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High-Resolution Synchrotron Terahertz Investigation of the Large-Amplitude Hydrogen Bond Librational Band of $(HCN)_2$

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SUPPLEMENTARY INFORMATION

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Table 1: Observed and Calculated Line Positions (Units of cm^{-1}) with Deviations and the Corresponding Rovibrational Assignments for the Observed ν_8^1 Band of $(HCN)_2$.

Observed	Calculated	Obs.–Calc.	Assignment
125.5700	125.5673	0.0027	R(50)
125.4320	125.4318	0.0002	R(49)
125.2960	125.2966	-0.0006	R(48)
125.1600	125.1617	-0.0017	R(47)
124.8920	124.8930	-0.0010	R(45)
124.7590	124.7592	-0.0002	R(44)
124.6240	124.6257	-0.0017	R(43)
124.4910	124.4926	-0.0016	R(42)
124.3600	124.3598	0.0002	R(41)
124.2270	124.2274	-0.0004	R(40)
124.0950	124.0953	-0.0003	R(39)
123.9640	123.9636	0.0004	R(38)
123.8323	123.8322	0.0001	R(37)
123.7030	123.7012	0.0018	R(36)
123.5710	123.5706	0.0004	R(35)
123.4410	123.4403	0.0007	R(34)
123.1810	123.1808	0.0002	R(32)
123.0510	123.0516	-0.0006	R(31)
122.9250	122.9227	0.0023	R(30)
122.7950	122.7942	0.0008	R(29)
122.6650	122.6661	-0.0011	R(28)
122.5370	122.5383	-0.0013	R(27)
122.4110	122.4109	0.0001	R(26)
122.2820	122.2839	-0.0019	R(25)
122.1570	122.1572	-0.0002	R(24)
122.0290	122.0309	-0.0019	R(23)
121.7760	121.7795	-0.0035	R(21)
121.6540	121.6543	-0.0003	R(20)
119.4805	119.4780	0.0025	Q(40)
119.4620	119.4602	0.0018	Q(39)
119.4430	119.4429	0.0001	Q(38)
119.4255	119.4260	-0.0005	Q(37)
119.4075	119.4096	-0.0021	Q(36)
119.3920	119.3936	-0.0016	Q(35)
119.3766	119.3781	-0.0015	Q(34)
119.3620	119.3630	-0.0010	Q(33)
119.3478	119.3483	-0.0005	Q(32)
119.3335	119.3342	-0.0007	Q(31)
119.3200	119.3204	-0.0004	Q(30)
119.3070	119.3072	-0.0002	Q(29)
119.2940	119.2943	-0.0003	Q(28)
119.2830	119.2819	0.0011	Q(27)
119.2700	119.2700	0.0000	Q(26)
119.2590	119.2585	0.0005	Q(25)

119.2485	119.2475	0.0010	Q(24)
119.2375	119.2369	0.0006	Q(23)
119.2270	119.2267	0.0003	Q(22)
119.2170	119.2170	0.0000	Q(21)
119.2090	119.2077	0.0013	Q(20)
119.2000	119.1989	0.0011	Q(19)
119.1920	119.1905	0.0015	Q(18)
119.1827	119.1826	0.0001	Q(17)
119.1750	119.1751	-0.0001	Q(16)
119.1680	119.1681	-0.0001	Q(15)
119.1600	119.1615	-0.0015	Q(14)
116.0150	116.0155	-0.0005	P(28)
115.9130	115.9114	0.0016	P(29)
115.8090	115.8077	0.0013	P(30)
115.7060	115.7044	0.0016	P(31)
115.6030	115.6017	0.0013	P(32)
115.5000	115.4994	0.0006	P(33)
115.3990	115.3976	0.0014	P(34)
115.2970	115.2963	0.0007	P(35)
115.1960	115.1955	0.0005	P(36)
114.9940	114.9954	-0.0014	P(38)
114.6990	114.6989	0.0001	P(41)

Table 2: Cartesian Coordinates (Å) for the CCSD(T)-F12b/aug-cc-pVQZ Optimized Geometries of HCN and $(HCN)_2$ with $C_{\infty V}$ Symmetry.

System	X	Y	Z
HCN	0.0	0.0	-3.8464938530
	0.0	0.0	-2.7798347168
	0.0	0.0	-1.6245812714
$(HCN)_2$	0.0	0.0	-3.8452184467
	0.0	0.0	-2.7779410151
	0.0	0.0	-1.6243343845
	0.0	0.0	2.8164101294
	0.0	0.0	1.6605333113
	0.0	0.0	0.5875299110

Table 3: The Predicted Absolute Electronic Energy E_{abs} (Units of Hartrees) for HCN and $(HCN)_2$ and Resulting Interaction Energies D_e (Units of kJ/mol) employing the CCSD(T) and CCSD(T)-F12b Methods with Dunning's Augmented Correlation-Consistent Basis Sets aug-cc-pV(T,Q,5,6)Z for CCSD(T)-F12b/aug-cc-pVQZ Geometries. The Complete Basis Set Limit (CBS) have been Calculated for the CCSD(T) Method.

Method	Basis Set	E_{abs} HCN	E_{abs} $(HCN)_2$	D_e
CCSD(T)-F12b	aug-cc-pVTZ	-93.3050358	-186.6178173	20.34
	aug-cc-pVQZ	-93.3121128	-186.6318676	20.06
	aug-cc-pV5Z	-93.3141756	-186.6359098	19.85
CCSD(T)	aug-cc-pVTZ	-93.2811176	-186.5704720	21.63
	aug-cc-pVQZ	-93.3034522	-186.6146783	20.41
	aug-cc-pV5Z	-93.3102516	-186.6280970	19.94
	aug-cc-pV6Z	-93.3126336	-186.6328338	19.87
	CBS(Q,5,6)	-93.3126592	-186.6328836	19.85

Table 4: The Predicted Harmonic Band Origins (Units of cm^{-1}) of the Vibrational Modes Associated with the Fundamental Transitions for HCN and $(HCN)_2$ at the CCSD(T)-F12b/aug-cc-pVQZ Level.

Normal mode	HCN	$(HCN)_2$
Acceptor Libration		48.02
CH···N Stretching		118.77
Donor Libration		137.18
HCN Bending	727.88	739.85
		814.20
CN Stretching	2127.07	2120.84
		2142.12
CH Stretching	3437.73	3356.45
		3435.01