  $I_b$  and  $I_c$  are the moments of inertia.  $P_{\alpha\alpha}$  ( $\alpha = a, b$  or  $c$ ) are the planar moments of inertia derived from the moments of inertia  $I_\alpha$  as for example  $P_{cc} = (I_a + I_b - I_c)/2$ . <sup>b</sup> This work, see Tables 1 and S8-S9. <sup>c</sup> Bocquet, R.; Demaison, J.; Poteau, L.; Liedtke, M.; Belov, S.; Yamada, K. M. T.; Winnemisser, 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<sub>4</sub> atom. The molecule exhibits a  $C_{2v}$  symmetry.

		$a$	$b$
$ r_s ^a$	N <sub>1</sub>	0.058(26) <sup>b</sup>	1.64469(92)
$r_0$		[0.0] <sup>c</sup>	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 $	C <sub>2</sub>	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 $	C <sub>3</sub>	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 $	C <sub>4</sub>	0.109(14) <sup>i</sup>	1.1102(13)
$r_0$		[0.0]	-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
DFT	F <sub>7</sub>	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
DFT	F <sub>8</sub>	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
DFT	F <sub>9</sub>	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

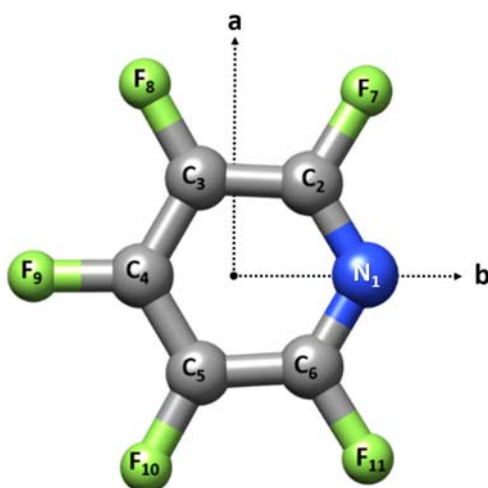


<sup>a</sup> Absolute values. <sup>b</sup> Errors quoted calculated according to van Eijck, B. P. Influence of Molecular Vibrations on Substitution Coordinates. *J. Mol. Spectrosc.* **1982**, *91*, 348–362. <sup>c</sup> Values in square brackets were kept fixed in the  $r_0$  fitting.

**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.

	$r_0$	$r_s$	$r_e$ (DFT)	$r_e$ (MP2(1))	$r_e$ (MP2(2))	$r_e$ (MP2(3))	$r_e$ (CCSD)
$r(N_1-C_2) / \text{\AA}$	1.3123(21) <sup>a</sup>	1.3125(15)	1.3096	1.3149	1.3244	1.3135	1.3122
$r(C_2-C_3) / \text{\AA}$	1.3827(21)	1.3675(41)	1.3879	1.3890	1.3993	1.3883	1.3871
$r(C_3-C_4) / \text{\AA}$	1.3868(24)	1.3929(23)	1.3901	1.3911	1.4014	1.3904	1.3887
$r(C_2-F_7)^b / \text{\AA}$	1.3319(24)		1.3308	1.3307	1.3445	1.3278	1.3252
$r(C_3-F_8)^b / \text{\AA}$	1.3319(26)		1.3318	1.3299	1.3431	1.3264	1.3287
$r(C_4-F_9) / \text{\AA}$	1.3283(35)		1.3249	1.3263	1.3395	1.3235	1.3219
$\angle N_1-C_2-C_3 / ^\circ$	124.04(17)	124.30(12)	123.6	123.7	124.0	123.7	123.8
$\angle C_2-C_3-C_4 / ^\circ$	117.41(19)	117.75(16)	117.3	117.4	117.4	117.3	117.4
$\angle C_3-C_4-C_5 / ^\circ$	119.21(21)	118.33(21)	119.3	119.3	119.1	119.4	119.3
$\angle C_2-N_1-C_6 / ^\circ$	117.88(16)	117.56(11)	118.8	118.5	118.0	118.5	118.3
$\angle F_7-C_2-N_1 / ^\circ$	117.32(11)		117.7	117.7	117.4	117.6	117.5
$\angle F_8-C_3-C_2 / ^\circ$	122.19(18)		122.1	122.1	122.1	122.2	122.0
$\angle F_9-C_4-C_3 / ^\circ$	120.40(12)		120.3	120.3	120.4	120.3	120.3

<sup>a</sup> Standard error in parenthesis in units of the last digit. <sup>b</sup> All  $C_2-F_7$  and  $C_3-F_8$  distances taken as equal.

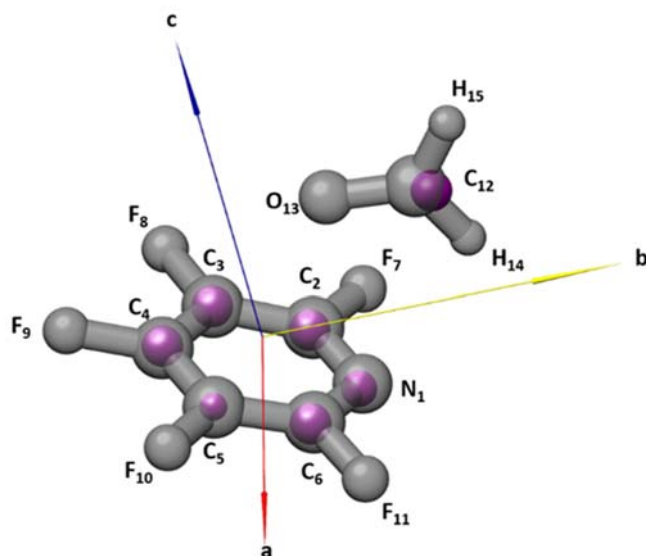




**Table S14.** The  $r_s$  coordinates (in Å) of pentafluoropyridine...formaldehyde and its comparison with the  $r_0$  and  $r_e$  (CCSD/6-311++G(2d,p) (CCSD), MP2/aug-cc-pVTZ) (MP2) or B3LYP-D3/6-311++G(2d,p) (DFT)) coordinates for the most stable conformer C1. The  $r_s$  method gives imaginary values for the  $a$  coordinates of C4 and C12 atom. These imaginary coordinates have been set to zero to draw the atom positions in the figure which compares the  $r_s$  and  $r_e$  structures. The complex has  $C_s$  symmetry.

		$a$	$b$	$c$
$ r_s ^a$	N <sub>1</sub>	[0.00] <sup>b</sup>	1.0721(14) <sup>c</sup>	1.1219(37)
$r_0$		[0.00]	1.0661(12)	-1.1237(14)
$r_e$ (CCSD)		0.00	1.0634	-1.1284
$r_e$ (MP2)		0.00	1.0605	-1.1280
$r_e$ (DFT)		0.00	1.0787	-1.0952
$ r_s $	C <sub>2</sub>	1.1162(14)	0.4706(32)	0.7944(19)
$r_0$		-1.12418(1)	0.47086(82)	-0.80103(89)
$r_e$ (CCSD)		-1.1241	0.4712	-0.8022
$r_e$ (MP2)		-1.1263	0.5219	-0.7638
$r_e$ (DFT)		-1.1254	0.4864	-0.7840
$ r_s $	C <sub>3</sub>	1.1949(13)	0.7253(21)	0.1588(96)
$r_0$		-1.19619(1)	-0.74298(5)	-0.14291(31)
$r_e$ (CCSD)		-1.1970	-0.7464	-1.1455
$r_e$ (MP2)		-1.1986	-0.7278	-0.1668
$r_e$ (DFT)		-1.1982	-0.7450	-0.1521
$ r_s $	C <sub>4</sub>	[0.00]	1.3447(11)	0.174(21)
$r_0$		[0.00]	-1.35983(36)	0.1915(15)
$r_e$ (CCSD)		0.00	-1.3635	0.1883
$r_e$ (MP2)		0.00	-1.3625	0.1325
$r_e$ (DFT)		0.00	-1.3696	0.1679
$ r_s $	C <sub>12</sub>	[0.00]	2.77152(54)	1.76847(94)
$r_0$		[0.00]	2.7447(43)	1.789(12)
$r_e$ (CCSD)		0.00	2.7415	1.8191
$r_e$ (MP2)		0.00	2.5871	1.8342
$r_e$ (DFT)		0.00	2.7041	1.7832

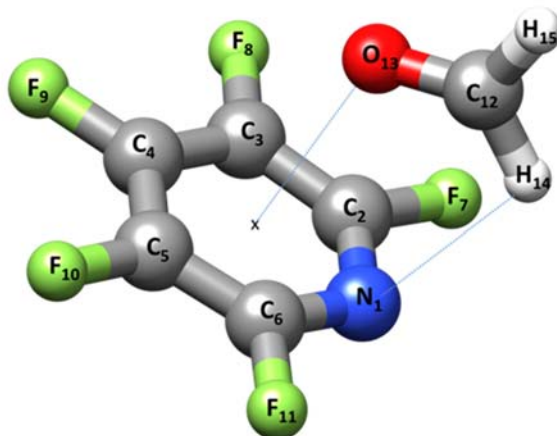
<sup>a</sup> Absolute values. <sup>b</sup> Values in square brackets were kept fixed in the  $r_0$  fitting. <sup>c</sup> Errors quoted calculated according to van Eijck, B. P. Influence of Molecular Vibrations on Substitution Coordinates. *J. Mol. Spectrosc.* **1982**, *91*, 348–362.



**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.

	$r_0$	$r_s$	$r_e(\text{DFT})$	$r_e(\text{MP2})$	$r_e(\text{CCSD})$
$r(\text{N}_1\text{-C}_2) / \text{\AA}$	[1.3119] <sup>a</sup>	1.3096(22)	1.3092	1.3131	1.3182
$r(\text{C}_2\text{-C}_3) / \text{\AA}$	[1.3812]	1.3566(57)	1.3859	1.3868	1.3856
$r(\text{C}_3\text{-C}_4) / \text{\AA}$	[1.3853]	1.3865(57)	1.3886	1.3889	1.3874
$r(\text{C}_2\text{-F}_7) / \text{\AA}$	[1.3349]		1.3334	1.3308	1.3279
$r(\text{C}_3\text{-F}_8) / \text{\AA}$	[1.3325]		1.3324	1.3270	1.3295
$r(\text{C}_4\text{-F}_9) / \text{\AA}$	[1.3289]		1.3253	1.3241	1.3223
$r(\text{N}_1\text{-C}_{12}) / \text{\AA}$	3.361(11) <sup>b</sup>	3.3530(34)	3.3057	3.2416	3.3918
$r(\text{N}_1\text{-O}_{13}) / \text{\AA}$	3.184(16)		3.1089	3.0572	3.1847
$r(\text{x-O}_{13}) / \text{\AA}$	3.024(14)		2.9580	2.8719	2.9768
$r(\text{x-N}_1) / \text{\AA}$	1.3806(16)		1.3775	1.3807	1.3806
$r(\text{N}_1\text{-H}_{14}) / \text{\AA}$	2.801(26)		2.7560	2.6869	2.8774
$r(\text{C}_{12}\text{-O}_{13}) / \text{\AA}$	[1.2091] <sup>c</sup>		1.2031	1.2158	1.2076
$r(\text{C}_{12}\text{-H}_{14}) / \text{\AA}$	[1.1174]		1.1065	1.1001	1.1042
$r(\text{C}_{12}\text{-H}_{15}) / \text{\AA}$	[1.1164]		1.1065	1.0991	1.1037
$\angle \text{N}_1\text{-C}_2\text{-C}_3 / ^\circ$	[124.23]	124.86(17)	123.7	123.9	124.0
$\angle \text{C}_2\text{-C}_3\text{-C}_4 / ^\circ$	[117.43]	117.15(40)	117.3	117.4	117.4
$\angle \text{C}_3\text{-C}_4\text{-C}_5 / ^\circ$	[119.12]	119.04(75)	119.3	119.3	119.2
$\angle \text{C}_2\text{-N}_1\text{-C}_6 / ^\circ$	[117.55]	116.94(23)	118.5	118.1	117.9
$\angle \text{F}_7\text{-C}_2\text{-N}_1 / ^\circ$	[117.07]		117.5	117.4	117.3
$\angle \text{F}_8\text{-C}_3\text{-C}_2 / ^\circ$	[122.06]		122.0	122.1	121.9
$\angle \text{F}_9\text{-C}_4\text{-C}_3 / ^\circ$	[120.44]		120.4	120.3	120.4
$\angle \text{C}_{12}\text{-N}_1\text{-C}_4 / ^\circ$	91.48(13)	92.25(40)	92.2	91.2	91.2
$\angle \text{O}_{13}\text{-C}_{12}\text{-N}_1 / ^\circ$	71.20(89)		70.1	70.4	67.9
$\angle \text{O}_{13}\text{-N}_1\text{-C}_4 / ^\circ$	70.41(65)		70.8	69.1	70.3
$\angle \text{x-O}_{13}\text{-C}_{12} / ^\circ$	113.3(1.1)		114.7	114.3	117.2
$\angle \text{O}_{13}\text{-x-N}_1 / ^\circ$	84.04(18)		80.8	82.5	82.0
$\angle \text{O}_{13}\text{-C}_{12}\text{-H}_{14} / ^\circ$	[122.47]		121.6	121.3	121.5
$\angle \text{O}_{13}\text{-C}_{12}\text{-H}_{15} / ^\circ$	[122.59]		121.7	121.4	121.5
$\angle \text{H}_{14}\text{-N}_1\text{-C}_4 / ^\circ$	109.62(52)		110.5	109.7	109.2

<sup>a</sup> Values in square brackets were kept fixed in the  $r_0$  fitting. <sup>b</sup> 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 C<sub>5</sub>F<sub>5</sub>N···CH<sub>2</sub>O and C<sub>5</sub>H<sub>5</sub>N···CH<sub>2</sub>O complexes.

Complex	Elect.	Exch.	Induct.	Dispers.	HF	SAPT
C <sub>5</sub> F <sub>5</sub> N···CH <sub>2</sub> O	-17.1	19.6	-2.0	-16.8	-1.2	-17.5
C <sub>5</sub> H <sub>5</sub> N···CH <sub>2</sub> O	-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	1	2106.6704	-0.0003
4	3	1	4	2	2	3	4	2185.5652	-0.0025
						5	4	2185.7570	-0.0031
						4	4	2186.5119	0.0021
						5	5	2187.2094	0.0002
						3	3	2187.3891	0.0000
						4	5	2187.9501	-0.0085
						4	3	2188.3411	0.0099
5	3	2	5	2	3	4	4	2358.8587	-0.0204
						6	6	2358.9102	0.0093
						5	5	2359.0071	0.0001
4	2	2	4	1	3	3	4	2362.7641	0.0000
						5	4	2363.1341	-0.0025
						3	3	2363.5151	-0.0008
						5	5	2363.7353	0.0004
						4	4	2364.5851	-0.0004
						4	5	2365.1873	0.0035
						4	3	2365.3333	-0.0040
						4	3	2461.4628	0.0000
3	3	0	3	2	1	3	3	2461.4628	0.0000
						4	3	2461.8990	0.0010
						2	3	2462.0523	0.0015
						3	4	2462.6331	-0.0019
						4	4	2463.0713	0.0010
						2	2	2463.6346	0.0015
						2	1	2574.4218	0.0029
						2	3	2574.7738	-0.0009
2	2	1	2	1	2	2	2	2575.4085	0.0005
						3	3	2575.4085	0.0005
						1	1	2575.4085	0.0005
						3	2	2576.0448	-0.0006
						1	2	2576.3982	0.0011
						2	2	2687.1778	0.0007
						4	4	2687.7431	0.0005
						4	3	2688.2551	-0.0041
3	1	2	3	0	3	3	2	2688.6598	0.0010
						3	4	2688.8448	0.0046
						3	3	2689.3568	0.0000
						3	3	2689.3568	0.0000
						1	0	2765.8686	-0.0013
						3	2	2767.6213	-0.0039
						2	1	2768.7665	-0.0011
2	0	2	1	1	1	1	1	2768.8363	0.0011
						1	1	2768.8363	0.0011

**Table S17 (Continued).**

<b>J'</b>	<b>K<sub>-1</sub>'</b>	<b>K<sub>+1</sub>'</b>	<b>J''</b>	<b>K<sub>-1</sub>''</b>	<b>K<sub>+1</sub>''</b>	<b>F'</b>	<b>F''</b>	<b>Obs.</b>	<b>Obs.-Cal.</b>
6	4	2	6	3	3	6	6	2881.6016	0.0015
						7	7	2882.1014	0.0003
						5	5	2882.1869	0.0012
7	4	3	7	3	4	8	8	3058.3174	0.0094
						7	7	3058.4443	0.0073
6	3	3	6	2	4	5	6	3160.4495	-0.0018
						7	6	3160.7304	0.0178
						5	5	3161.4501	0.0002
						7	7	3161.5678	0.0008
						6	6	3162.2610	0.0009
						6	7	3163.1179	0.0034
						6	5	3163.2398	-0.0186
5	4	1	5	3	2	5	5	3241.9377	0.0000
						6	6	3243.0324	0.0029
						4	4	3243.2508	-0.0013
						5	4	3243.5908	-0.0087
4	2	3	3	3	0	3	2	3250.9850	0.0015
						3	4	3251.1463	0.0101
						4	3	3251.6730	0.0026
3	3	1	3	2	2	3	3	3278.6178	0.0001
						3	4	3278.6178	0.0001
						4	3	3279.2638	0.0008
						4	4	3279.2638	0.0008
						2	2	3279.4896	0.0008
						2	3	3279.4896	0.0008
						2	1	3349.9291	0.0000
2	1	2	1	0	1	2	2	3350.5171	-0.0018
						1	1	3350.9210	-0.0024
						3	2	3351.1566	-0.0008
						1	2	3351.5118	-0.0015
						1	0	3352.3967	-0.0011
						3	2	3370.8059	0.0003
3	2	2	3	1	3	2	2	3370.8059	0.0003
						3	4	3371.0414	0.0004
						4	4	3371.0414	0.0004
						3	3	3371.7119	-0.0014
						4	3	3371.7119	-0.0014
						2	3	3371.7119	-0.0014
						8	5	3	8
5	2	3	5	1	4	9	9	3544.0561	0.0092
						4	5	3616.9719	0.0066
						4	4	3617.1414	-0.0001
						6	6	3617.3728	0.0012
						5	5	3618.4994	0.0001

**Table S17 (Continued).**

<b>J'</b>	<b>K<sub>-1</sub>'</b>	<b>K<sub>+1</sub>'</b>	<b>J''</b>	<b>K<sub>-1</sub>''</b>	<b>K<sub>+1</sub>''</b>	<b>F'</b>	<b>F''</b>	<b>Obs.</b>	<b>Obs.-Cal.</b>
9	5	4	9	4	5	8	8	3741.2299	0.0123
						10	10	3741.2299	0.0123
4	4	0	4	3	1	4	4	3755.8963	-0.0002
						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).**

<b>J'</b>	<b>K<sub>-1</sub>'</b>	<b>K<sub>+1</sub>'</b>	<b>J''</b>	<b>K<sub>-1</sub>''</b>	<b>K<sub>+1</sub>''</b>	<b>F'</b>	<b>F''</b>	<b>Obs.</b>	<b>Obs.-Cal.</b>
3	1	2	2	2	1	2	1	4357.3277	-0.0008
						4	3	4358.0638	-0.0005
						2	2	4358.3107	-0.0017
						3	3	4359.1634	0.0015
4	2	3	4	1	4	3	2	4359.7949	0.0008
						3	3	4390.0597	0.0004
						4	3	4390.1581	0.0000
						5	5	4390.2827	0.0009
5	4	2	5	3	3	4	4	4391.1462	-0.0004
						5	5	4399.8660	0.0015
						6	6	4400.2100	0.0010
						4	4	4400.2818	0.0027
3	1	3	2	0	2	3	2	4476.0760	-0.0009
						4	3	4476.7063	0.0005
						2	1	4476.9172	-0.0005
						2	2	4476.9896	0.0044
7	3	4	7	2	5	6	6	4518.4606	0.0097
						8	8	4518.5905	0.0076
						7	7	4519.4991	0.0017
						4	4	4525.4309	0.0018
5	3	3	5	2	4	6	6	4525.5152	0.0026
						5	5	4525.9129	0.0010
						4	3	4553.2108	0.0000
						6	5	4553.4704	0.0036
6	5	1	6	4	2	5	4	4554.5464	0.0101
						6	6	4610.0565	0.0006
						7	7	4611.1342	0.0024
						5	5	4611.3146	0.0011
9	6	3	9	5	4	9	9	4651.7023	0.0069
						10	10	4652.4267	0.0096
						8	8	4652.5021	0.0042
						11	11	4711.6119	-0.0043
10	5	5	10	4	6	10	10	4712.1710	-0.0078
						5	5	4865.9668	-0.0008
						7	7	4865.9668	-0.0008
						6	6	4865.9668	-0.0008
2	2	1	1	1	0	2	1	5066.8679	0.0000
						2	2	5067.4623	-0.0012
						1	1	5067.8525	0.0006
						3	2	5068.0955	-0.0001
5	5	0	5	4	1	1	2	5068.4503	0.0028
						1	0	5069.3398	-0.0014
						5	5	5076.9153	0.0002
						6	6	5078.0428	-0.0007
						4	4	5078.2752	0.0020

**Table S17 (Continued).**

<b>J'</b>	<b>K<sub>-1</sub>'</b>	<b>K<sub>+1</sub>'</b>	<b>J''</b>	<b>K<sub>-1</sub>''</b>	<b>K<sub>+1</sub>''</b>	<b>F'</b>	<b>F''</b>	<b>Obs.</b>	<b>Obs.-Cal.</b>
6	2	4	6	1	5	5	5	5092.4221	0.0006
						5	6	5092.5899	0.0111
						6	6	5093.5772	0.0000
5	5	1	5	4	2	5	5	5254.1489	-0.0002
						6	6	5255.0308	0.0021
						4	4	5255.2099	0.0020
6	5	2	6	4	3	6	6	5265.2841	0.0047
						7	7	5265.8217	0.0027
						5	5	5265.9146	0.0045
4	2	2	3	3	1	3	2	5365.1460	0.0007
						5	4	5365.7451	0.0011
						3	3	5366.0075	-0.0092
						4	3	5367.8403	0.0021
9	4	5	9	3	6	8	8	5402.0646	-0.0010
						10	10	5402.1649	0.0108
						9	9	5402.9448	-0.0005
8	6	2	8	5	3	8	8	5407.6821	0.0034
						9	9	5408.5809	0.0095
						7	7	5408.6858	0.0019
5	1	4	5	0	5	4	4	5439.8626	0.0000
						6	6	5440.0735	0.0009
						5	6	5440.2309	0.0116
						5	5	5441.1009	-0.0009
7	5	3	7	4	4	7	7	5456.4011	0.0070
						8	8	5456.6240	0.0040
6	3	4	6	2	5	5	5	5523.9982	0.0011
						7	7	5524.0953	0.0019
						6	6	5524.6631	0.0016
5	2	4	5	1	5	4	4	5547.4041	0.0012
						6	6	5547.5775	0.0011
						5	5	5548.4368	-0.0019
4	0	4	3	1	3	4	4	5576.2260	0.0023
						4	3	5576.9090	0.0130
						5	4	5576.9693	-0.0068
						3	3	5577.8423	-0.0002
7	4	4	7	3	5	6	6	5618.2365	0.0063
						8	8	5618.2365	0.0063
						7	7	5618.5511	0.0050
4	1	4	3	0	3	4	4	5643.6225	0.0021
						4	3	5644.1391	0.0020
						5	4	5644.4002	-0.0060
						3	3	5645.1251	-0.0003



**Table S17 (Continued).**

<b>J'</b>	<b>K<sub>-1</sub>'</b>	<b>K<sub>+1</sub>'</b>	<b>J''</b>	<b>K<sub>-1</sub>''</b>	<b>K<sub>+1</sub>''</b>	<b>F'</b>	<b>F''</b>	<b>Obs.</b>	<b>Obs.-Cal.</b>
2	2	0	1	1	1	1	0	5741.0556	0.0005
						3	2	5742.8598	0.0021
						1	1	5744.0198	-0.0002
8	5	4	8	4	5	2	1	5744.0859	-0.0010
						7	7	5915.9931	0.0016
						9	9	5915.9931	0.0016
5	3	2	4	4	1	8	8	5915.9931	0.0016
						4	3	5916.3701	-0.0050
						6	5	5916.8521	0.0028
7	6	1	7	5	2	5	4	5918.9790	-0.0002
						7	7	6010.0545	0.0038
						8	8	6010.9255	0.0011
8	3	5	8	2	6	6	6	6011.0486	-0.0018
						7	7	6080.2263	-0.0051
						9	9	6080.3386	0.0052
10	7	3	10	6	4	8	8	6081.1497	0.0082
						10	10	6160.1627	-0.0087
						11	11	6160.9387	-0.0137
4	1	3	3	2	2	9	9	6161.0337	0.0029
						3	2	6281.1189	0.0008
						3	3	6281.1189	0.0008
8	6	3	8	5	4	3	4	6281.1189	0.0008
						5	4	6281.2732	0.0010
						4	3	6281.8717	0.0013
7	6	2	7	5	3	4	4	6281.8717	0.0013
						8	8	6286.4161	-0.0037
						7	7	6297.7760	-0.0003
3	2	2	2	1	1	8	8	6298.3919	0.0063
						6	6	6298.4697	-0.0037
						3	2	6313.0904	0.0008
6	6	0	6	5	1	2	2	6313.0904	0.0008
						3	3	6314.3608	0.0007
						4	3	6314.3608	0.0007
6	6	1	6	5	2	2	3	6314.3608	0.0007
						2	1	6315.0664	0.0000
						6	6	6333.5726	-0.0035
9	6	4	9	5	5	7	7	6334.4751	-0.0034
						5	5	6334.6325	0.0017
						6	6	6392.6635	-0.0040
9	6	4	9	5	5	7	7	6393.4937	0.0044
						5	5	6393.6268	-0.0011
						9	9	6467.8294	0.0029
8	6	4	9	5	5	10	10	6468.0127	0.0154
						8	8	6468.0127	0.0154

**Table S17 (Continued).**

<b>J'</b>	<b>K<sub>-1</sub>'</b>	<b>K<sub>+1</sub>'</b>	<b>J''</b>	<b>K<sub>-1</sub>''</b>	<b>K<sub>+1</sub>''</b>	<b>F'</b>	<b>F''</b>	<b>Obs.</b>	<b>Obs.-Cal.</b>
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
						7	7	6673.9061	-0.0017
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

**Table S17 (Continued).**

<b>J'</b>	<b>K<sub>-1</sub>'</b>	<b>K<sub>+1</sub>'</b>	<b>J''</b>	<b>K<sub>-1</sub>''</b>	<b>K<sub>+1</sub>''</b>	<b>F'</b>	<b>F''</b>	<b>Obs.</b>	<b>Obs.-Cal.</b>
8	7	2	8	6	3	8	8	7426.5922	-0.0102
						9	9	7427.2156	0.0077
						7	7	7427.2846	0.0004
11	7	5	11	6	6	11	11	7445.4378	-0.0156
						12	12	7445.5789	-0.0027
						10	10	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	8	8	7564.4259	0.0059
						4	3	7752.1220	0.0033
						6	5	7752.3534	0.0028
9	4	6	9	3	7	5	4	7753.5214	0.0050
						10	10	7763.9996	-0.0125
						9	9	7764.4740	-0.0152
8	2	6	8	1	7	7	7	7847.1356	-0.0029
						9	9	7847.2200	0.0015
						7	7	7895.0730	-0.0129
8	3	6	8	2	7	9	9	7895.1644	0.0048
						8	8	7895.7396	-0.0037
						4	3	7897.2853	0.0037
5	1	4	4	2	3	6	5	7897.2853	0.0037
						5	4	7897.3562	0.0031
						6	5	8099.4284	0.0016
6	0	6	5	1	5	5	4	8099.5148	0.0156
						7	6	8099.5148	0.0156
						6	5	8103.0840	0.0017
6	1	6	5	0	5	5	4	8103.1731	0.0100
						7	6	8103.1731	0.0100
						3	2	8151.0870	-0.0017
3	3	1	2	2	0	4	3	8151.7745	-0.0029
						2	1	8152.0233	-0.0037
						5	4	8335.6130	-0.0032
5	2	4	4	1	3	6	5	8336.2406	-0.0006
						4	3	8336.3947	-0.0081
						3	1	8453.6491	-0.0054
3	3	0	2	2	1	4	3	8453.8494	-0.0041
						3	2	8454.0455	-0.0049
						2	2	8454.6342	-0.0042
3	2	1	2	1	2	2	1	8565.4128	-0.0115
						4	3	8566.1842	-0.0060
						3	2	8567.9943	-0.0066
6	1	5	5	2	4	6	5	9289.7962	-0.0020
						7	6	9289.9078	-0.0042
						5	4	9289.9078	-0.0042

**Table S17 (Continued).**

<b>J'</b>	<b>K<sub>-1</sub>'</b>	<b>K<sub>+1</sub>'</b>	<b>J''</b>	<b>K<sub>-1</sub>''</b>	<b>K<sub>+1</sub>''</b>	<b>F'</b>	<b>F''</b>	<b>Obs.</b>	<b>Obs.-Cal.</b>
7	0	7	6	1	6	6	5	9346.8536	0.0003
						8	7	9346.8536	0.0003
7	1	7	6	0	6	6	5	9347.6198	0.0018
						8	7	9347.6198	0.0018
6	2	5	5	1	4	6	5	9431.1216	-0.0099
						7	6	9431.4506	-0.0081
						5	4	9431.5004	-0.0190
4	3	2	3	2	1	4	3	9475.4592	-0.0098
						5	4	9476.5255	-0.0071
						3	2	9476.9102	-0.0049
6	2	4	5	3	3	5	4	9856.9043	-0.0089
						7	6	9856.9686	-0.0131
						6	5	9857.4552	-0.0084

**Table S18.** Observed rotational transitions and residuals (all the values in MHz) for the  $^{15}\text{N}_1$  isotopologue of pentafluoropyridine molecule in the ground vibrational state.

$J'$	$K_{-1}'$	$K_{+1}'$	$J''$	$K_{-1}''$	$K_{+1}''$	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  $^{13}\text{C}_2$  isotopologue of pentafluoropyridine molecule in the ground vibrational state. (see Table S13 for atom labelling).

$J'$	$K_{-1}'$	$K_{+1}'$	$J''$	$K_{-1}''$	$K_{+1}''$	$F'$	$F''$	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	3	4233.7881	-0.0040
3	0	3	2	1	2	2	1	4234.1339	-0.0004
						4	3	4234.3072	-0.0015
						3	2	4234.4286	-0.0019
						2	2	4235.1271	-0.0015
						2	1	4345.6692	-0.0079
3	1	2	2	2	1	4	3	4346.4074	-0.0056
						3	2	4348.1398	-0.0029
						2	2	4378.2231	-0.0003
4	2	3	4	1	4	5	5	4378.4480	0.0020
						4	4	4379.3077	-0.0031
						5	5	4387.9016	0.0019
						6	6	4388.2356	-0.0085
5	4	2	5	3	3	4	4	4388.3173	0.0029
						3	2	4464.0080	-0.0021
						4	3	4464.6379	-0.0011
						2	1	4464.8486	-0.0023
5	3	3	5	2	4	2	2	4464.9215	0.0030
						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
						6	6	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).**

<b>J'</b>	<b>K<sub>-1</sub>'</b>	<b>K<sub>+1</sub>'</b>	<b>J''</b>	<b>K<sub>-1</sub>''</b>	<b>K<sub>+1</sub>''</b>	<b>F'</b>	<b>F''</b>	<b>Obs.</b>	<b>Obs.-Cal.</b>
5	1	4	5	0	5	4	4	5425.2332	0.0026
						6	6	5425.4385	-0.0018
						5	5	5426.4649	-0.0046
6	3	4	6	2	5	7	7	5509.1941	-0.0127
						6	6	5509.7805	0.0056
5	2	4	5	1	5	4	4	5532.4577	-0.0030
						6	6	5532.6362	0.0018
						5	5	5533.4979	0.0012
4	0	4	3	1	3	4	3	5561.8941	0.0109
						3	2	5561.9540	0.0061
						5	4	5561.9540	0.0061
4	1	4	3	0	3	4	4	5628.4051	-0.0102
						4	3	5628.9311	-0.0008
						5	4	5629.1934	-0.0156
						3	2	5629.1934	-0.0156
						3	3	5629.9256	0.0052
						2	0	5725.5661	0.0021
2	2	0	1	1	1	3	2	5727.3680	0.0013
						1	1	5728.5257	-0.0033
						2	1	5728.5955	-0.0004
						3	2	6264.2657	-0.0004
						3	3	6264.2657	-0.0004
4	1	3	3	2	2	5	4	6264.4214	0.0011
						4	3	6265.0176	-0.0008
						4	4	6265.0176	-0.0008
						3	2	6296.0432	0.0014
						2	2	6296.0432	0.0014
						3	3	6297.3127	0.0005
						4	3	6297.3127	0.0005
						2	1	6298.0180	-0.0005
7	2	5	7	1	6	6	6	6498.6583	0.0087
						8	8	6498.7667	0.0058
						7	7	6499.5263	-0.0058
5	0	5	4	1	4	5	4	6828.9615	0.0012
						6	5	6829.0694	0.0124
5	1	5	4	0	4	5	4	6845.3838	0.0041
						4	3	6845.5170	0.0057
						6	5	6845.5170	0.0057
4	2	3	3	1	2	4	3	7326.0986	0.0005
						5	4	7327.1174	0.0008
						6	5	7327.4838	0.0031
5	2	3	4	3	2	4	3	7731.4038	0.0044
						6	4	7731.6292	-0.0020
						5	2	7732.7949	-0.0019

**Table S19 (Continued).**

<b>J'</b>	<b>K<sub>-1</sub>'</b>	<b>K<sub>+1</sub>'</b>	<b>J''</b>	<b>K<sub>-1</sub>''</b>	<b>K<sub>+1</sub>''</b>	<b>F'</b>	<b>F''</b>	<b>Obs.</b>	<b>Obs.-Cal.</b>
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  $^{13}\text{C}_3$  isotopologue of pentafluoropyridine molecule in the ground vibrational state. (see Table S13 for atom labelling).

$J'$	$K_{-1}'$	$K_{+1}'$	$J''$	$K_{-1}''$	$K_{+1}''$	$F'$	$F''$	Obs.	Obs.-Cal.
2	1	2	1	0	1	2	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	2	2	3368.1897	-0.0066
						4	4	3368.4323	0.0008
						3	3	3369.1013	-0.0015
4	1	3	4	0	4	3	3	4061.9855	-0.0032
						5	5	4062.3393	0.0014
						4	4	4063.7027	0.0088
3	0	3	2	1	2	2	1	4235.2075	-0.0003
						4	3	4235.3826	-0.0009
						3	2	4235.5086	0.0000
3	1	2	2	2	1	2	1	4335.6529	-0.0197
						4	3	4336.4127	0.0028
						3	2	4338.1459	0.0023
4	2	3	4	1	4	5	5	4383.1148	0.0077
						4	4	4383.9699	-0.0020
						3	2	4469.1710	-0.0022
3	1	3	2	0	2	3	2	4469.1710	-0.0022
						4	3	4469.8052	0.0000
						2	1	4470.0190	-0.0001
						2	2	4470.0862	0.0057
						4	4	4521.5258	-0.0080
5	3	3	5	2	4	4	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	4868.1816	0.0151
6	4	3	6	3	4	5	5	4868.1816	0.0151
						7	7	4868.1816	0.0151
						6	6	4868.1816	0.0151
2	2	1	1	1	0	2	1	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	7	7	5514.2254	-0.0031
						6	6	5514.7962	0.0005
5	2	4	5	1	5	4	4	5536.2350	-0.0044
						6	6	5536.4331	-0.0017
						5	5	5537.2871	-0.0017
4	0	4	3	1	3	4	3	5565.2331	0.0086
						5	4	5565.2963	-0.0071

**Table S20 (Continued).**

<b>J'</b>	<b>K<sub>-1</sub>'</b>	<b>K<sub>+1</sub>'</b>	<b>J''</b>	<b>K<sub>-1</sub>''</b>	<b>K<sub>+1</sub>''</b>	<b>F'</b>	<b>F''</b>	<b>Obs.</b>	<b>Obs.-Cal.</b>
4	1	4	3	0	3	4	3	5634.0043	0.0015
						5	4	5634.2663	-0.0159
						3	2	5634.2663	-0.0159
2	2	0	1	1	1	1	0	5733.4373	-0.0025
						3	2	5735.2425	0.0020
						2	1	5736.4659	0.0003
4	1	3	3	2	2	3	2	6259.0601	0.0063
						3	3	6259.0601	0.0063
						5	4	6259.2102	0.0003
						4	3	6259.8203	0.0049
						4	4	6259.8203	0.0049
3	2	2	2	1	1	3	2	6307.4117	0.0005
						2	2	6307.4117	0.0005
						3	3	6308.6809	-0.0007
						4	3	6308.6809	-0.0007
						2	1	6309.3855	-0.0024
5	0	5	4	1	4	5	4	6833.8083	0.0020
						6	5	6833.9173	0.0144
5	1	5	4	0	4	5	4	6850.7887	0.0049
						4	3	6850.9212	0.0048
						6	5	6850.9212	0.0048
4	2	3	3	1	2	4	3	7338.3190	0.0001
						5	4	7339.3393	-0.0006
						3	2	7339.7040	-0.0011
3	3	1	2	2	0	4	3	8147.3185	-0.0025
						3	2	8146.6246	-0.0108

**Table S21.** Observed rotational transitions and residuals (all the values in MHz) for the  $^{13}\text{C}_4$  isotopologue of pentafluoropyridine molecule in the ground vibrational state. (see Table S13 for atom labelling).

$J'$	$K_{-1}'$	$K_{+1}'$	$J''$	$K_{-1}''$	$K_{+1}''$	$F'$	$F''$	Obs.	Obs.-Cal.
2	1	2	1	0	1	2	1	3341.7957	-0.0028
						3	2	3343.0229	-0.0038
3	0	3	2	1	2	2	1	4242.0947	0.0091
						4	3	4242.2660	0.0077
						3	2	4242.3825	0.0070
3	1	3	2	0	2	3	2	4466.8207	-0.0063
						4	3	4467.4453	-0.0063
						2	1	4467.6545	-0.0064
2	2	1	1	1	0	2	1	5049.9267	0.0029
						2	2	5050.5234	0.0040
						1	1	5050.9145	0.0067
						3	2	5051.1536	0.0021
						1	0	5052.4015	0.0043
6	2	4	6	1	5	5	5	5098.9030	-0.0044
						7	7	5099.0737	0.0003
4	0	4	3	1	3	4	3	5569.6725	0.0140
						5	4	5569.7347	-0.0056
4	1	4	3	0	3	4	3	5634.4900	-0.0007
						5	4	5634.7505	-0.0066
3	2	2	2	1	1	3	2	6294.2833	-0.0002
						2	2	6294.2833	-0.0002
						3	3	6295.5548	0.0008
						4	3	6295.5548	0.0008
						2	1	6296.2571	-0.0032
5	1	5	4	0	4	5	4	6853.1902	0.0000
						4	3	6853.3184	-0.0022
						6	5	6853.3184	-0.0022
4	2	3	3	1	2	4	3	7325.4767	-0.0071
						5	4	7326.4962	-0.0025
						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  $0^+$  ( $v=0$ ) and  $0^-$  ( $v=1$ ) torsion states.

$J'$	$K_{-1}'$	$K_{+1}'$	$J''$	$K_{-1}''$	$K_{+1}''$	$v$	$F'$	$F''$	Obs.	Obs.-Cal.	
2	0	2	1	1	1	0	1	0	2406.9517	-0.0144	
							3	2	2408.0715	0.0066	
							2	1	2408.7670	0.0039	
						1	1	0	2406.8766	0.0046	
							3	2	2407.9693	-0.0013	
							2	1	2408.6606	-0.0083	
2	1	2	1	0	1	0	2	1	2445.5073	0.0029	
							3	2	2446.2717	0.0040	
							1	0	2447.2652	0.0137	
						1	2	1	2445.4466	-0.0010	
							3	2	2446.2087	-0.0023	
							1	0	2447.1968	0.0020	
2	2	1	1	1	0	1	2	1	2893.8910	-0.0080	
							3	2	2894.6879	-0.0051	
							1	0	2895.2699	-0.0158	
2	2	0	1	1	1	0	3	2	3245.4512	0.0015	
							1	3	3245.3772	0.0069	
							2	1	3246.1758	-0.0002	
3	0	3	2	1	2	0	4	3	3537.4203	0.0023	
							3	2	3537.4203	0.0023	
							1	4	3	3537.3076	0.0024
						1	3	2	3537.3076	0.0024	
							4	3	3541.8814	0.0000	
							2	1	3541.9328	0.0152	
3	1	3	2	0	2	0	3	2	3541.7836	0.0081	
							1	4	3	3541.7836	0.0081
							2	1	3541.7836	0.0081	
						1	3	2	3541.6428	-0.0006	
							2	1	3883.1054	-0.0018	
							4	3	3883.5605	-0.0026	
3	2	2	2	2	1	0	3	2	3884.4901	-0.0015	
							1	2	1	3882.9183	-0.0006
							4	3	3883.3741	-0.0008	
						1	3	2	3884.3035	-0.0001	
							3	2	4004.8519	-0.0007	
							4	3	4005.6628	0.0045	
3	3	1	2	2	0	0	2	1	4006.1034	-0.0027	
							1	3	2	4004.7875	-0.0028
							4	3	4005.5935	-0.0024	
						1	2	1	4006.0427	-0.0011	
							3	2	4468.6124	0.0000	
							4	3	4469.3163	0.0015	
3	3	1	2	2	0	0	2	1	4469.5741	0.0030	

**Table S22 (Continued).**

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

**Table S22 (Continued).**

<b>J'</b>	<b>K<sub>1</sub>'</b>	<b>K<sub>+1</sub>'</b>	<b>J''</b>	<b>K<sub>1</sub>''</b>	<b>K<sub>+1</sub>''</b>	<b>v</b>	<b>F'</b>	<b>F''</b>	<b>Obs.</b>	<b>Obs.-Cal.</b>
5	0	5	4	1	4	0	5	4	5761.3293	0.0013
							6	5	5761.3568	0.0010
						1	5	4	5761.1505	0.0031
							6	5	5761.1769	0.0018
						0	4	3	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
						0	4	3	5761.3789	0.0046
							6	5	5761.3789	0.0046
						1	4	3	5761.1981	0.0044
							6	5	5761.1981	0.0044
4	4	1	3	3	0	0	4	4	6053.0397	-0.0034
						1	4	4	6053.0397	-0.0034
						0	4	3	6053.1515	-0.0080
						1	4	3	6053.1515	-0.0080
						0	5	4	6053.7314	-0.0059
						1	5	4	6053.7314	-0.0059
						0	3	2	6053.8682	-0.0064
						1	3	2	6053.8682	-0.0064
4	4	0	3	3	0	0	4	3	6139.9469	0.0004
							5	4	6140.1482	-0.0008
							3	2	6140.1897	-0.0004
						1	4	3	6139.8663	0.0006
							5	4	6140.0677	-0.0006
							3	2	6140.1110	0.0016
5	1	4	4	2	3	0	5	4	6173.8002	0.0030
							6	5	6173.8530	-0.0028
							4	3	6173.8530	-0.0028
						1	5	4	6173.6083	-0.0034
							6	5	6173.6680	-0.0024
							4	3	6173.6680	-0.0024
5	2	4	4	1	3	0	5	4	6176.1382	-0.0005
							6	5	6176.2249	0.0000
							4	3	6176.2445	-0.0007
						1	5	4	6175.9599	0.0000
							6	5	6176.0460	0.0000
							4	3	6176.0644	-0.0019
4	4	1	3	3	1	0	3	2	6177.1275	0.0003
							4	3	6177.1275	0.0003
							5	4	6177.1745	0.0002
						1	3	2	6177.0575	0.0008
							4	3	6177.0575	0.0008
							5	4	6177.1041	0.0003

**Table S22 (Continued).**

<b>J'</b>	<b>K<sub>1</sub>'</b>	<b>K<sub>+1</sub>'</b>	<b>J''</b>	<b>K<sub>1</sub>''</b>	<b>K<sub>+1</sub>''</b>	<b>v</b>	<b>F'</b>	<b>F''</b>	<b>Obs.</b>	<b>Obs.-Cal.</b>	
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	
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	
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	
6	0	6	5	1	5	0	7	6	6872.2508	0.0006	
							6	5	6872.2309	0.0002	
							6	5	6872.2309	0.0002	
							5	4	6872.2444	-0.0009	
							5	4	6872.2444	-0.0009	
							6	5	6872.0145	0.0004	
							6	5	6872.0145	0.0004	
							5	4	6872.0269	-0.0018	
							5	4	6872.0269	-0.0018	
							7	6	6872.0346	0.0004	
6	1	6	5	0	5	1	7	6	6872.0346	0.0004	
							7	6	6872.0346	0.0004	
							0	7	6	6872.2524	0.0010
							5	4	7174.5688	0.0000	
							6	5	7175.3362	-0.0010	
5	4	2	5	3	1	0	4	3	7175.5360	-0.0006	
							4	3	7175.5360	-0.0006	

**Table S22 (Continued).**

<b>J'</b>	<b>K<sub>1</sub>'</b>	<b>K<sub>+1</sub>'</b>	<b>J''</b>	<b>K<sub>1</sub>''</b>	<b>K<sub>+1</sub>''</b>	<b>v</b>	<b>F'</b>	<b>F''</b>	<b>Obs.</b>	<b>Obs.-Cal.</b>
5	4	2	4	3	1	1	5	4	7174.5409	0.0008
							6	5	7175.3082	-0.0002
							4	3	7175.5074	-0.0004
6	1	5	5	2	4	0	6	5	7285.4906	-0.0062
							7	6	7285.5442	-0.0007
							5	4	7285.5546	0.0026
							1	6	7285.2773	-0.0007
							7	6	7285.3249	-0.0012
							5	4	7285.3338	0.0007
6	2	5	5	1	4	0	6	5	7285.6858	0.0001
							7	6	7285.7368	0.0006
							5	4	7285.7448	0.0012
							1	6	7285.4674	-0.0001
							7	6	7285.5188	0.0008
							5	4	7285.5266	0.0012
5	5	1	4	4	0	0	4	3	7640.8695	-0.0072
							5	4	7640.3647	-0.0042
							1	5	7640.3647	-0.0042
							0	6	7640.8018	0.0006
							1	6	7640.8018	0.0006
							4	3	7640.8702	0.0030
6	2	4	5	3	3	0	6	5	7695.8842	-0.0003
							7	6	7695.9239	-0.0003
							5	4	7695.9369	0.0011
							1	6	7695.6542	0.0001
							7	6	7695.6935	-0.0003
							5	4	7695.7068	0.0014
5	5	0	4	4	0	0	5	4	7696.1260	0.0008
							6	5	7696.3203	-0.0001
							4	3	7696.3415	-0.0015
							1	5	7696.0502	0.0002
							6	5	7696.2454	0.0001
							4	3	7696.2668	-0.0010
6	3	4	5	2	3	0	6	5	7705.3081	0.0031
							7	6	7705.4316	-0.0001
							5	4	7705.4605	-0.0001
							1	6	7705.1013	0.0009
							7	6	7705.2277	0.0005
							5	4	7705.2548	-0.0013
5	5	1	4	4	1	0	5	4	7727.1578	0.0027
							4	3	7727.1875	0.0007
							6	5	7727.2123	0.0000
							1	5	7727.0764	0.0005
							4	3	7727.1058	-0.0016
							6	5	7727.1325	-0.0005



**Table S22 (Continued).**

<b>J'</b>	<b>K<sub>1</sub>'</b>	<b>K<sub>+1</sub>'</b>	<b>J''</b>	<b>K<sub>1</sub>''</b>	<b>K<sub>+1</sub>''</b>	<b>v</b>	<b>F'</b>	<b>F''</b>	<b>Obs.</b>	<b>Obs.-Cal.</b>
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
							8	7	8396.3745	0.0002
							6	5	8396.3745	0.0002
						1	7	6	8396.0780	-0.0030
							6	5	8396.1201	0.0004
							8	7	8396.1201	0.0004
7	2	6	6	1	5	0	7	6	8396.3469	-0.0017
							6	5	8396.3921	0.0047
							8	7	8396.3921	0.0047
						1	7	6	8396.0947	0.0005
							6	5	8396.1378	0.0049
							8	7	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	7	6	9093.6690	0.0002
8	1	8	7	0	7	1	7	6	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
							7	6	10010.4305	-0.0005
							6	5	10011.1450	-0.0009
						1	5	4	10009.8470	0.0000
							7	6	10009.9639	0.0009
							6	5	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  $0^+$  ( $v=0$ ) and  $0^-$  ( $v=1$ ) torsion states. (see Table S15 for atom labelling).

$J'$	$K_{-1}'$	$K_{+1}'$	$J''$	$K_{-1}''$	$K_{+1}''$	$v$	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  $^{13}\text{C}_2$  isotopologue of pentafluoropyridine···formaldehyde adduct in the  $0^+$  ( $\nu=0$ ) and  $0^-$  ( $\nu=1$ ) torsion states. (see Table S15 for atom labelling).

$J'$	$K_{-1}'$	$K_{+1}'$	$J''$	$K_{-1}''$	$K_{+1}''$	$\nu$	$F'$	$F''$	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	-0.0020
							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	3	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	7271.3601	0.0074
							5	4	7271.3665	0.0068
						1	6	5	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	7271.5648	-0.0025
							5	4	7271.5735	-0.0014
						1	6	5	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	7681.4667	-0.0011
							5	4	7681.4789	-0.0002
						1	6	5	7681.1942	-0.0037
							7	6	7681.2355	-0.0007
							5	4	7681.2480	0.0005

**Table S24 (Continued).**

<b>J'</b>	<b>K<sub>1</sub>'</b>	<b>K<sub>+1</sub>'</b>	<b>J''</b>	<b>K<sub>1</sub>''</b>	<b>K<sub>+1</sub>''</b>	<b>v</b>	<b>F'</b>	<b>F''</b>	<b>Obs.</b>	<b>Obs.-Cal.</b>
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  $^{13}\text{C}_3$  isotopologue of pentafluoropyridine···formaldehyde adduct in the  $0^+$  ( $v=0$ ) and  $0^-$  ( $v=1$ ) torsion states. (see Table S15 for atom labelling).

$J'$	$K_{-1}'$	$K_{+1}'$	$J''$	$K_{-1}''$	$K_{+1}''$	$v$	$F'$	$F''$	Obs.	Obs.-Cal.
5	0	5	4	1	4	1	5	4	5751.5082	0.0023
							4	3	5751.5267	-0.0006
							6	5	5751.5336	0.0000
						0	5	4	5751.6897	-0.0014
							6	5	5751.7179	-0.0010
							4	3	5751.7142	0.0003
5	1	5	4	0	4	0	5	4	5751.7142	0.0003
							4	3	5751.7390	0.0021
							6	5	5751.7427	-0.0004
						1	5	4	5751.5295	-0.0002
							4	3	5751.5513	-0.0005
							6	5	5751.5589	0.0008
5	2	3	4	3	2	1	4	3	6543.4063	-0.0008
							6	5	6543.4407	-0.0013
							5	4	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	7272.4991	-0.0006
							5	4	7272.5071	0.0003
							6	5	7272.6676	-0.0011
6	2	5	5	1	4	1	7	6	7272.7165	-0.0033
							5	4	7272.7310	0.0035
							6	5	7681.0606	-0.0013
6	2	4	5	3	3	1	7	6	7681.1002	0.0003
							5	4	7681.1139	0.0027
							7	6	7969.8857	0.0037
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).**

<b>J'</b>	<b>K<sub>1</sub>'</b>	<b>K<sub>+1</sub>'</b>	<b>J''</b>	<b>K<sub>1</sub>''</b>	<b>K<sub>+1</sub>''</b>	<b>v</b>	<b>F'</b>	<b>F''</b>	<b>Obs.</b>	<b>Obs.-Cal.</b>
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	8381.4710	-0.0004
							8	7	8381.5071	-0.0019
							6	5	8381.5100	-0.0023
7	2	6	6	1	5	0	7	6	8381.7833	-0.0027
							6	5	8381.8279	0.0028
							8	7	8381.8279	0.0028
						1	7	6	8381.4867	-0.0003
							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  $^{13}\text{C}_4$  isotopologue of pentafluoropyridine...formaldehyde adduct in the  $0^+$  ( $v=0$ ) and  $0^-$  ( $v=1$ ) torsion states. (see Table S15 for atom labelling).

$J'$	$K_{-1}'$	$K_{+1}'$	$J''$	$K_{-1}''$	$K_{+1}''$	$v$	$F'$	$F''$	Obs.	Obs.-Cal.
5	2	3	4	3	2	1	4	3	6551.2377	-0.0025
							6	5	6551.2731	0.0036
							5	4	6551.4253	0.0009
6	0	6	5	1	5	0	6	5	6859.0675	-0.0003
6	1	6	5	0	5	0	6	5	6859.0675	-0.0003
6	0	6	5	1	5	0	5	4	6859.0804	-0.0017
6	1	6	5	0	5	0	5	4	6859.0804	-0.0017
6	0	6	5	1	5	0	7	6	6859.0893	0.0017
6	1	6	5	0	5	0	7	6	6859.0893	0.0017
6	0	6	5	1	5	1	6	5	6858.8500	-0.0023
6	1	6	5	0	5	1	6	5	6858.8500	-0.0023
6	0	6	5	1	5	1	5	4	6858.8642	-0.0024
6	1	6	5	0	5	1	5	4	6858.8642	-0.0024
6	0	6	5	1	5	1	7	6	6858.8726	0.0005
6	1	6	5	0	5	1	7	6	6858.8726	0.0005
6	1	5	5	2	4	1	6	5	7272.1935	-0.0015
							7	6	7272.2427	0.0002
							5	4	7272.2526	0.0034
6	2	5	5	1	4	1	6	5	7272.3409	0.0023
							7	6	7272.3903	0.0022
							5	4	7272.3967	0.0017
6	2	4	5	3	3	1	6	5	7683.2742	-0.0043
							7	6	7683.3151	-0.0062
							5	4	7683.3313	-0.0018
7	0	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
							8	7	8380.8349	0.0041
7	2	6	6	1	5	0	8	7	8380.8349	0.0041
							6	5	8380.8427	0.0036
							7	6	8380.8026	0.0034

**Table S26 (Continued).**

<b>J'</b>	<b>K<sub>1</sub>'</b>	<b>K<sub>+1</sub>'</b>	<b>J''</b>	<b>K<sub>1</sub>''</b>	<b>K<sub>+1</sub>''</b>	<b>v</b>	<b>F'</b>	<b>F''</b>	<b>Obs.</b>	<b>Obs.-Cal.</b>
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	7	1	9	8	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  $0^+$  ( $v=0$ ) and  $0^-$  ( $v=1$ ) torsion states. (see Table S15 for atom labelling).

$J'$	$K_{-1}'$	$K_{+1}'$	$J''$	$K_{-1}''$	$K_{+1}''$	$v$	$F'$	$F''$	Obs.	Obs.-Cal.
5	0	5	4	1	4	0	4	3	5711.2898	-0.0037
							6	5	5711.3012	0.0005
						1	5	4	5711.0933	-0.0021
							4	3	5711.1141	-0.0005
5	1	5	4	0	4	1	6	5	5711.1222	0.0009
							4	3	5711.1222	0.0009
						0	6	5	5711.1286	0.0009
							5	4	5711.1004	-0.0008
5	2	3	4	3	2	1	4	3	5711.2993	0.0000
							6	5	5711.3078	0.0013
						0	6	5	6510.5153	-0.0014
							5	4	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
						0	5	4	7219.7985	-0.0011
							6	5	7219.8030	0.0023
7	0	7	6	1	6	0	8	7	7914.2482	-0.0030
							7	6	7914.2482	-0.0030
						1	7	6	7913.9844	0.0004
							6	5	7913.9908	-0.0029
7	1	7	6	0	6	1	8	7	7913.9982	-0.0002
							7	6	7913.9844	0.0004
						0	7	6	7913.9844	0.0004
							6	5	7913.9908	-0.0029
7	0	7	6	1	6	1	8	7	7913.9982	-0.0002
							7	6	7913.9982	-0.0002
						1	7	6	7913.9982	-0.0002
							6	5	7913.9982	-0.0002

**Table S27 (Continued).**

<b>J'</b>	<b>K<sub>1</sub>'</b>	<b>K<sub>+1</sub>'</b>	<b>J''</b>	<b>K<sub>1</sub>''</b>	<b>K<sub>+1</sub>''</b>	<b>v</b>	<b>F'</b>	<b>F''</b>	<b>Obs.</b>	<b>Obs.-Cal.</b>
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
						1	6	5	8321.1704	0.0029
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