NMR and X-ray Study Revealing the Rigidity of Zeolitic Imidazolate Frameworks (ZIFs)

Supplementary Material

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Section S1: Single crystal x-ray diffraction (SXRD) analysis of ZIF-8 and ZIF-4

Table S1.A. Crystal data and structure refinement for ZIF-8_298k.

Identification code	ZIF-8_298K	
Empirical formula	$C_{24}H_{30}N_{12}Zn_3$	
Formula weight	682.4	
Temperature	298(2) K	
Wavelength	1.54178 Å	
Crystal system	cubic	
Space group	I-43m	
Unit cell dimensions	a = 17.0095(8) Å	α= 90°.
	b = 17.0095(8) Å	β= 90°.
	c = 17.0095(8) Å	γ = 90°.
Volume	4921.2(4) $Å^3$	
Z	4	
Density (calculated)	0.921 Mg/m^3	
Absorption coefficient	1.879 mm^{-1}	
F(000)	1392	
Crystal size	0.20 x 0.20 x 0.20 mm^3	
Theta range for data collection	3.67 to 49.56°.	
Index ranges	-16<=h<=16, -16<=k<=16, -15<=l<=16	
Reflections collected	10627	
Independent reflections	500 [R(int) = 0.0362]	
Completeness to theta = 49.56∞	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7050 and 0.7050	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	500 / 0 / 34	
Goodness-of-fit on F^2	1.624	
Final R indices [I>2sigma(I)]	R1 = 0.0477, wR2 = 0.1595	
R indices (all data)	R1 = 0.0477, wR2 = 0.1595	
Absolute structure parameter	-0.04(11)	
Largest diff. peak and hole	0.964 and -0.262 e. $Å^{-3}$	

Table S1.B. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for ZIF-8_298k. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zn(1)	0	5000	7500	63(1)
N(1)	904(3)	5309(3)	8173(3)	67(1)
C(2)	1233(2)	4914(7)	8767(2)	62(2)
C(1)	1322(5)	6000(4)	8127(5)	86(2)
C(4)	949(5)	4128(6)	9051(5)	90(3)

Table S1.C. Bond lengths [Å] and angles [˚] for ZIF-8 (298 K).

Zn(1)-N(1)#1	1.987(5)
Zn(1)-N(1)#2	1.987(5)
Zn(1)-N(1)#3	1.987(5)
Zn(1)-N(1)	1.987(5)
N(1)-C(2)	1.337(8)
N(1)-C(1)	1.376(9)
C(2)-N(1)#4	1.337(8)
C(2)-C(4)	1.501(16)
C(1)-C(1)#4	1.325(14)
N(1)#1-Zn(1)-N(1)#2	109.39(16)
N(1)#1-Zn(1)-N(1)#3	109.6(3)
N(1)#2-Zn(1)-N(1)#3	109.39(16)
N(1)#1-Zn(1)-N(1)	109.39(16)
N(1)#2-Zn(1)-N(1)	109.6(3)
N(1)#3-Zn(1)-N(1)	109.38(16)
C(2)-N(1)-C(1)	104.8(6)
C(2)-N(1)-Zn(1)	128.8(5)
C(1)-N(1)-Zn(1)	126.4(5)
N(1)-C(2)-N(1)#4	112.4(9)
N(1)-C(2)-C(4)	123.8(4)
N(1)#4-C(2)-C(4)	123.8(4)
C(1)#4-C(1)-N(1)	109.0(4)

Symmetry transformations used to generate equivalent atoms:

#1 y-1/2,-x+1/2,-z+3/2 #2 -x,-y+1,z #3 -y+1/2,x+1/2,-z+3/2

#4 -z+1,y,-x+1

Table S1.D. Anisotropic displacement parameters ($Å^2$ x 10^3) for ZIF-8_298K. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zn(1)	65(1)	65(1)	59(1)	0	0	0
N(1)	71(3)	67(3)	64(3)	6(2)	-9(2)	-4(2)
C(2)	68(3)	50(5)	68(3)	-1(3)	6(4)	1(3)
C(1)	91(5)	71(4)	95(5)	25(4)	-21(3)	-12(4)
C(4)	98(5)	76(6)	98(5)	15(4)	-28(6)	-15(4)

Table S2.A. Crystal data and structure refinement for ZIF-8_240K.

Identification code	zif8_240k_0m	
Empirical formula	C24 H30 N12 O4 Zn3	
Formula weight	746.70	
Temperature	240(2) K	
Wavelength	1.54178 Å	
Crystal system	cubic	
Space group	I-43m	
Unit cell dimensions	a = 16.993(2) Å	α= 90°.
	b = 16.993(2) Å	β= 90°.
	c = 16.993(2) Å	γ = 90°.
Volume	4906.8(10) $Å^3$	
Z	4	
Density (calculated)	1.011 Mg/m^3	
Absorption coefficient	1.984 mm^{-1}	
F(000)	1520	
Crystal size	0.20 x 0.20 x 0.20 mm^3	
Theta range for data collection	3.68 to 43.94°.	
Index ranges	-15<=h<=15, -15<=k<=14, -15<=l<=15	
Reflections collected	8313	
Independent reflections	385 [R(int) = 0.0411]	
Completeness to theta = 43.94°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6924 and 0.6924	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	385 / 0 / 40	
Goodness-of-fit on F^2	1.393	
Final R indices [I>2sigma(I)]	R1 = 0.0510, wR2 = 0.1424	
R indices (all data)	R1 = 0.0512, wR2 = 0.1431	
Absolute structure parameter	0.07(12)	
Largest diff. peak and hole	0.556 and -0.260 $e.Å^{-3}$	

Table S2.B. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for zif-8-240k. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zn(1)	5000	2500	0	58(1)
N(1)	5895(4)	3169(4)	-327(4)	57(2)
C(1)	6234(3)	3766(3)	68(10)	53(3)
C(2)	5954(6)	4046(6)	856(7)	81(4)
C(4)	6304(5)	3135(6)	-1014(5)	73(3)
O(1)	6883(16)	3117(16)	6883(16)	235(18)
O(2)	8350(20)	1650(20)	8350(20)	500(60)

Table S2.C. Bond lengths [Å] and angles [°] for zif-8-240k.

Zn(1)-N(1)#1	1.979(6)
Zn(1)-N(1)#2	1.979(6)
Zn(1)-N(1)#3	1.979(6)
Zn(1)-N(1)	1.979(6)
N(1)-C(1)	1.345(9)
N(1)-C(4)	1.359(10)
C(1)-N(1)#4	1.345(9)
C(1)-C(2)	1.50(2)
C(4)-C(4)#4	1.349(16)
N(1)#1-Zn(1)-N(1)#2	109.8(4)
N(1)#1-Zn(1)-N(1)#3	109.3(2)
N(1)#2-Zn(1)-N(1)#3	109.3(2)
N(1)#1-Zn(1)-N(1)	109.3(2)
N(1)#2-Zn(1)-N(1)	109.3(2)
N(1)#3-Zn(1)-N(1)	109.8(4)
C(1)-N(1)-C(4)	104.0(9)
C(1)-N(1)-Zn(1)	128.5(6)
C(4)-N(1)-Zn(1)	127.5(6)
N(1)-C(1)-N(1)#4	113.4(12)

N(1)-C(1)-C(2)	123.3(6)
N(1)#4-C(1)-C(2)	123.3(6)
C(4)#4-C(4)-N(1)	109.3(5)

Symmetry transformations used to generate equivalent atoms:

#1 z+1/2,-y+1/2,-x+1/2 #2 -z+1/2,-y+1/2,x-1/2

#3 -x+1,y,-z #4 -y+1,-x+1,z

Table S2.D. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for zif-8-240k. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zn(1)	60(1)	55(1)	60(1)	0	0	0
N(1)	56(4)	53(4)	63(5)	-6(3)	7(3)	-6(3)
C(1)	54(4)	54(4)	51(7)	-2(5)	2(5)	4(6)
C(2)	88(5)	88(5)	66(9)	-8(6)	8(6)	-13(8)
C(4)	77(6)	89(6)	54(5)	-18(4)	8(5)	-22(4)
O(1)	235(18)	235(18)	235(18)	-30(20)	30(20)	-30(20)
O(2)	500(60)	500(60)	500(60)	130(50)	-130(50)	130(50)

Table S3.A. Crystal data and structure refinement for zif-8-200k.

Identification code	zif8_200k_0m	
Empirical formula	C24 H30 N12 O4 Zn3	
Formula weight	746.7	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	Cubic	
Space group	I-43m	
Unit cell dimensions	a = 16.9122(9) Å	α= 90°.
	b = 16.9122(9) Å	β= 90°.
	c = 16.9122(9) Å	γ = 90°.
Volume	4837.3(4) $Å^3$	
Z	4	
Density (calculated)	1.025 Mg/m^3	
Absorption coefficient	2.013 mm^{-1}	
F(000)	1520	
Crystal size	0.20 x 0.20 x 0.20 mm^3	
Theta range for data collection	3.70 to 53.13°.	
Index ranges	-17<=h<=15, -17<=k<=16, -17<=l<=15	
Reflections collected	10867	
Independent reflections	565 [R(int) = 0.0417]	
Completeness to theta = 53.13°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6890 and 0.6890	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	565 / 0 / 40	
Goodness-of-fit on F^2	1.391	
Final R indices [I>2sigma(I)]	R1 = 0.0513, wR2 = 0.1382	
R indices (all data)	R1 = 0.0513, wR2 = 0.1382	
Absolute structure parameter	-0.03(7)	
Largest diff. peak and hole	0.822 and -0.260 $e.Å^{-3}$	

Table S3.B. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for zif-8-200k. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zn(1)	5000	10000	2500	50(1)
N(1)	5894(3)	10332(2)	3178(2)	54(1)
C(1)	6295(4)	11048(3)	3147(4)	69(2)
C(2)	6235(2)	9929(6)	3765(2)	50(2)
C(4)	5971(4)	9132(5)	4029(4)	71(2)
O(2)	6896(10)	3104(10)	3104(10)	173(8)
O(1)	8440(40)	1560(40)	1560(40)	650(70)

Table S3.C. Bond lengths [Å] and angles [°] for zif-8-200k.

Zn(1)-N(1)#1	1.978(4)
Zn(1)-N(1)#2	1.978(4)
Zn(1)-N(1)#3	1.978(4)
Zn(1)-N(1)	1.978(4)
N(1)-C(2)	1.335(7)
N(1)-C(1)	1.390(7)
C(1)-C(1)#4	1.334(12)
C(2)-N(1)#4	1.335(7)
C(2)-C(4)	1.489(13)
N(1)#1-Zn(1)-N(1)#2	109.63(13)
N(1)#1-Zn(1)-N(1)#3	109.2(3)
N(1)#2-Zn(1)-N(1)#3	109.63(13)
N(1)#1-Zn(1)-N(1)	109.63(13)
N(1)#2-Zn(1)-N(1)	109.2(3)
N(1)#3-Zn(1)-N(1)	109.63(13)
C(2)-N(1)-C(1)	105.2(5)
C(2)-N(1)-Zn(1)	128.1(4)
C(1)-N(1)-Zn(1)	126.8(4)

C(1)#4-C(1)-N(1)	108.6(3)
N(1)-C(2)-N(1)#4	112.5(8)
N(1)-C(2)-C(4)	123.7(4)
N(1)#4-C(2)-C(4)	123.7(4)

Symmetry transformations used to generate equivalent atoms:

#1 y-1/2,-x+3/2,-z+1/2 #2 -x+1,-y+2,z #3 -y+3/2,x+1/2,-z+1/2

#4 -z+1,y,-x+1

Table S3.D. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for zif-8-200k. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zn(1)	51(1)	51(1)	47(1)	0	0	0
N(1)	57(2)	53(2)	53(2)	3(2)	-7(2)	-4(2)
C(1)	76(3)	55(3)	77(3)	14(3)	-22(3)	-8(3)
C(2)	54(2)	42(4)	54(2)	1(2)	3(3)	-1(2)
C(4)	74(3)	66(4)	74(3)	10(3)	-16(4)	-10(3)
O(2)	173(8)	173(8)	173(8)	22(11)	-22(11)	-22(11)
O(1)	650(70)	650(70)	650(70)	0(110)	0(110)	0(110)

Table S4.A. Crystal data and structure refinement for zif-8-100k.

Identification code	zif8_100k_0m	
Empirical formula	C24 H30 N12 O4 Zn3	
Formula weight	746.7	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Cubic	
Space group	I-43m	
Unit cell dimensions	a = 16.8509(3) Å	α= 90°.
	b = 16.8509(3) Å	β= 90°.
	c = 16.8509(3) Å	γ = 90°.
Volume	4784.86(15) $Å^3$	
Z	4	
Density (calculated)	1.037 Mg/m^3	
Absorption coefficient	2.035 mm^{-1}	
F(000)	1520	
Crystal size	0.20 x 0.20 x 0.20 mm^3	
Theta range for data collection	3.71 to 53.91°.	
Index ranges	-15<=h<=17, -17<=k<=15, -17<=l<=17	
Reflections collected	11078	
Independent reflections	573 [R(int) = 0.0358]	
Completeness to theta = 53.91°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6864 and 0.6864	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	573 / 0 / 40	
Goodness-of-fit on F^2	2.098	
Final R indices [I>2sigma(I)]	R1 = 0.0688, wR2 = 0.2089	
R indices (all data)	R1 = 0.0689, wR2 = 0.2090	
Absolute structure parameter	0.04(12)	
Largest diff. peak and hole	0.949 and -0.443 $e.Å^{-3}$	

Table S4.B. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for zif-8-100k. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zn(1)	5000	0	2500	50(1)
C(3)	6240(3)	53(10)	3760(3)	49(2)
N(1)	5883(4)	-357(3)	3173(4)	53(1)
C(1)	6276(5)	-1088(4)	3160(6)	63(2)
C(4)	5985(6)	861(6)	4015(6)	62(3)
O(1)	6920(11)	6920(11)	3080(11)	126(8)
O(2)	8160(30)	8160(30)	1840(30)	510(90)

Table S4.C. Bond lengths [Å] and angles [°] for zif-8-100k.

Zn(1)-N(1)	1.966(6)
Zn(1)-N(1)#1	1.966(6)
Zn(1)-N(1)#2	1.966(6)
Zn(1)-N(1)#3	1.966(6)
C(3)-N(1)	1.347(10)
C(3)-N(1)#4	1.347(10)
C(3)-C(4)	1.49(2)
N(1)-C(1)	1.399(10)
C(1)-C(1)#4	1.344(16)
N(1)-Zn(1)-N(1)#1	109.5(2)
N(1)-Zn(1)-N(1)#2	109.5(2)
N(1)#1-Zn(1)-N(1)#2	109.5(4)
N(1)-Zn(1)-N(1)#3	109.5(4)
N(1)#1-Zn(1)-N(1)#3	109.5(2)
N(1)#2-Zn(1)-N(1)#3	109.5(2)
N(1)-C(3)-N(1)#4	113.1(12)
N(1)-C(3)-C(4)	123.4(6)
N(1)#4-C(3)-C(4)	123.4(6)

C(3)-N(1)-C(1)	104.6(9)
C(3)-N(1)-Zn(1)	127.2(7)
C(1)-N(1)-Zn(1)	128.2(6)
C(1)#4-C(1)-N(1)	108.8(5)

Symmetry transformations used to generate equivalent atoms:

#1 y+1/2,-x+1/2,-z+1/2 #2 -y+1/2,x-1/2,-z+1/2

#3 -x+1,-y,z #4 -z+1,y,-x+1

Table S4.D. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for zif-8-100k. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zn(1)	51(1)	51(1)	50(1)	0	0	0
C(3)	53(3)	41(5)	53(3)	-1(4)	5(4)	1(4)
N(1)	56(3)	49(3)	54(3)	-2(3)	-7(3)	1(3)
C(1)	71(5)	46(4)	71(5)	-9(4)	-17(4)	7(4)
C(4)	64(4)	57(6)	64(4)	-5(4)	-10(6)	5(4)
O(1)	126(8)	126(8)	126(8)	-11(9)	-11(9)	11(9)
O(2)	510(90)	510(90)	510(90)	110(70)	110(70)	-110(70)

Section S2: Variable-contact-time ^{13}C CP/MAS analysis of ZIF-8 and ZIF-4

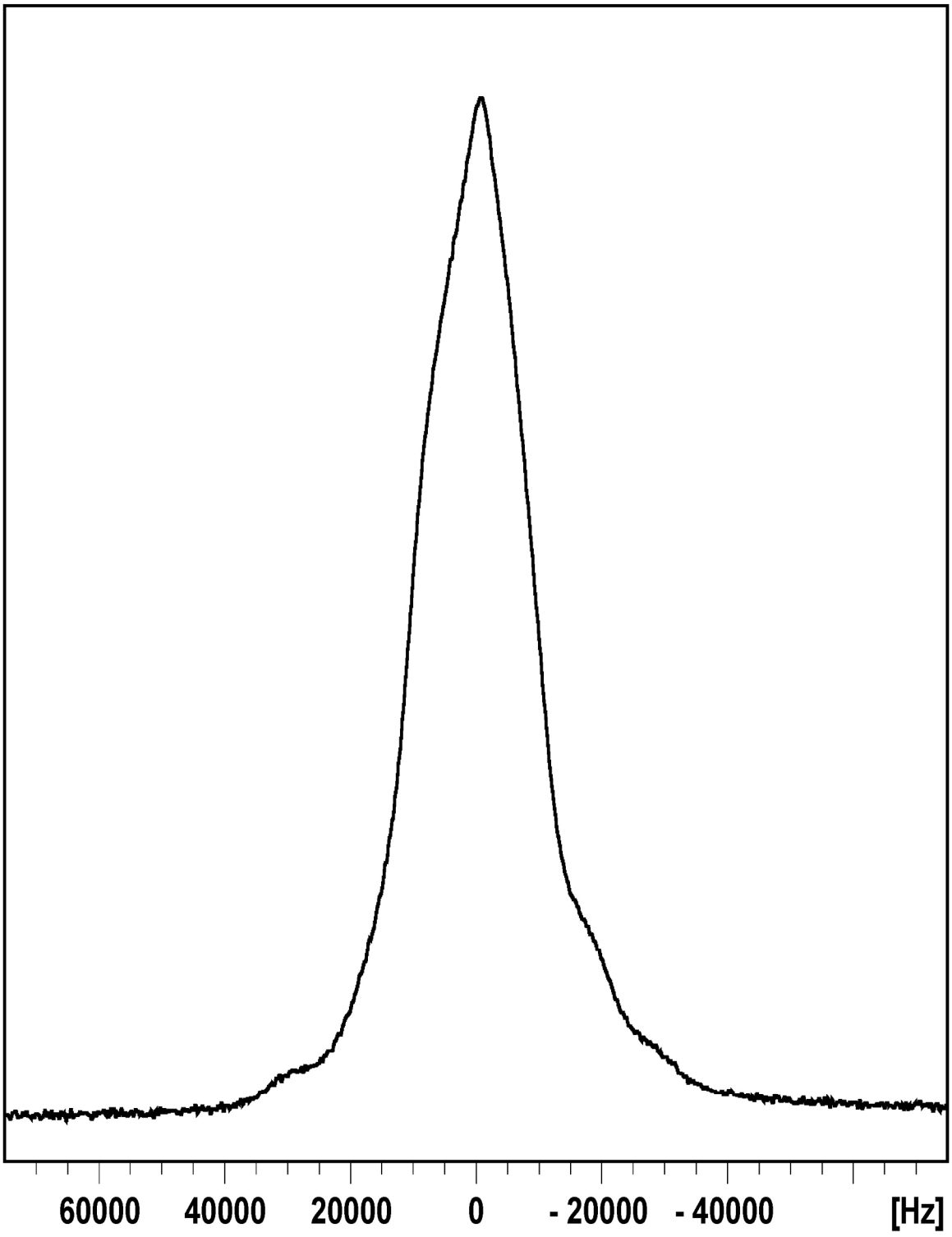

Figure S1. ^{1}H wideline NMR spectrum of ZIF-8 at 273 K.

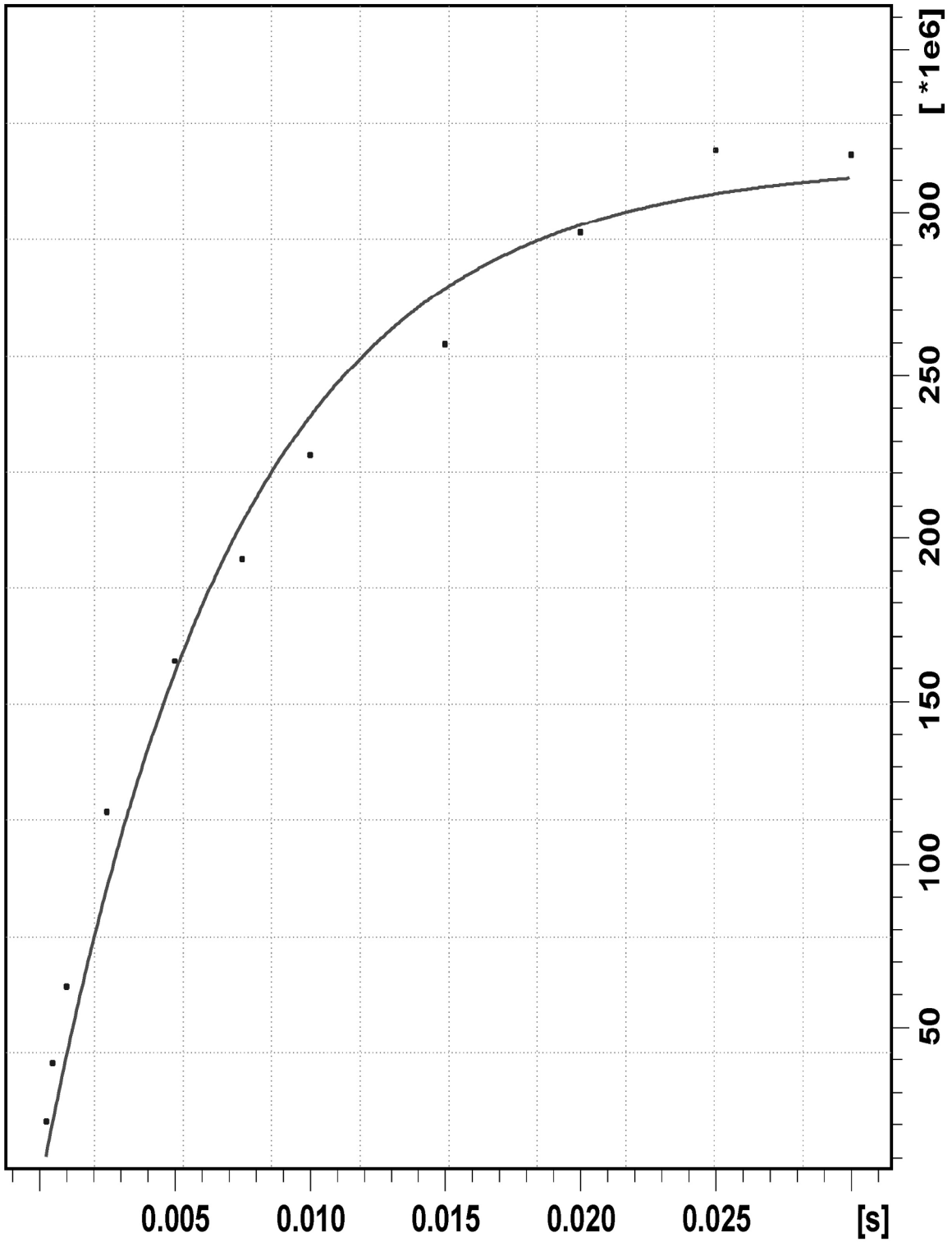

Figure S2. Variable-contact-time ^{15}N CP/MAS data for ZIF-8 in air at 296 K.

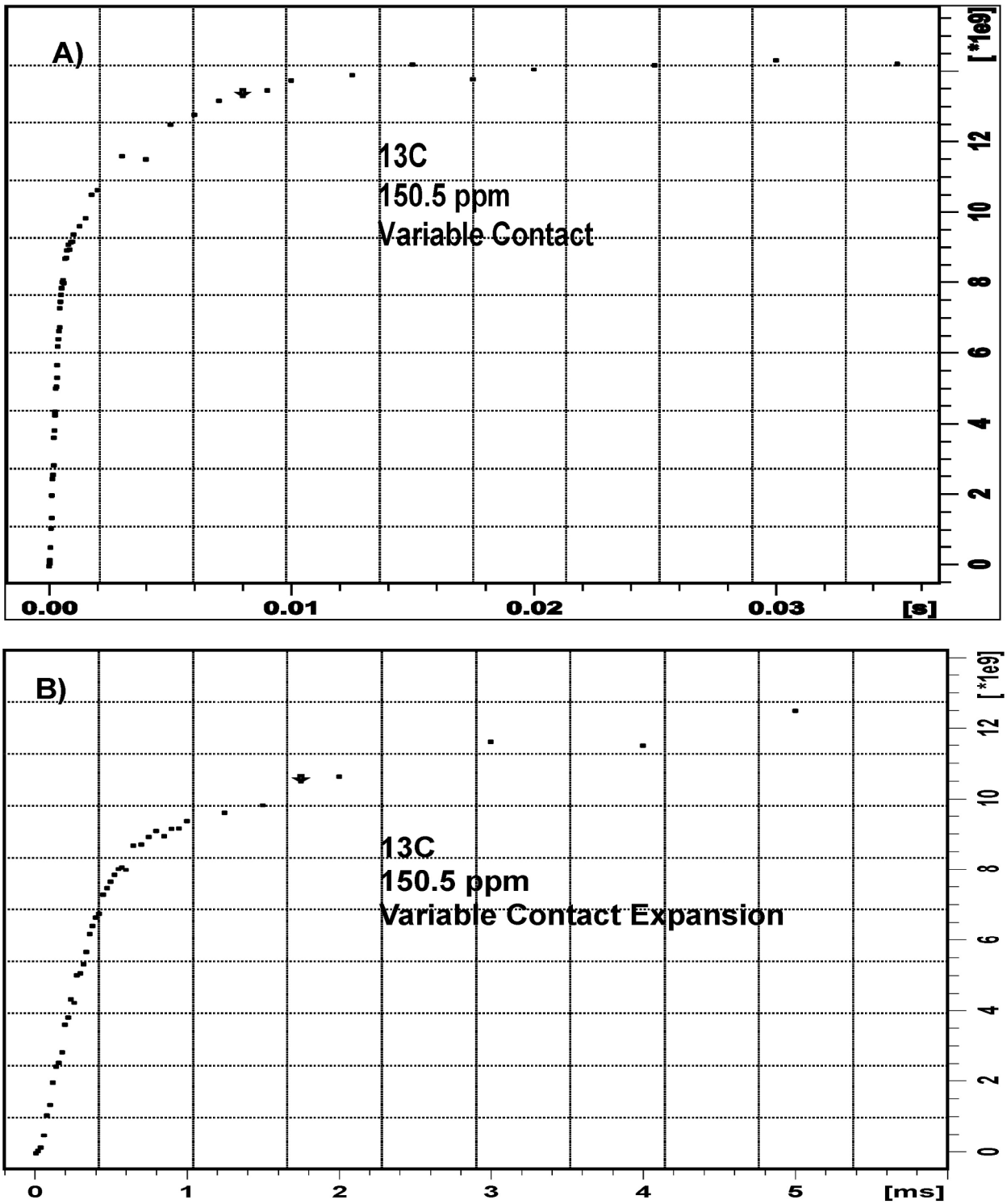

Figure S3. Variable-contact-time ^{13}C CP/MAS data (A) and expansion (B) for the resonance at 150.5 ppm of ZIF-8 in air at 298 K. The non-monotonic behavior is discussed in the text.

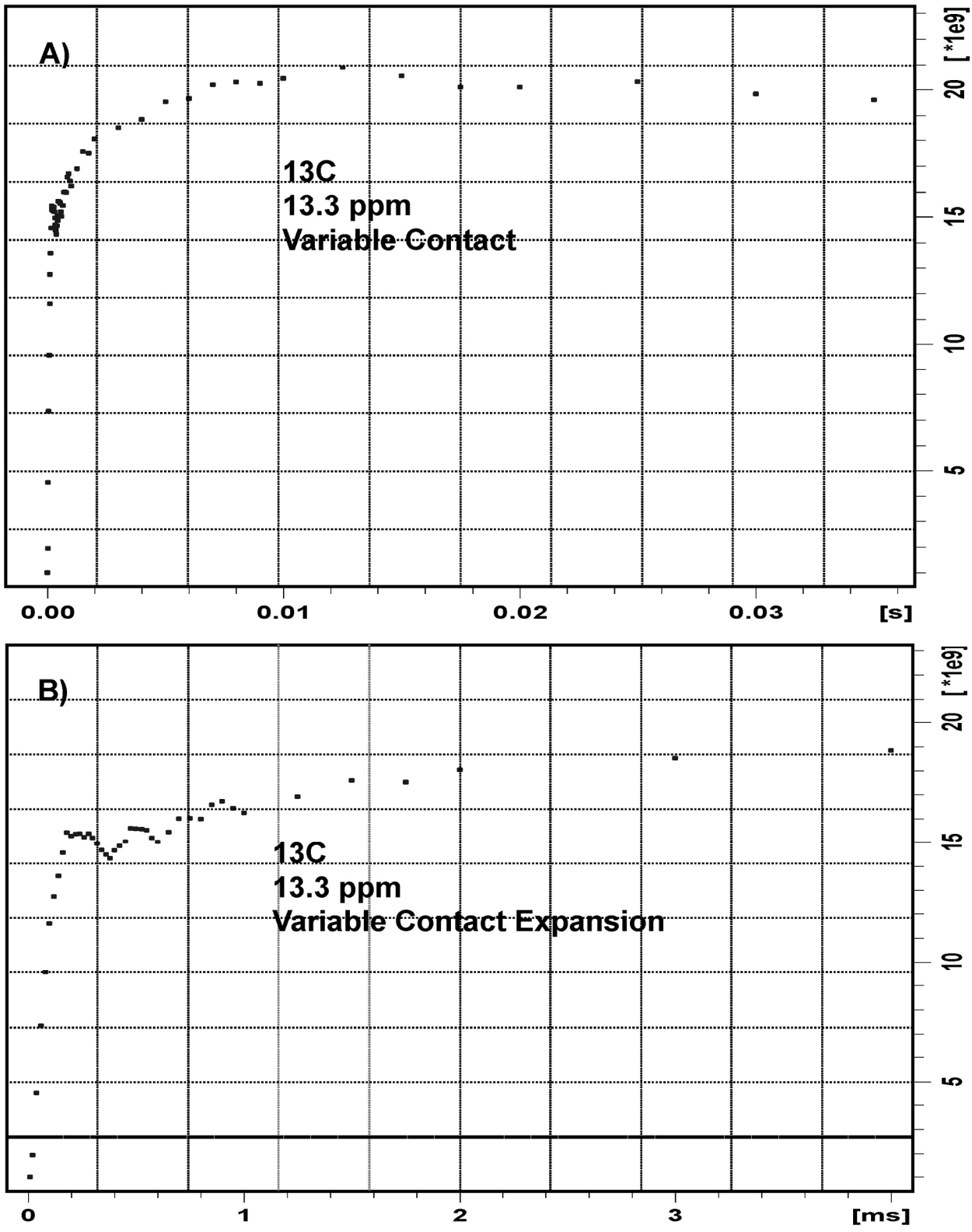

Figure S4. Variable-contact-time ^{13}C CP/MAS data (A) and expansion (B) for the resonance at 13.3 ppm of ZIF-8 in air at 298 K. The non-monotonic behavior is discussed in the text.