Electronic supplementary information (ESI)
for
Dynamics of proton transfer in imidazole hydrogen-bond chains

*Worapong Bua-ngern, Sermsiri Chaiwongwattana, Parichart Suwannakham, and Kritsana Sagarik**

School of Chemistry, Institute of Science, Suranaree University of Technology
Nakhon Ratchasima 30000
Thailand

Figure S1 Correlations of the static results of $H^+(Im)_2$ obtained from the RIMP2/TZVP and B3LYP/TZVP calculations in the gas phase ($\varepsilon = 1$) and continuum solvent ($\varepsilon = 23$).

a) Interaction (ΔE) and solvation (ΔE^{sol}) energies.

b) $R_{N\text{-}N}$ distance.

c) Asymmetric stretching coordinate (Δd_{DA}).

d) Asymmetric N-H stretching frequency (ν^{NH}).

e) Isotropic shielding constant (σ_{H^+}).

Figure S2 Potential energy curves obtained from B3LYP/TZVP calculations in the gas phase.

a) Proton displacement in H-bond **(1)** of $H^+(Im)_2$.

b) Rotation (ω_1) of H-bond **(1)** in $H^+(Im)_2$.

c) Axial rotation (θ) of V_2 reference vector in $H^+(Im)_3$.

d) Proton displacement in H-bond **(2)** of $H^+(Im)_4$.

e) Rotation (ω_2) of H-bond **(2)** in $H^+(Im)_4$.

E^{rel} = relative energy.

Figure S3 a) – c) Proton transfer profiles and time evolutions of dihedral angle (ω_2) of H-bond **(2)** in structure **G4-[1]**$^{(\omega_1=-92)}$ obtained from BOMD simulations at 350 K. **L** and **S** = large- and small-amplitude N-N vibrations, respectively.

Figure S4 a) Vibrational spectra of H-bond **(2)** in structure **G4-[1]**$^{(\omega_1=-92)}$ obtained from BOMD simulations at 350 K.

b) Vibrational spectra for torsional oscillation (ω_2) of H-bond **(2)** in structure **G4-[1]**$^{(\omega_1=-92)}$ obtained from BOMD simulations at 350 K.

c) Arrhenius plot for proton transfer in H-bond **(2)** of structure **G4-[1]**$^{(\omega_1=-92)}$ obtained from BOMD simulations over the temperature range of 298 to 500 K.

A and **B** = oscillatory shuttling and structural diffusion peaks, respectively; **C** = characteristic peak of the N-H stretching mode in the imidazolium cation ($H^+(Im)$); **P** = primary vibrational peak; $\Delta E^{\ddagger,Arr}$ = activation energy obtained from the slope of the linear relationship between ln (k) and 1000/T.

Figure S5 a) – c) VACF plots of N-N vibration in structure **G4-[1]$^{(\omega_1 = -92)}$** obtained from BOMD simulations at 350, 400 and 450 K, respectively.

Figure S6 Proton transfer profiles and time evolutions of dihedral angles (ω_1, ω_2 and ω_3) of H-bonds in structure **G4-[1]$^{(\omega_1 = -92)}$** obtained from BOMD simulations at 350 K.

Figure S7 Proton transfer profiles and time evolutions of dihedral angles (ω_1, ω_2 and ω_3) of H-bonds in structure **G4-[1]$^{(\omega_1 = -92)}$** obtained from BOMD simulations at 298 K.

Figure S8 a) – c) Proton transfer profiles and time evolutions of dihedral angle (ω_2) of H-bond **(2)** in structure **G4-[1]$^{(\omega_1 = -92)}$** obtained from BOMD simulations at 298 K. **L** and **S** = large- and small-amplitude N-N vibrations, respectively.

Table S1 Static results of $H^+(Im)_n$, n = 2 – 4, obtained from B3LYP/TZVP calculations. Energies, distances, vibrational frequencies, ^{1}H NMR isotropic shielding constants and chemical shifts are in kJ/mol, Å, cm^{-1}, and ppm, respectively.

Table S2 Static results of $H^+(Im)_n$, n = 2 – 4, obtained from RIMP2/TZVP calculations. Energies, distances, vibrational frequencies, ^{1}H NMR isotropic shielding constants and chemical shifts are in kJ/mol, Å, cm^{-1}, and ppm, respectively.

Table S3 ^{1}H NMR chemical shifts ($\delta_{H^+}^{MD}$) and line widths ($\Delta\delta_{H^+}^{MD}$) of proton in H-bond **(1)** of structure **G2-[1]$^{(\omega_1 = -94)}$** obtained from BOMD simulations over the temperature range of 298 – 500 K. $\delta_{H^+}^{MD}$, $\Delta\delta_{H^+}^{MD}$ and temperature are in ppm and K, respectively.

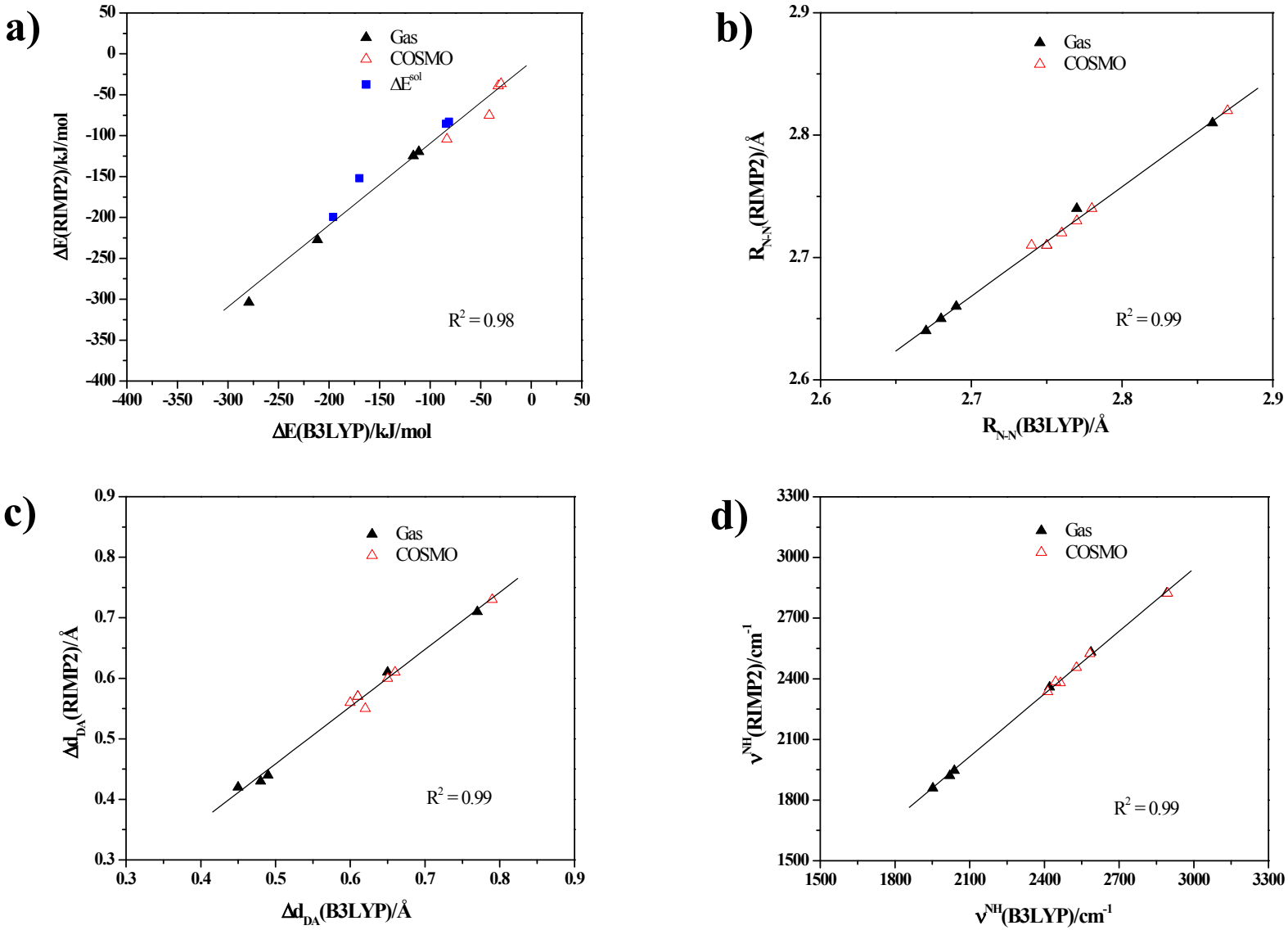

a)
Gas
COSMO
ΔE^sol
R^2 = 0.98
ΔE(RIMP2)/kJ/mol
ΔE(B3LYP)/kJ/mol
b)
Gas
COSMO
R^2 = 0.99
R_N-N(RIMP2)/Å
R_N-N(B3LYP)/Å
c)
Gas
COSMO
R^2 = 0.99
Δd_DA(RIMP2)/Å
Δd_DA(B3LYP)/Å
d)
Gas
COSMO
R^2 = 0.99
ν^NH(RIMP2)/cm^-1
ν^NH(B3LYP)/cm^-1

Figure S1

e)

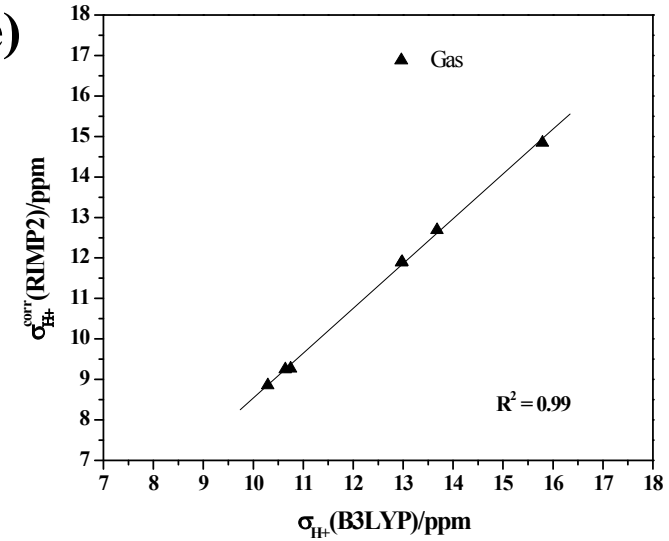


Figure S1 (cont.)

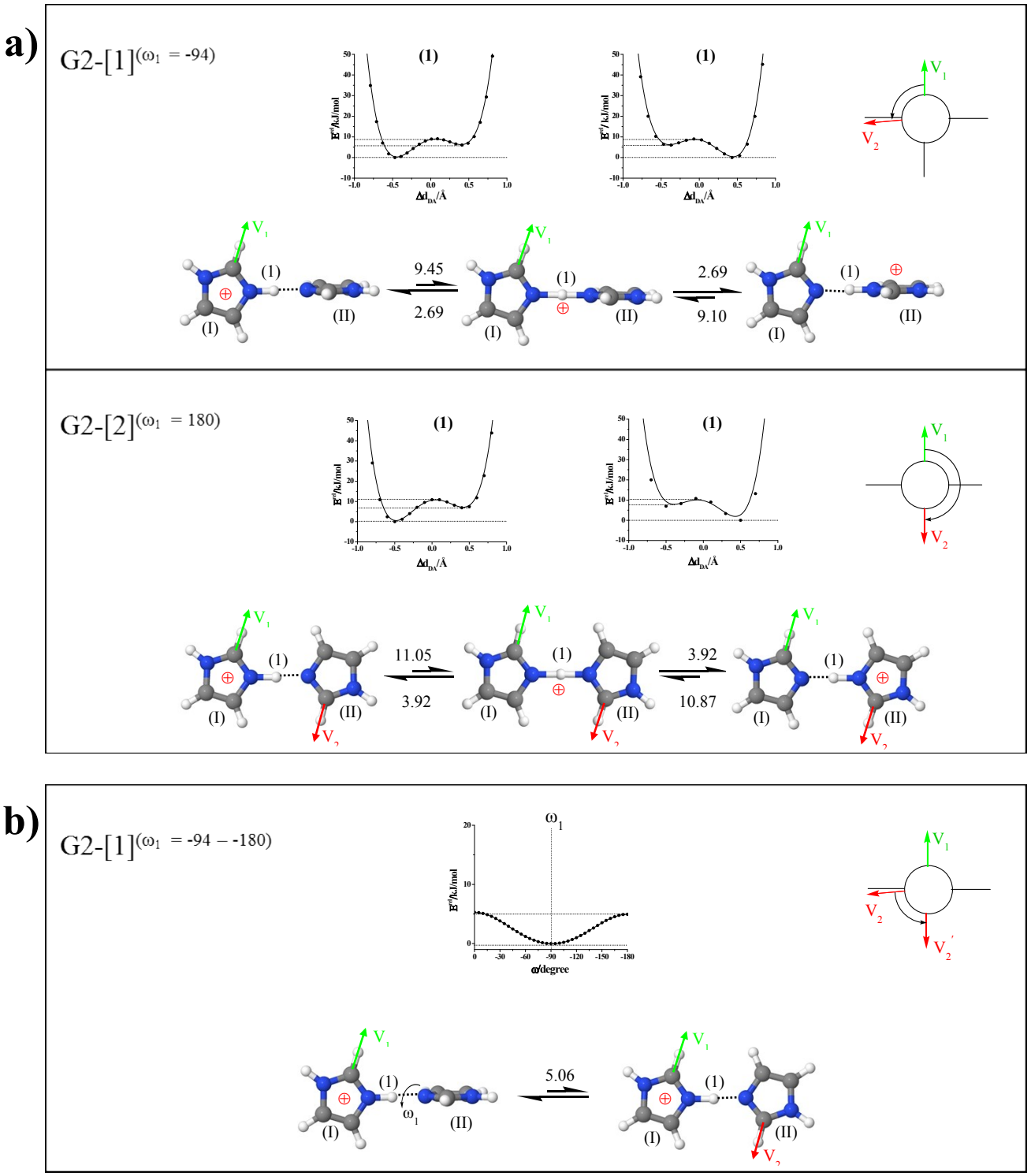

a)
G2-[1](ω1 = -94)
(1)
(1)
V1
V2
9.45
2.69
2.69
9.10
(I)
(II)
G2-[2](ω1 = 180)
11.05
3.92
3.92
10.87
b)
G2-[1](ω1 = -94 – -180)
ω1
ω/degree
5.06
V2′

Figure S2

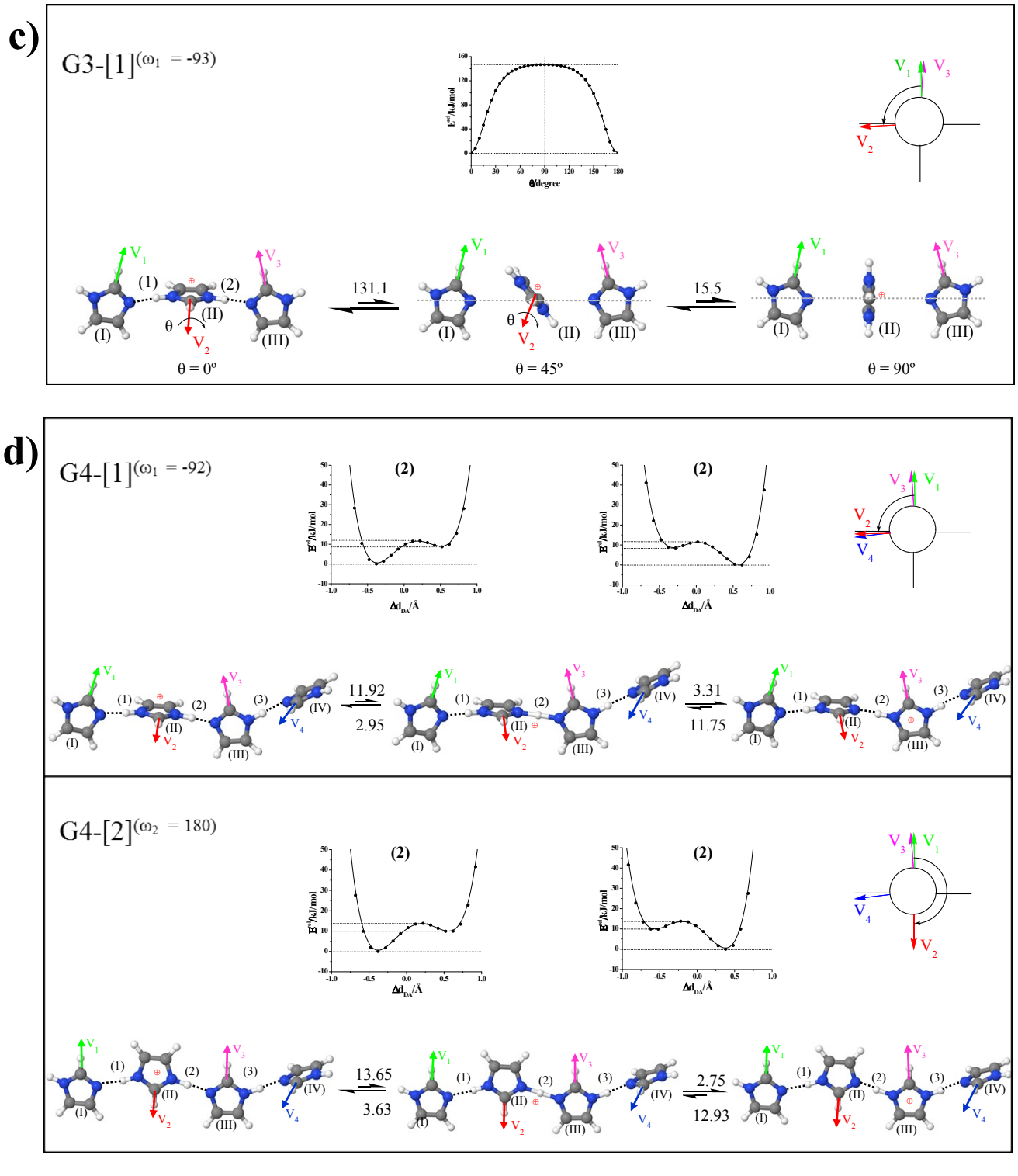


Figure S2 (cont.)

e)

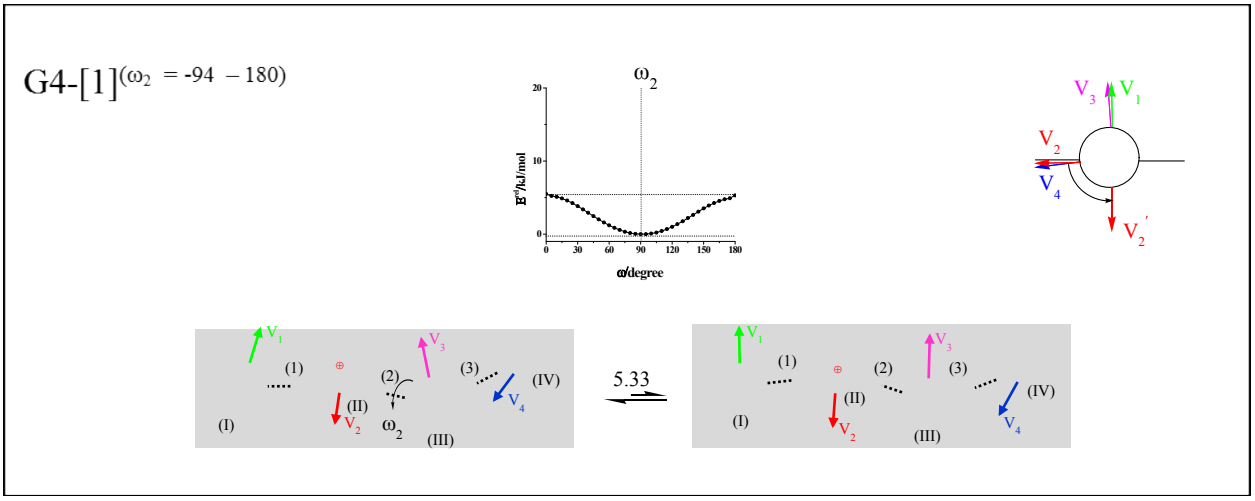


Figure S2 (cont.)

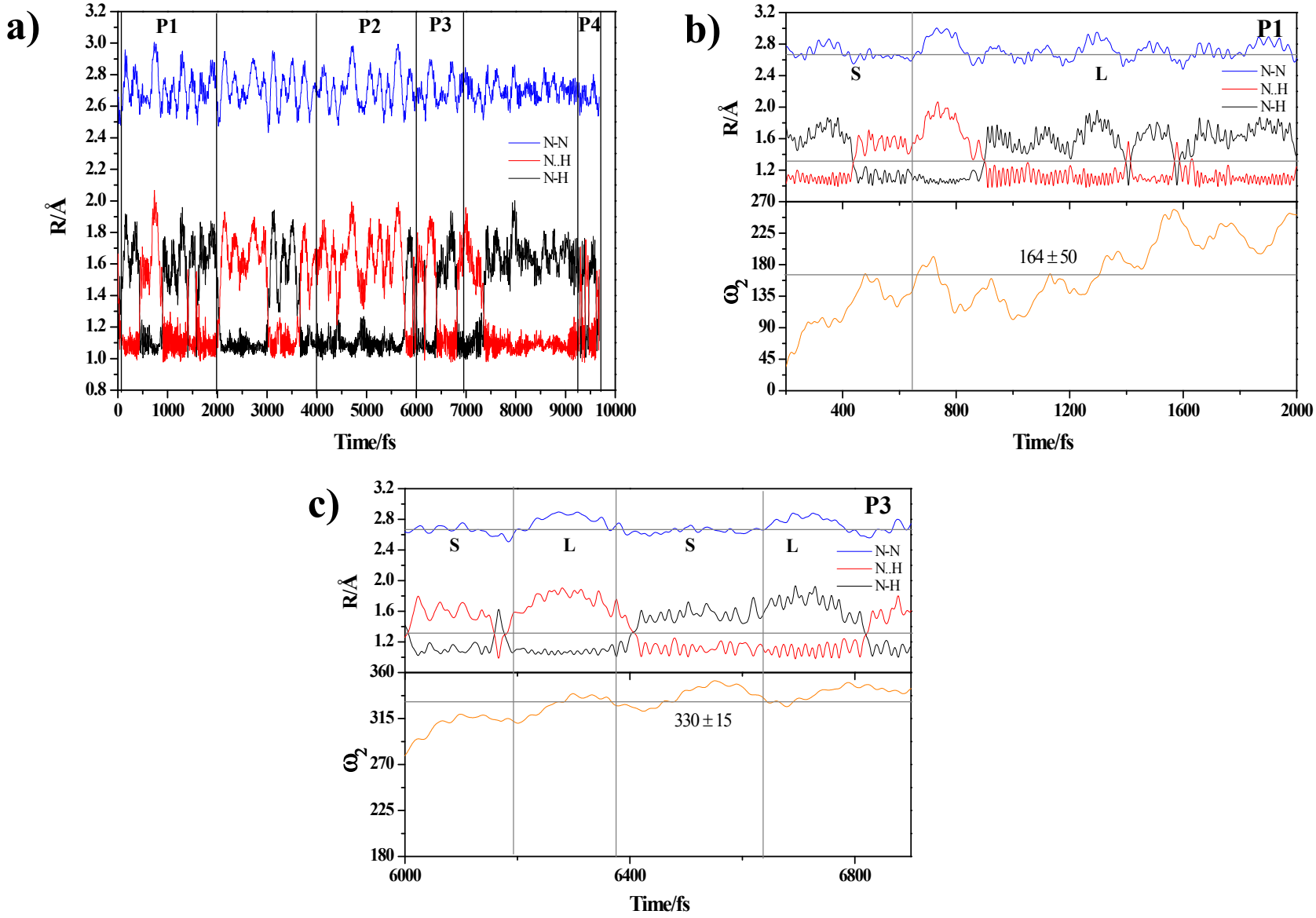

a)
P1
P2
P3
P4
N-N
N..H
N-H
R/Å
Time/fs
b)
P1
S
L
N-N
N..H
N-H
R/Å
164 ± 50
ω2
Time/fs
c)
P3
S
L
S
L
N-N
N..H
N-H
R/Å
330 ± 15
ω2
Time/fs

Figure S3

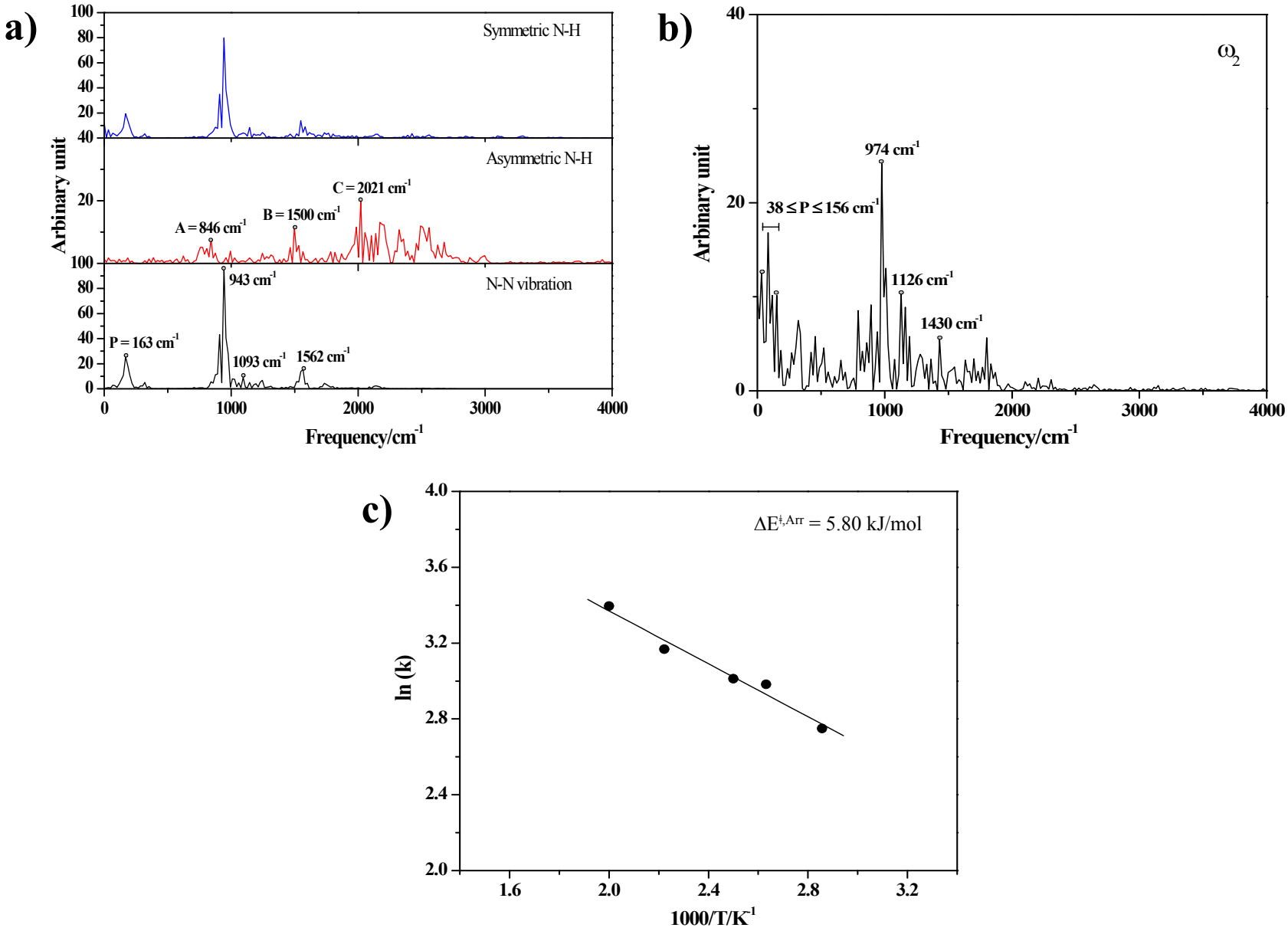
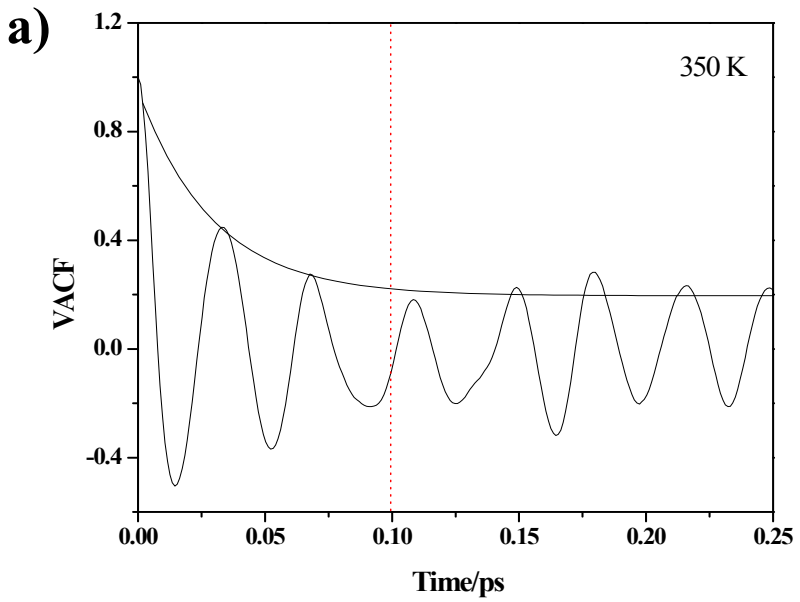
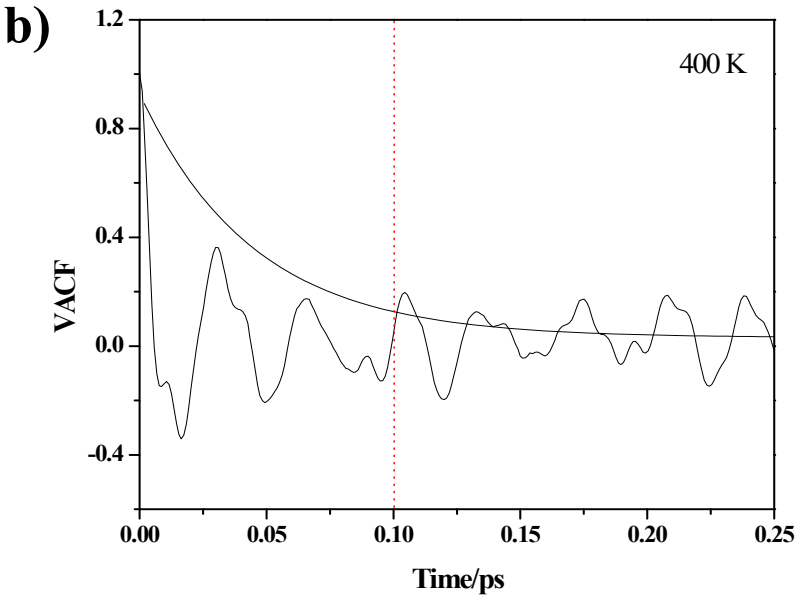

a)
Symmetric N-H
Asymmetric N-H
N-N vibration
A = 846 cm-1
B = 1500 cm-1
C = 2021 cm-1
P = 163 cm-1
943 cm-1
1093 cm-1
1562 cm-1
Arbinary unit
Frequency/cm-1
b)
ω2
974 cm-1
38 ≤ P ≤ 156 cm-1
1126 cm-1
1430 cm-1
Arbinary unit
Frequency/cm-1
c)
ΔE‡,Arr = 5.80 kJ/mol
ln (k)
1000/T/K-1

Figure S4


a)
350 K
VACF
Time/ps
1.2
0.8
0.4
0.0
-0.4
0.00
0.05
0.10
0.15
0.20
0.25


b)
400 K
VACF
Time/ps
1.2
0.8
0.4
0.0
-0.4
0.00
0.05
0.10
0.15
0.20
0.25

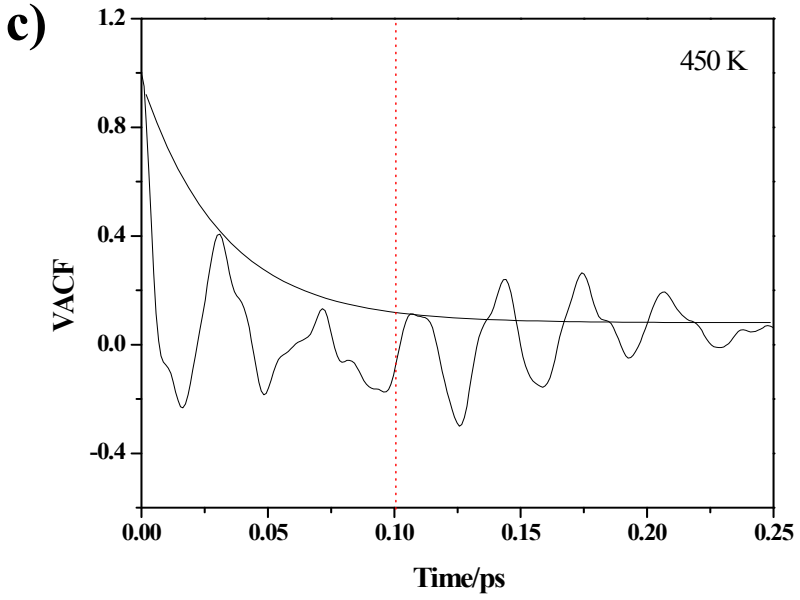

c)
450 K
VACF
Time/ps
1.2
0.8
0.4
0.0
-0.4
0.00
0.05
0.10
0.15
0.20
0.25

Figure S5

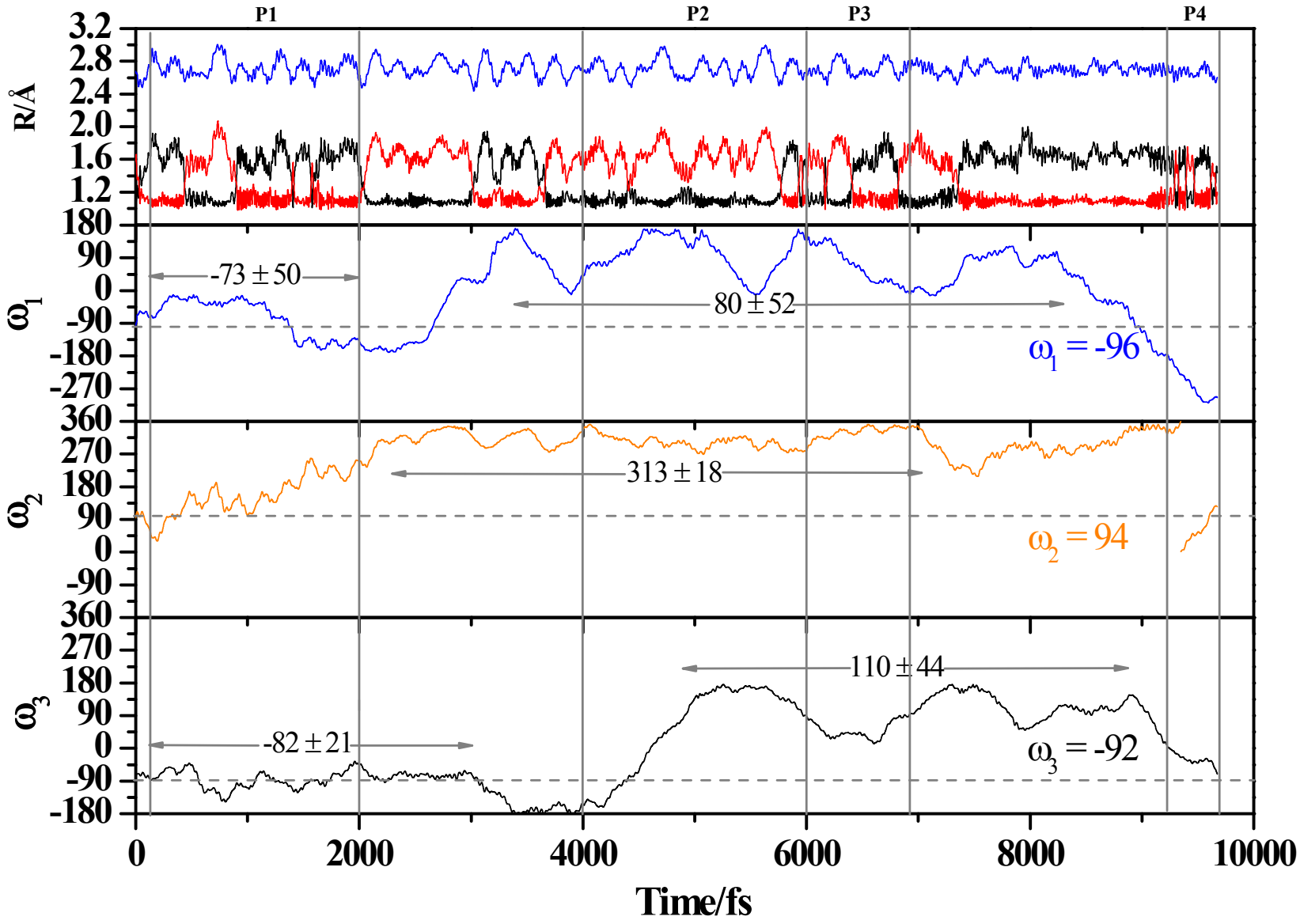

P1
P2
P3
P4
R/Å
3.2
2.8
2.4
2.0
1.6
1.2
ω1
180
90
0
-90
-180
-270
360
-73 ± 50
80 ± 52
ω1 = -96
ω2
270
180
90
0
-90
360
313 ± 18
ω2 = 94
ω3
270
180
90
0
-90
-180
110 ± 44
-82 ± 21
ω3 = -92
0
2000
4000
6000
8000
10000
Time/fs

Figure S6

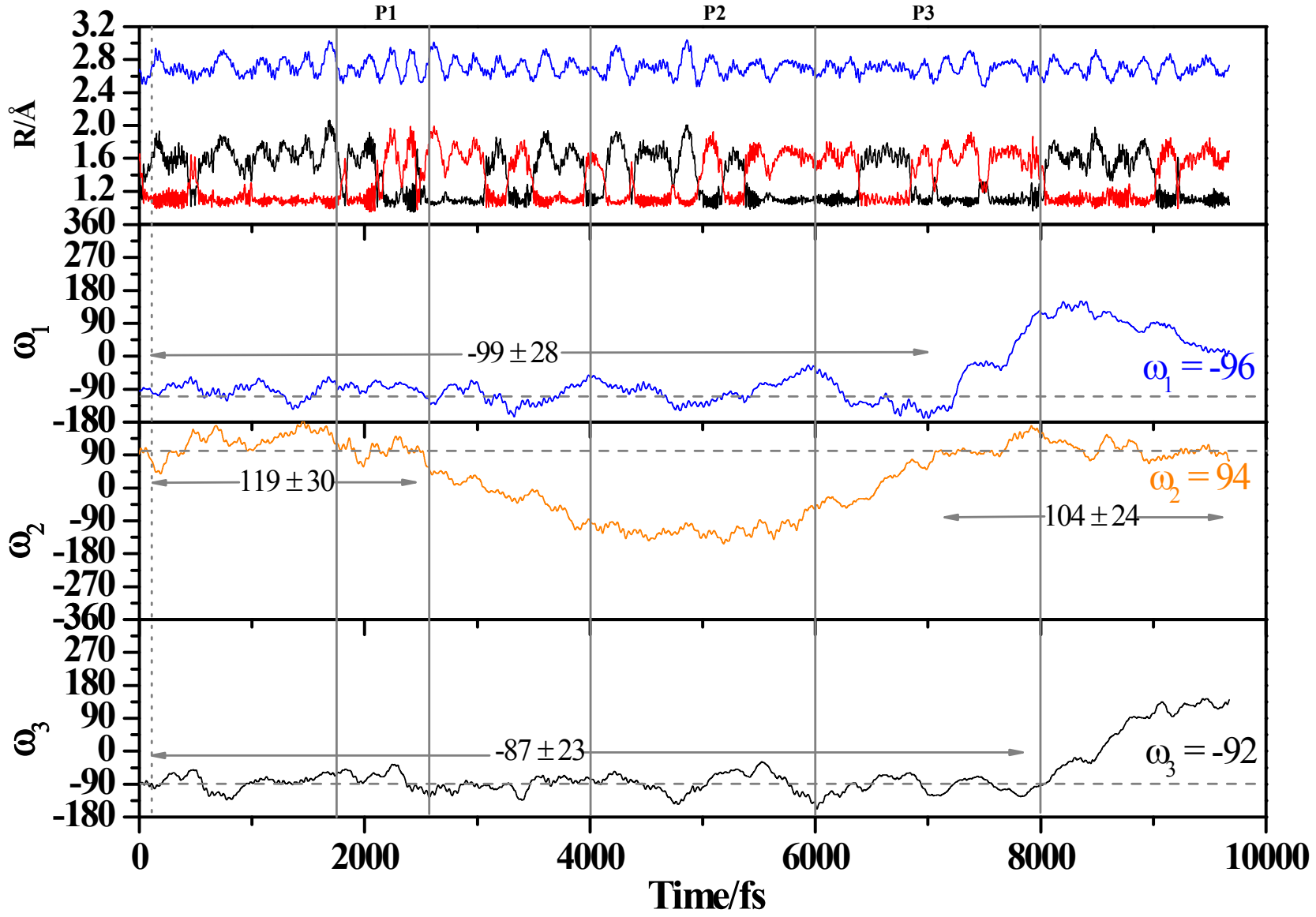

P1
P2
P3
R/Å
3.2
2.8
2.4
2.0
1.6
1.2
ω1
360
270
180
90
0
-90
-180
-99 ± 28
ω1 = -96
ω2
90
0
-90
-180
-270
-360
119 ± 30
ω2 = 94
104 ± 24
ω3
270
180
90
0
-90
-180
-87 ± 23
ω3 = -92
0
2000
4000
6000
8000
10000
Time/fs

Figure S7

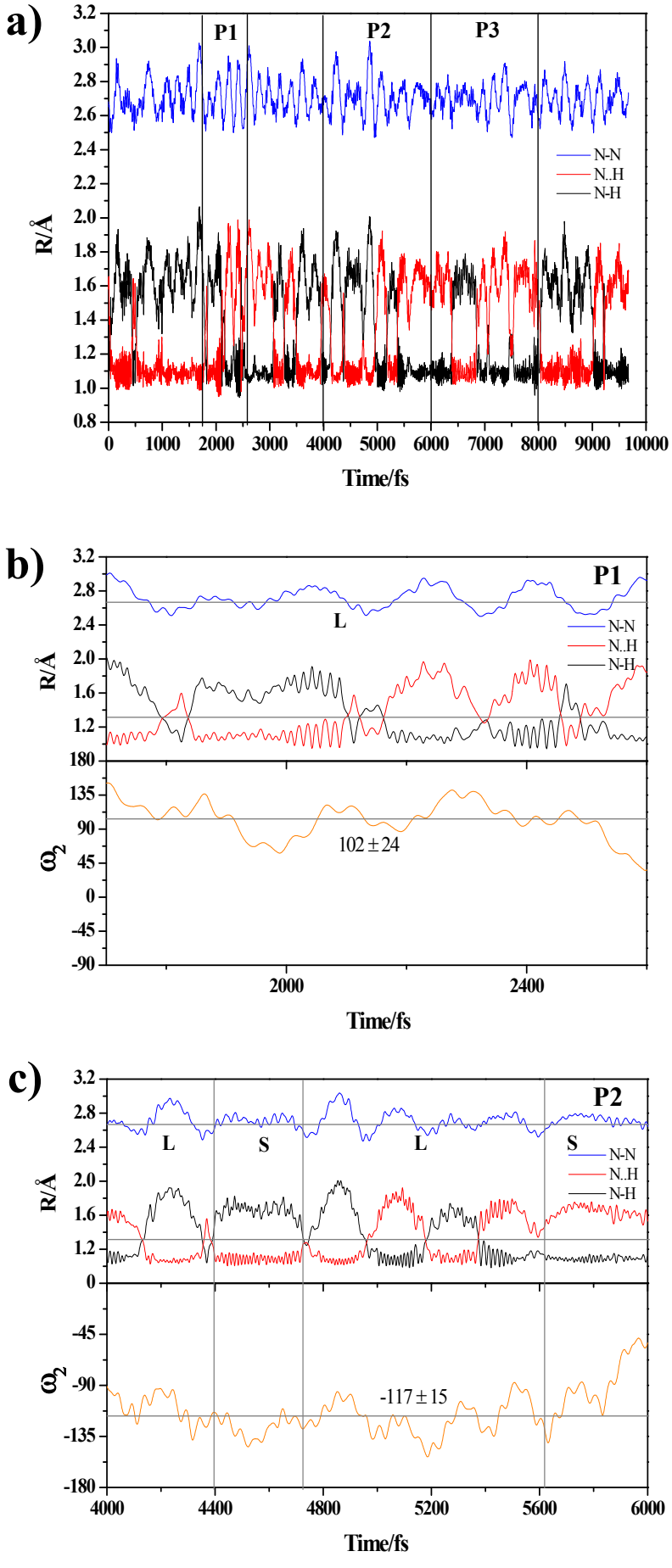
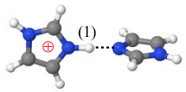
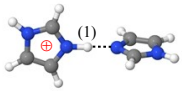
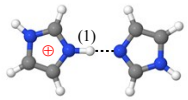
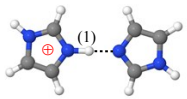
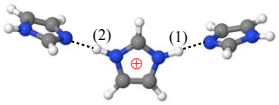
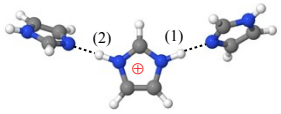
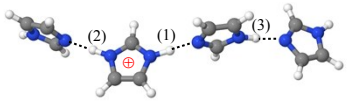
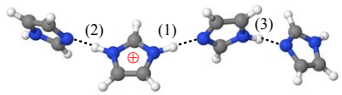

a)
P1
P2
P3
N-N
N..H
N-H
R/Å
Time/fs
b)
P1
L
N-N
N..H
N-H
R/Å
ω2
102 ± 24
Time/fs
c)
P2
L
S
L
S
N-N
N..H
N-H
R/Å
ω2
-117 ± 15
Time/fs

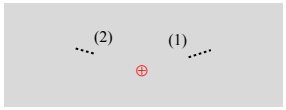
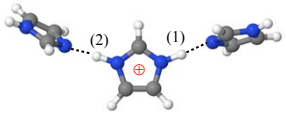
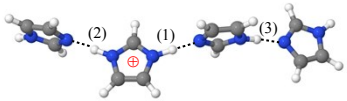
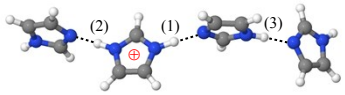
Figure S8

Table S1 Static results of $H^+(Im)_n$, n = 2 – 4, obtained from B3LYP/TZVP calculations. Energies, distances, vibrational frequencies, ^1H NMR isotropic shielding constants and chemical shifts are in kJ/mol, Å, cm^{-1}, and ppm, respectively.

Gas	COSMO	H-bond	R_{N-N}	Δd_{DA}	ν^{NH}	σ_{H+}	δ_{H+}	ΔE	ΔE^{sol}
G2-[1](ω_1 = −94) 	C2-[1](ω_1 = −94) 	(1)	2.67 (2.74)	0.45 (0.60)	1952 (2414)	10.29 -	21.68 -	-116.7 (-32.6)	-84.2 -
G2-[2](ω_1 = 180) 	C2-[2](ω_1 = -175) 	(1)	2.69 (2.76)	0.49 (0.63)	2020 (2464)	10.75 -	21.22 -	-111.1 (-29.8)	-81.3 -
G3-[1](ω_1 = −93) 	C3-[1](ω_1 = −61) 	(1) (2)	2.75 (2.78) 2.75 (2.77)	0.61 (0.66) 0.61 (0.65)	2421 (2529) 2421 (2529)	12.97 - 12.98 -	19.00 - 18.99 -	-211.4 (-41.5) - -	-169.9 - - -
G4-[1](ω_1 = 93) 	C4-[1](ω_1 = 92) 	(1) (2) (3)	2.68 (2.75) 2.77 (2.78) 2.86 (2.87)	0.48 (0.61) 0.65 (0.66) 0.77 (0.79)	2039 (2445) 2587 (2583) 2892 (2895)	10.64 - 13.68 - 15.79 -	21.33 - 18.29 - 16.18 -	-279.3 (-83.4) - - -	-195.9 - - - -

R_{N-N} = H-bond distance; Δd_{DA} = asymmetric stretching coordinate; ΔE = interaction energy; ΔE^{sol} = solvation energy; ν^{NH} = asymmetric N-H stretching frequency; σ_{H+} = ^1H NMR isotropic shielding constants; δ_{H+} = ^1H NMR chemical shift; (..) = continuum liquid (COSMO, ε = 23).

Table S2 Static results of $H^+(Im)_n$, n = 2 – 4, obtained from RIMP2/TZVP calculations. Energies, distances, vibrational frequencies, ^1H NMR isotropic shielding constants and chemical shifts are in kJ/mol, Å, cm^{-1}, and ppm, respectively.

Gas	COSMO	H-bond	$R_{N\text{-}N}$	Δd_{DA}	ν^{NH}	σ_{H+}^{corr}	δ_{H+}^{corr}	ΔE	ΔE^{sol}
G2-[1](ω_1 = – 98) 	C2-[1](ω_1 = – 83) 	(1)	2.64 (2.71)	0.42 (0.56)	1859 (2336)	8.86 -	23.10 -	-124.8 (-39.1)	-85.6 -
G2-[2](ω_1 = 180) 	C2-[2](ω_1 = 180) 	(1)	2.66 (2.72)	0.44 (0.58)	1921 (2380)	9.27 -	22.69 -	-119.6 (-36.5)	-83.1 -
G3-[1](ω_1 = – 99) 	C3-[1](ω_1 = – 84) 	(1) (2)	2.71 (2.74) 2.71 (2.73)	0.57 (0.61) 0.57 (0.60)	2359 (2456) 2359 (2456)	11.89 - 11.90 -	20.07 - 20.06 -	-227.3 (-75.2) - -	-152.0 - - -
G4-[3](ω_1 = 167) 	C4-[3](ω_1 = 146) 	(1) (2) (3)	2.65 (2.71) 2.74 (2.74) 2.81 (2.82)	0.43 (0.57) 0.61 (0.61) 0.71 (0.73)	1946 (2385) 2532 (2524) 2823 (2823)	9.25 - 12.69 - 14.85 -	22.72 - 19.27 - 17.12 -	-303.8 (-104.3) - - -	-199.4 - - - -

$R_{N\text{-}N}$ = H-bond distance; Δd_{DA} = asymmetric stretching coordinate; ΔE = interaction energy; ΔE^{sol} = solvation energy; ν^{NH} = asymmetric N-H stretching frequency; σ_{H+}^{corr} = isotropic shielding constants; δ_{H+}^{corr} = ^1H NMR chemical shift; (..) = continuum liquid (COSMO, ε = 23).

Table S3 ^{1}H NMR chemical shifts ($\delta_{H^+}^{MD}$) and line widths ($\Delta\delta_{H^+}^{MD}$) of proton in H-bond **(1)** of structure **G2-[1]**$^{(\omega_1 = -94)}$ obtained from BOMD simulations over the temperature range of 298 – 500 K. $\delta_{H^+}^{MD}$, $\Delta\delta_{H^+}^{MD}$ and temperature are in ppm and K, respectively.

T	Peak	$\delta_{H^+}^{MD}$	$\Delta\delta_{H^+}^{MD}$
298	**A**	24.39	1.45
	B	20.96	3.76
	C	17.63	2.47
350	**A**	24.68	0.90
	B	22.25	2.83
	C	19.54	3.00
380	**A**	24.50	0.77
	B	21.16	3.47
	C	17.77	3.28
400	**A**	24.03	2.18
	B	20.66	2.98
	C	17.69	3.57
450	**A**	24.39	1.19
	B	22.45	1.95
	C	19.96	2.87
500	**A**	24.64	1.04
	B	21.57	3.30
	C	18.41	2.66

A = oscillatory shuttling peak; B = structural diffusion peak;

C = characteristic peak of proton in imidazolium cation (H^+(Im)).