Supporting Information

Importance of Polarization and Charge Transfer Effects to Model the Infrared Spectra of Peptides in Solution

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Table 1: Atomic charges (atomic units) for cis and trans NMA as obtained in the gas phase from molecular dynamics with the Amber03 force field and from SEBOMD with a PM3 Hamiltonian. The average standard deviation on the quantum charges is 0.02 e.

	Amber03	SEBOMD-Mulliken	
Atom		cis	trans
C_{ACE}	-0.19	-0.13	-0.14
H_{ACE}	0.08	0.07	0.06
H_{ACE}	0.08	0.07	0.06
H_{ACE}	0.08	0.07	0.06
C	0.51	0.24	0.24
O	-0.55	-0.37	-0.36
N	-0.42	-0.06	-0.05
H	0.29	0.08	0.07
C_{NMet}	-0.05	-0.09	-0.08
H_{NMet}	0.06	0.04	0.05
H_{NMet}	0.06	0.04	0.05
H_{NMet}	0.06	0.04	0.05
		SEBOMD-CM1	
Atom		cis	trans
C_{ACE}		-0.14	-0.14
H_{ACE}		0.07	0.07
H_{ACE}		0.07	0.07
H_{ACE}		0.07	0.07
C		0.41	0.41
O		-0.45	-0.44
N		-0.51	-0.51
H		0.35	0.33
C_{NMet}		0.00	0.01
H_{NMet}		0.05	0.05
H_{NMet}		0.05	0.05
H_{NMet}		0.05	0.05
		SEBOMD-CM2	
Atom		cis	trans
C_{ACE}		-0.14	-0.14
H_{ACE}		0.07	0.07
H_{ACE}		0.07	0.07
H_{ACE}		0.07	0.07
C		0.49	0.49
O		-0.47	-0.47
N		-0.59	-0.59
H		0.33	0.32
C_{NMet}		0.03	0.04
H_{NMet}		0.05	0.05
H_{NMet}		0.05	0.05
H_{NMet}		0.05	0.05

Table 2: Atomic charges (atomic units) for cis and trans NMA as obtained in water from SEBOMD with a PM3 Hamiltonian and PIF corrections. The average standard deviation on the quantum charges is 0.03 e.

	SEBOMD-Mulliken	
Atom	cis	trans
C_{ACE}	-0.17	-0.17
H_{ACE}	0.09	0.10
H_{ACE}	0.09	0.10
H_{ACE}	0.09	0.10
C	0.24	0.23
O	-0.52	-0.52
N	0.02	0.04
H	0.10	0.12
C_{NMet}	-0.12	-0.13
H_{NMet}	0.08	0.07
H_{NMet}	0.08	0.06
H_{NMet}	0.09	0.06
	SEBOMD-CM1	
Atom	cis	trans
C_{ACE}	-0.17	-0.17
H_{ACE}	0.09	0.10
H_{ACE}	0.09	0.10
H_{ACE}	0.10	0.10
C	0.42	0.41
O	-0.61	-0.60
N	-0.44	-0.42
H	0.37	0.38
C_{NMet}	-0.04	-0.04
H_{NMet}	0.09	0.07
H_{NMet}	0.09	0.06
H_{NMet}	0.09	0.07
	SEBOMD-CM2	
Atom	cis	trans
C_{ACE}	-0.17	-0.17
H_{ACE}	0.10	0.10
H_{ACE}	0.10	0.10
H_{ACE}	0.10	0.10
C	0.49	0.48
O	-0.60	-0.60
N	-0.52	-0.50
H	0.35	0.37
C_{NMet}	0.00	0.00
H_{NMet}	0.09	0.07
H_{NMet}	0.09	0.06
H_{NMet}	0.09 3	0.07

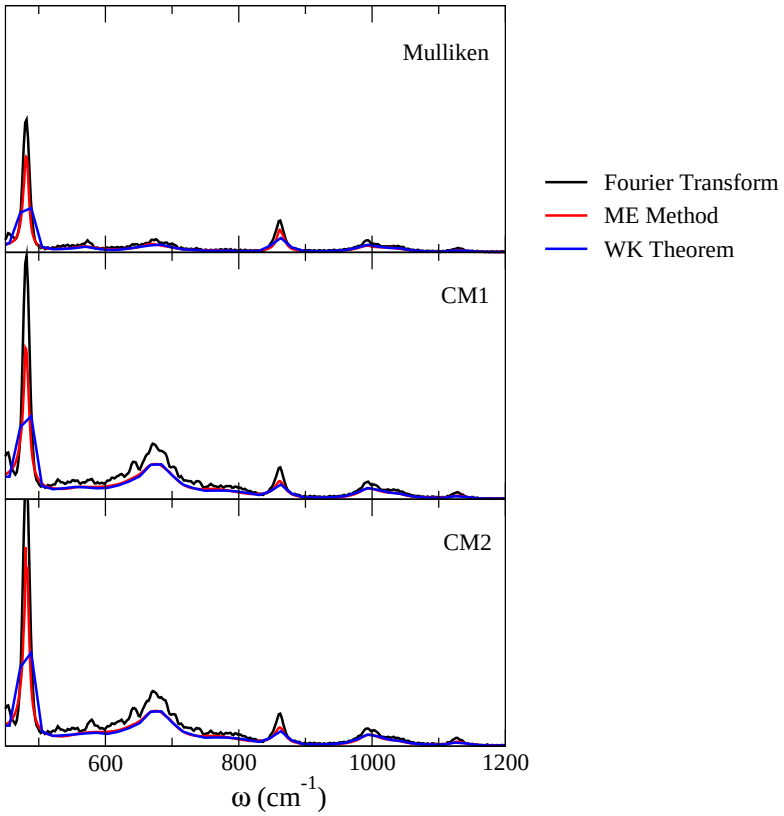

Figure 1: Comparison of different methods to calculate the infrared spectrum (between 450 and 1200 cm^{-1}) from simulations. Black curve: results from direct integration of the dipole correlation function. Red curve: maximum entropy method. Blue curve: Wiener-Khinchin theorem. Results are shown for trans NMA in the gas phase, semi-empirical Hamiltonian (three different charge schemes were used).

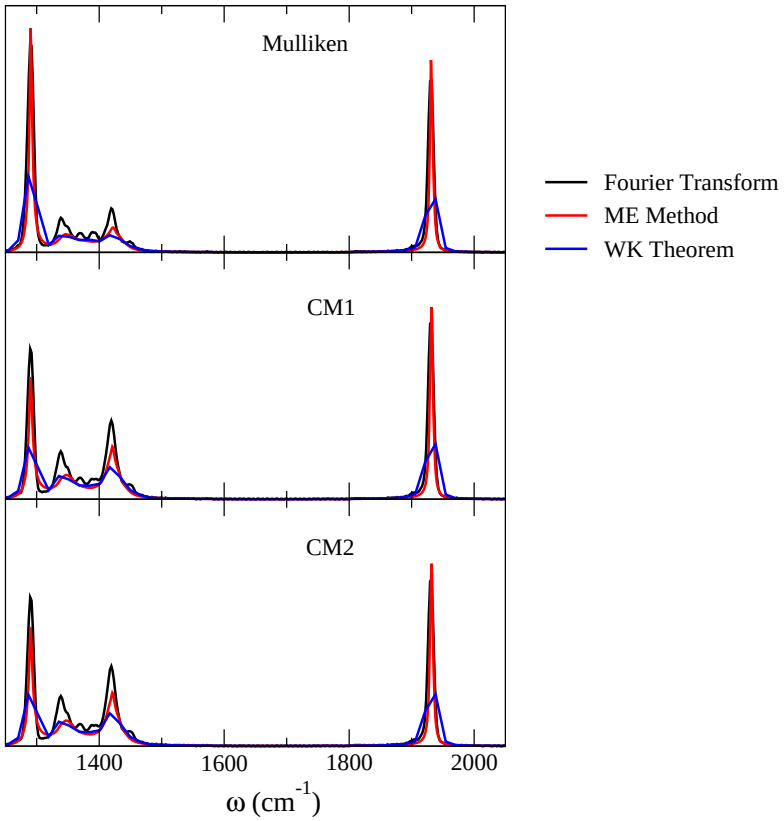

Figure 2: Comparison of different methods to calculate the infrared spectrum (between 1250 and 2250 cm^{-1}) from simulations. Black curve: results from direct integration of the dipole correlation function. Red curve: maximum entropy method. Blue curve: Wiener-Khinchin theorem. Results are shown for trans NMA in the gas phase, semi-empirical Hamiltonian (three different charge schemes were used).

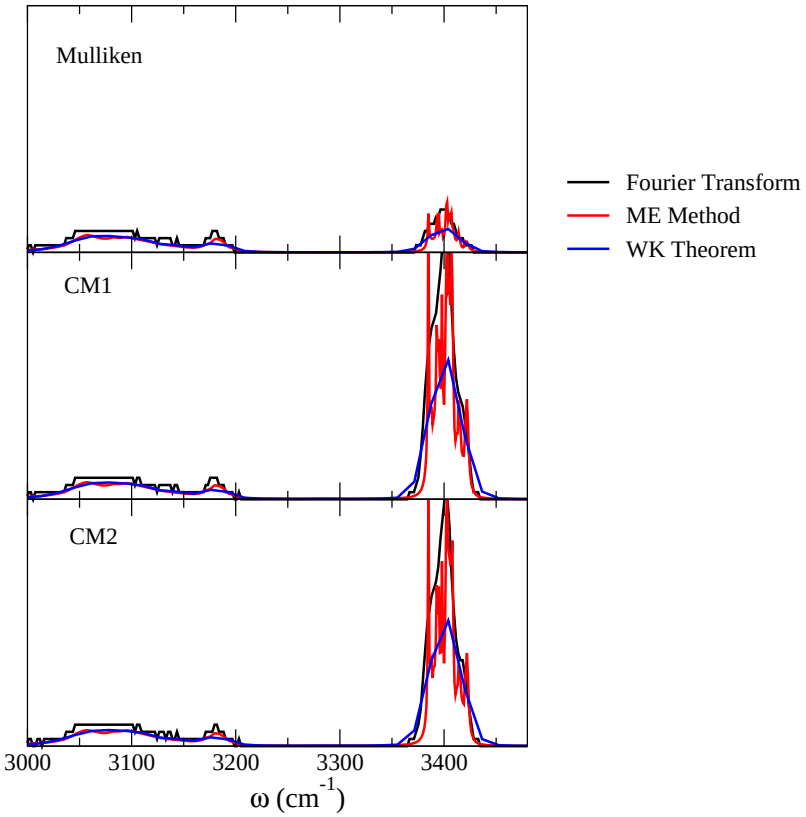

Figure 3: Comparison of different methods to calculate the infrared spectrum (between 3000 and 3500 cm^{-1}) from simulations. Black curve: results from direct integration of the dipole correlation function. Red curve: maximum entropy method. Blue curve: Wiener-Khinchin theorem. Results are shown for trans NMA in the gas phase, semi-empirical Hamiltonian (three different charge schemes were used).

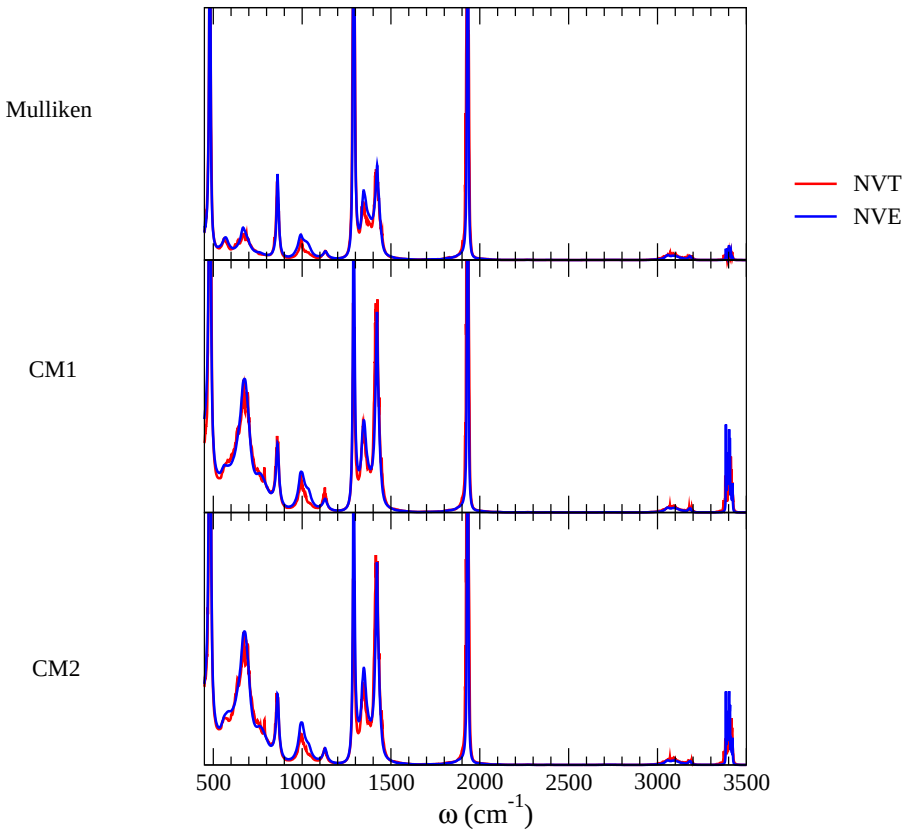

Figure 4: Comparison of the results obtained in different simulation ensembles (NVT in red, NVE in blue). Results are shown for trans NMA in the gas phase, semi-empirical Hamiltonian (three different charge schemes were used).

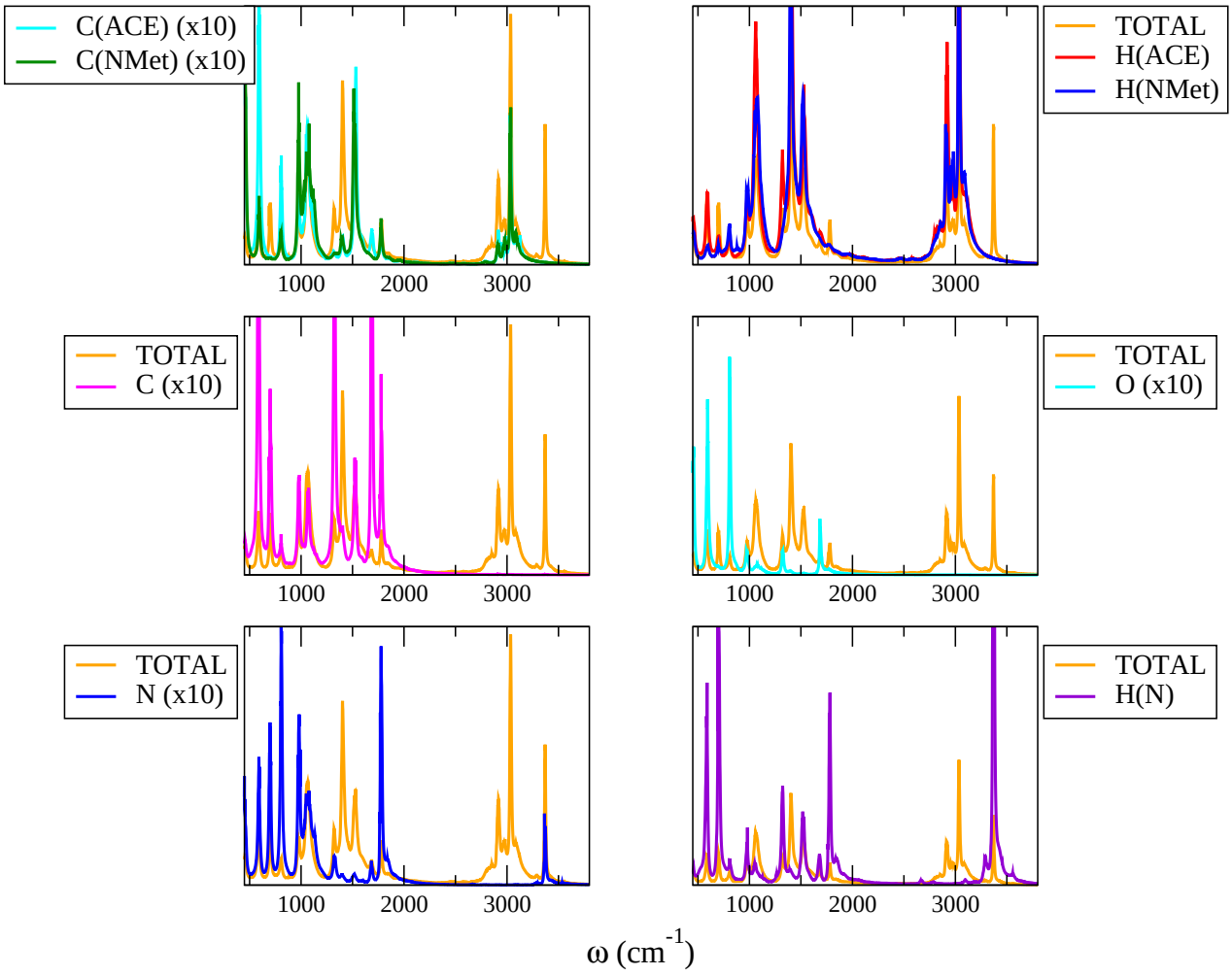

Figure 5: Trans NMA in the gas phase, MM force field. Atomic contributions to the total VDOS (reported in orange). Intensities are in arbitrary units.

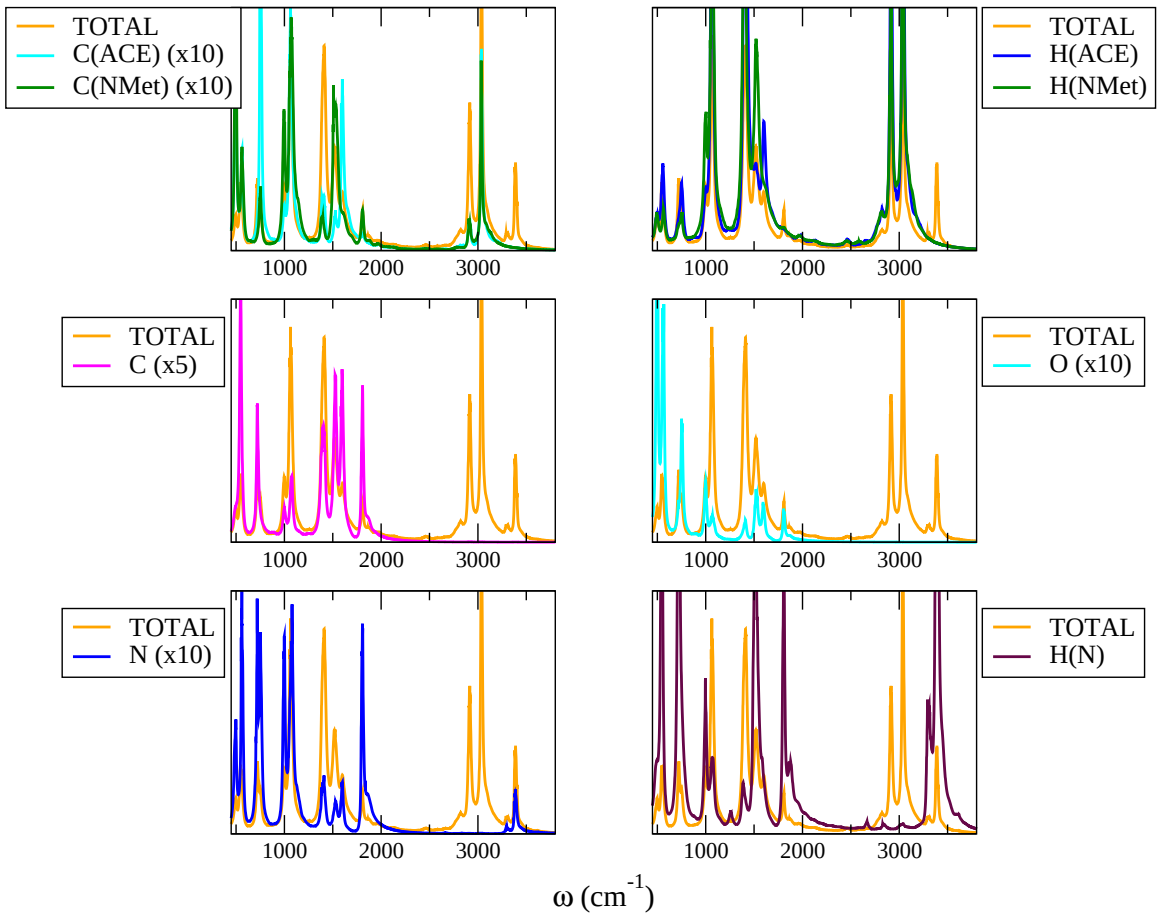

Figure 6: Cis NMA in the gas phase, MM force field. Atomic contributions to the total VDOS (reported in orange). Intensities are in arbitrary units.

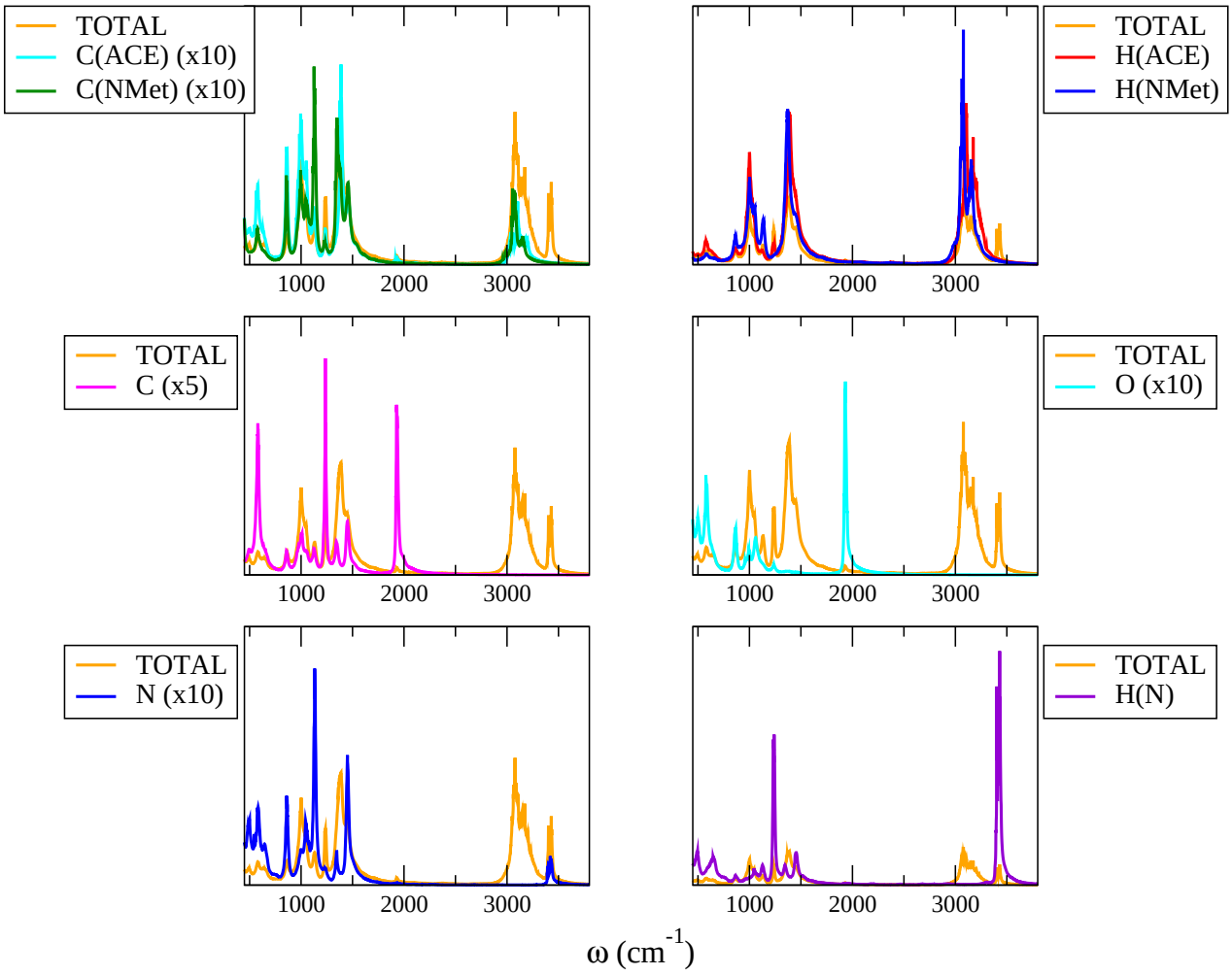

Figure 7: Trans NMA in the gas phase, semi-empirical Hamiltonian. Atomic contributions to the total VDOS (reported in orange). Intensities are in arbitrary units.

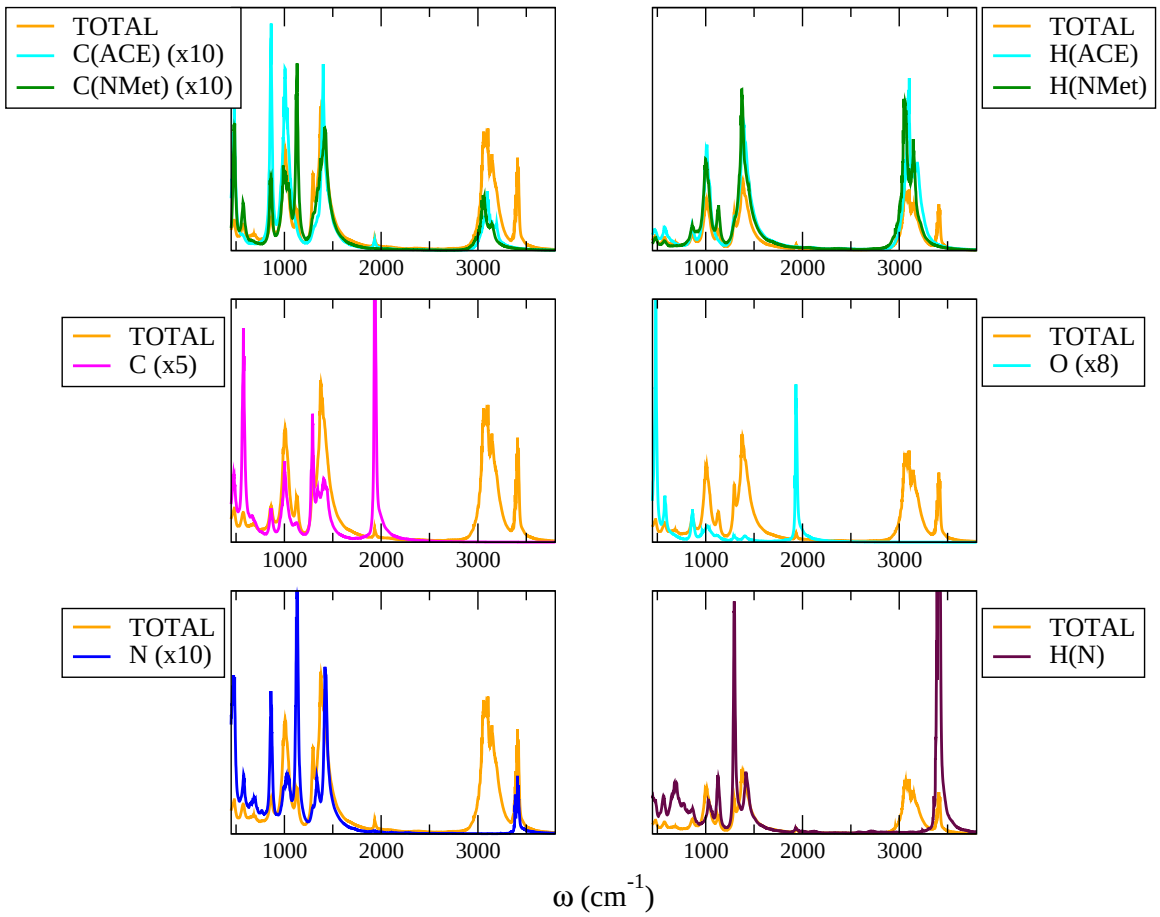

Figure 8: Cis NMA in the gas phase, semi-empirical Hamiltonian. Atomic contributions to the total VDOS (reported in orange). Intensities are in arbitrary units.

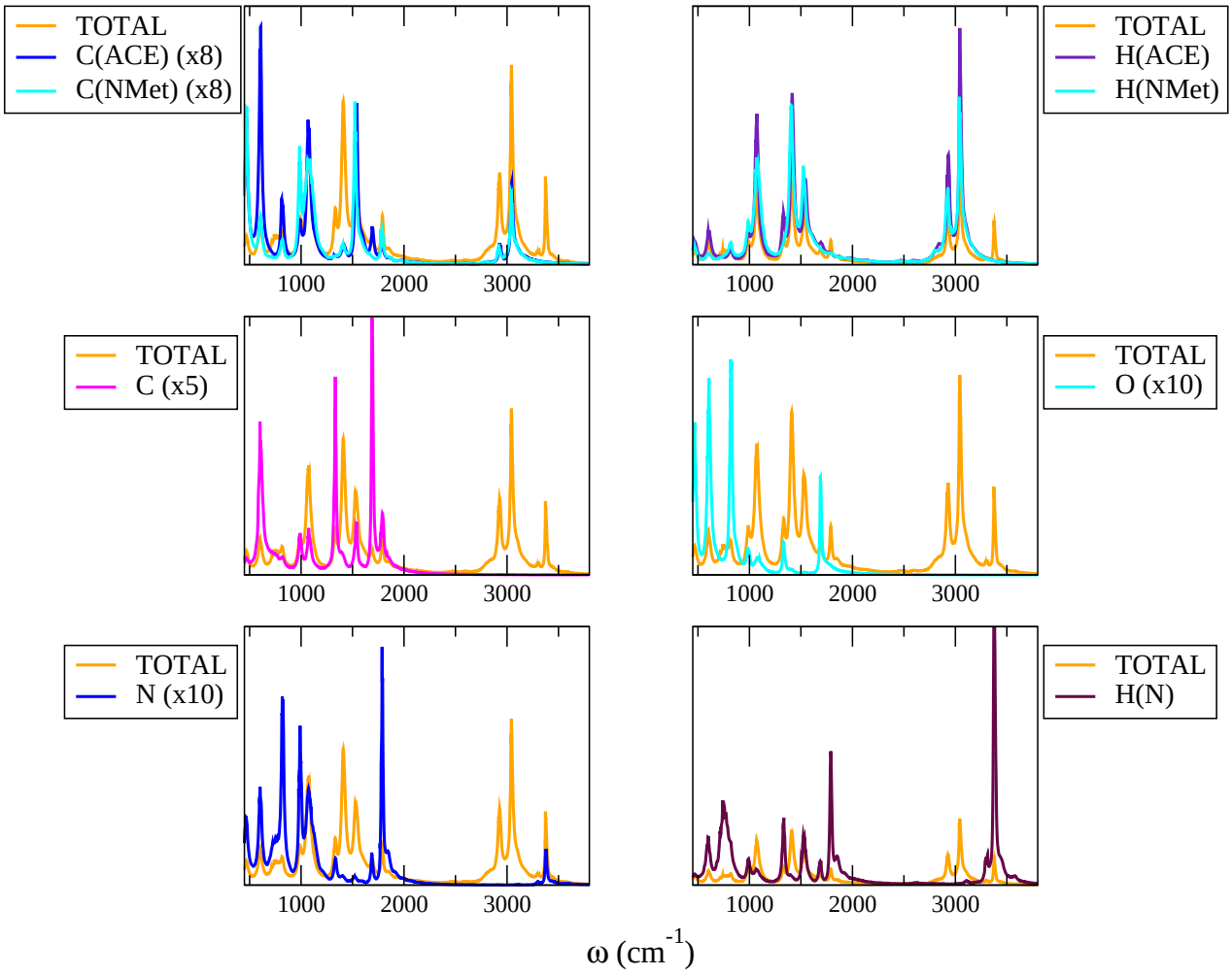

Figure 9: Trans NMA in water, MM force field. Atomic contributions to the total VDOS (reported in orange). Intensities are in arbitrary units.

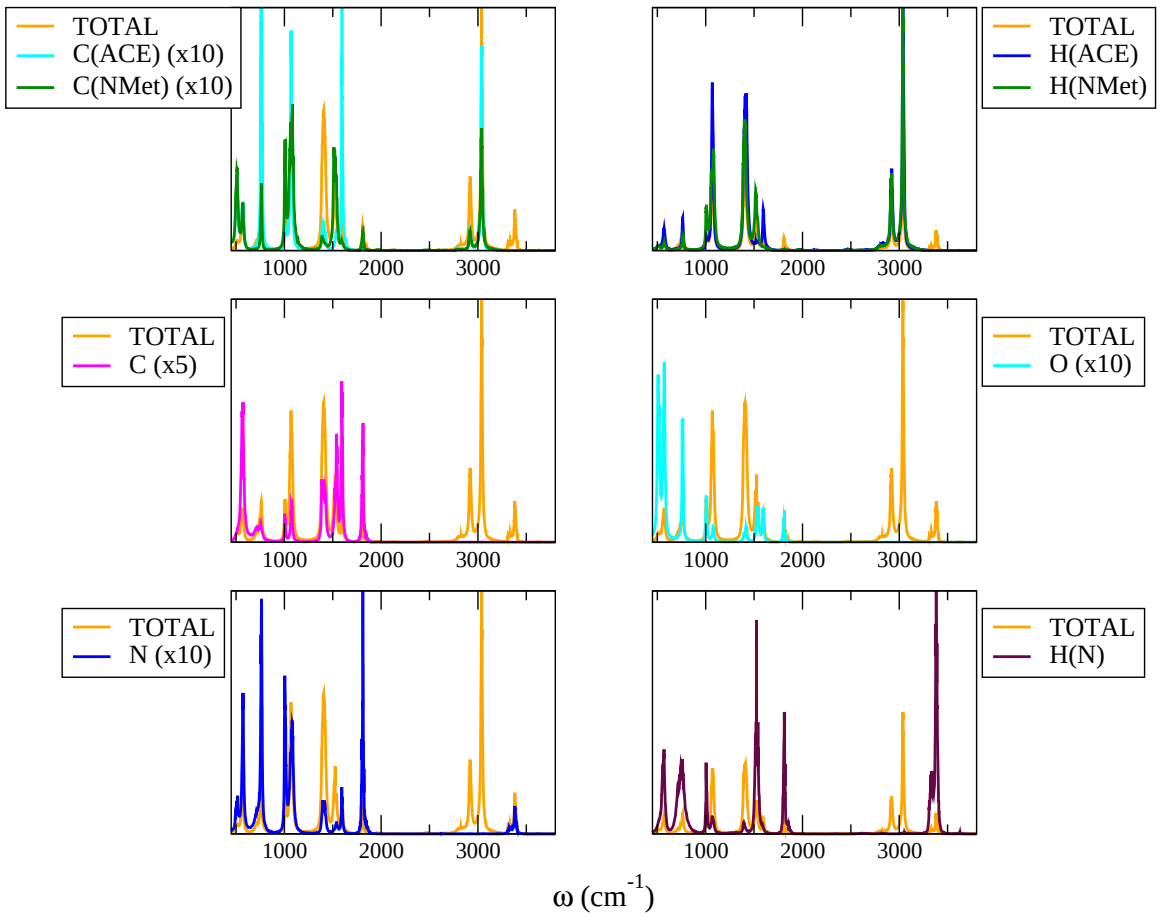

Figure 10: Cis NMA in water, MM force field. Atomic contributions to the total VDOS (reported in orange). Intensities are in arbitrary units.

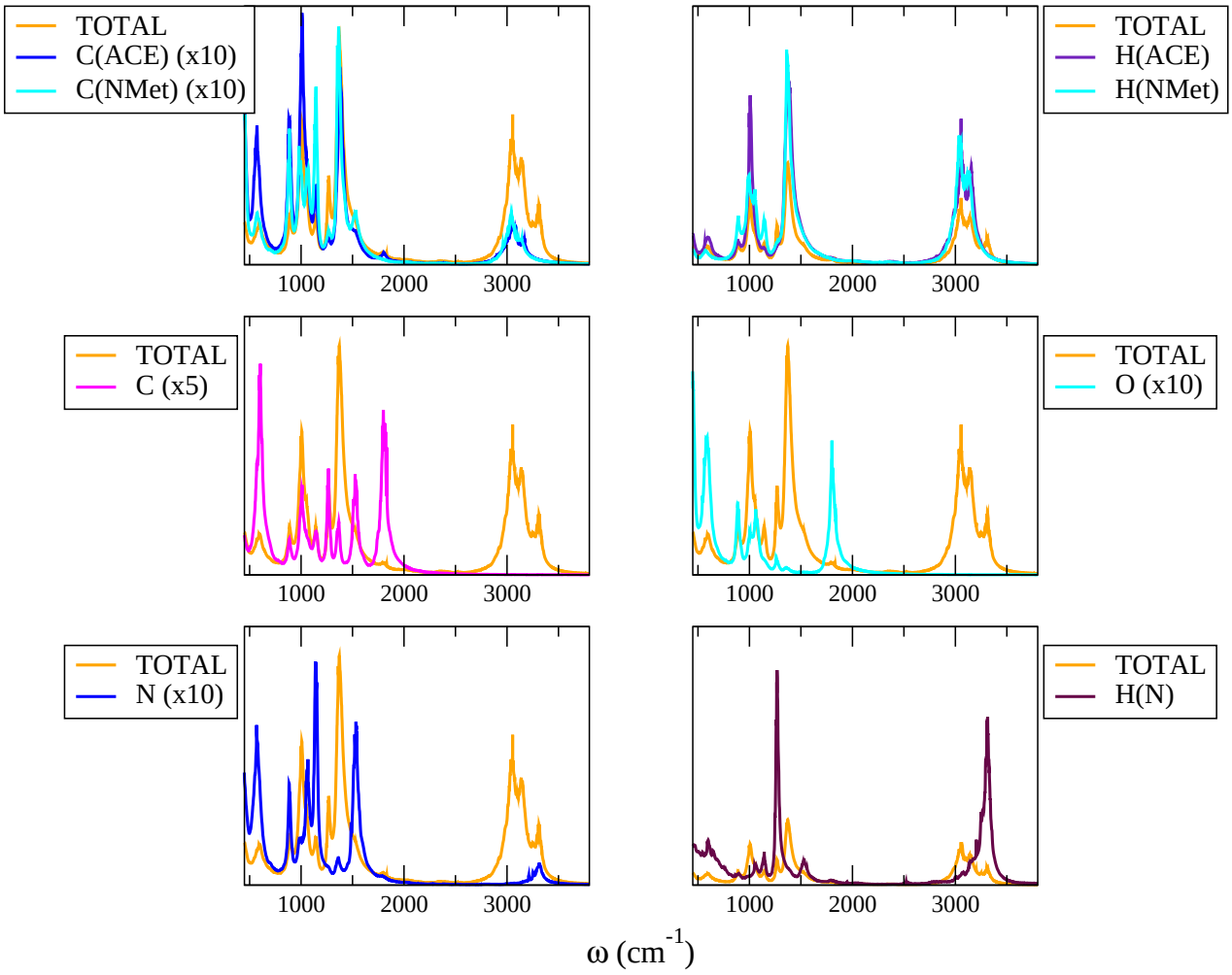

Figure 11: Trans NMA in water, semi-empirical Hamiltonian. Atomic contributions to the total VDOS (reported in orange). Intensities are in arbitrary units.