Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Nuclear quadrupole resonance supported by periodic quantum calculations: a sensitive tool for precise structural characterization of short hydrogen bonds.

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SUPPLEMENTARY INFORMATION

Gas phase model: impact of basis set and model Hamlitonian on computed NQCC values. In Table S1 and S2 are listed NQCC values computed with different basis sets and model chemistries (B3LYP vs. MP2). These calculations are performed on an isolated PANO molecule frozen in the experimental geometry measured by ND (ref. 18 in the text). Since this model completely disregards the effects of crystalline environment, its use is limited to the testing of computational settings. The tabulated results are briefly discussed in Section 3.2.

Table S1. NQCC values for selected PANO atoms (see Fig. 1) calculated with different basis sets with the B3LYP functional for an isolated PANO molecule in the experimental geometry. Experimental values are also listed.

Basis set	NQCC [kHz]		
	N	O_{don}	O_{acc}
6-31G	1316	7507	16739
6-31G(d)	1365	6882	15777
6-31G(d,p)	1358	6858	15831
6-31G(2d,2p)	1324	6599	15675
6-31G(3d,3p)	1421	6641	15747
6-31G(3df,3pd)	1368	6557	15627
6-31+G(d,p)	1468	6720	15729
6-31++G(d,p)	1471	6720	15735
6-31++G(3df,3pd)	1401	6383	15465
6-311G	1789	8745	18662
6-311G(d)	1605	7453	17532
6-311G(d,p)	1595	7417	17538
6-311G(2d,2p)	1558	7345	17382
6-311G(3d,3p)	1588	7158	17292
6-311G(3df,3pd)	1514	7008	17015
6-311+G(d,p)	1667	7140	17238
6-311++G(d,p)	1667	7140	17274
6-311++G(3df,3pd)	1572	6870	16793
cc-pVDZ	1252	7050	16204
cc-pVTZ	1486	6972	16907
cc-pVQZ	1580	6978	17088
cc-pV5Z	1606	7002	17166
aug-cc-pVDZ	1464	6629	15885
aug-cc-pVTZ	1522	6828	16739
aug-cc-pVQZ	1587	6918	17015
EXP.	**1886**	**6470**	**15320**

Table S2. NQCC values computed by the B3LYP and MP2 method and several basis sets for selected atoms of an isolated PANO molecule in the experimental geometry. Experimental NQCC values are also listed.

Basis set	NQCC [kHz]					
	N		O_{don}		O_{acc}	
	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
6-31G(d,p)	1358	1256	6858	6305	15831	15050
6-311G(d,p)	1595	1421	7417	6972	17538	17015
6-311++G(3df,3pd)	1572	1493	6870	6251	16793	15819
cc-pVDZ	1252	1088	7050	6503	16204	15621
cc-pVTZ	1486	1375	6972	6419	16907	16126
cc-pVQZ	1580	1494	6978	6389	17088	16144
EXP.	**1886**		**6470**		**15320**	

Gas phase vs. periodic model. Since DFT calculations can be performed with periodic boundary conditions at affordable cost, periodic DFT calculations represent an essential part of the modeling of

crystalline solids. Table S3 lists NQCC values computed by the isolated and the periodic model, all else being equal – that is, the same B3LYP functional, the same basis set and the same molecular geometry (measured by ND) were used in both models. The results are discussed in Section 3.2.

Table S3. Comparison of NQCC values computed by an isolated and periodic model of PANO using the B3LYP functional and various basis sets. Experimental values are also listed.

Basis set	NQCC [kHz]					
	N		O_{don}		O_{acc}	
	isolated	solid	isolated	solid	isolated	solid
6-31G	1316	1956	7507	7357	16739	16198
6-31G(d)	1365	1906	6882	6780	15777	15363
6-31G(d,p)	1358	1897	6858	6768	15831	15417
6-31G(2d,2p)	1324	1895	6599	6485	15675	15188
6-311G	1789	2474	8745	8294	18662	18067
6-311G(d)	1605	2238	7453	7273	17532	16967
6-311G(d,p)	1595	2224	7417	7237	17538	16979
6-311G(2d,2p)	1558	2172	7345	7146	17382	16781
cc-pVDZ	1252	1847	7050	6888	16204	15687
cc-pVTZ	1486	2083	6972	6870	16907	16366
EXP.	**1886**		**6470**		**15320**	

2D nuclear quantum treatment: potential energy surface. Figure S1 shows the potential energy surface computed for crystalline PANO by varying the proton location (R_{OH}) and donor…acceptor distance (R_{OO}). The surface is typical of very short, asymmetric H-bonds with single well potentials. Accordingly, proton dynamics features large-amplitude displacements with pronounced nuclear quantum effects and significant coupling with other degrees of freedom, in the first place donor…acceptor oscillations. Nuclear quantum treatment along herein used coordinates has been routinely used in short H-bonds, imposing substantial effects on geometry and other observables, as discussed in Section 3.2.

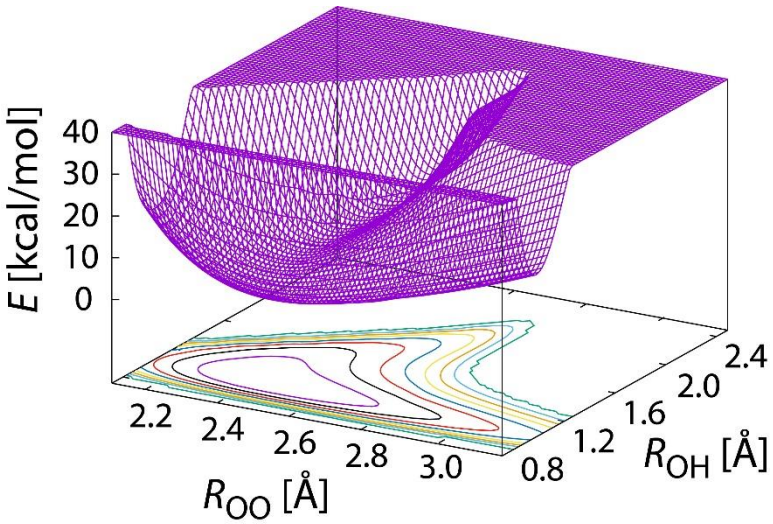

Figure S1. 2D potential energy surface in crystalline PANO computed at the B3LYP/6-31G(d,p) level along the O_{don}...O_{acc} (R_{OO}) and O_{don}—H (R_{OH}) distance. The resolution of contours is 5 kcal/mol.