Infrared Spectroscopy from Ab Initio Molecular Dynamics - the MeCN-HCl Molecular Complex

Nicolai Bork,^{1,2} Ville Loukonen,² Henrik G. Kjaergaard,^{*,1} and Hanna Vehkamäki²

October 3, 2014

Supporting Information

 Department of Chemistry, University of Copenhagen, Universitetsparken 5 ,DK-2100 Copenhagen Ø, Denmark
Department of Physics, University of Helsinki, P.O. Box 64, FI-00014 Helsinki, Finland
* Correspondence to: hgk@chem.ku.dk



Figure S1: Convergence of potential energy and dipole moment as function of length of the cubic unit cell, using the PBE functional and the aug-TZV2P basis set. A $(30 \text{ Å})^3$ cell was chosen.



Figure S2: Convergence of potential energy and dipole moment as function of basis set using the PBE functional and a $(30 \text{ Å})^3$ cell. The aug-TZV2P basis set was chosen.



Figure S3: Quantum correction factors to Equation 1 in the main article applied to the 55 ps MD simulation. $\beta = (k_B T)^{-1}$ where k_B is Boltzmanns constant and T=298 K. \hbar is the reduced Planck constant.



Figure S4: N-Cl distance as function of step number.



Figure S5: Dipole moment as function of step number.



Figure S6: Comparison of Fourier transform of dipole moment autocorrelation function of the 55 ps MD run and the experimental FTIR spectrum. The modelled spectrum is vertically scaled and red-shifted 100 cm⁻¹ for clarity.

Table S1: XYZ coordinates of the optimized MeCN-HCl geometry using PBE/aug-TZV2P. This structure is used as starting configuration for the MD run. Units are Å.

Atom	Х	Υ	Z
С	0.0000000480	-0.0005804741	-2.0700911209
\mathbf{C}	0.0000022126	-0.0001709087	-0.6171001600
Ν	-0.0000008878	0.0000684174	0.5468957862
Cl	0.0000062867	0.0040473574	3.7463773610
Η	0.8941797700	-0.5169452410	-2.4478407585
Η	-0.8941604645	-0.5169792889	-2.4478396282
Η	-0.0000198152	1.0317894539	-2.4483356092
Η	0.0000043989	0.0022401634	2.4230332684

HCl		MeCN	MeCN-HCl		
				177.3	(0.0024)
				178.2	(0.0016)
				178.3	(0.0015)
		389.1	(0.00019)	394.0	(0.00027)
		389.1	(0.00019)	394.0	(0.00027)
				533.3	(0.0036)
				533.4	(0.0036)
		934.9	(0.00051)	944.1	(0.0018)
		1016.2	(0.0012)	1015.5	(0.0015)
		1016.2	(0.0012)	1015.6	(0.0015)
		1349.5	(0.0015)	1349.1	(0.0013)
		1418.3	(0.0026)	1414.5	(0.0027)
		1418.3	(0.0026)	1414.5	(0.0027)
		2276.5	(0.0026)	2295.6	(0.0041)
2876.8	(0.0050)			2520.7	(0.028)
		2974.6	(0.0011)	2977.7	(0.00029)
		3057.0	(0.00038)	3062.4	(0.00023)
		3057.1	(0.00038)	3062.5	(0.00023)

Table S2: Vibrational frequencies (in $\rm cm^{-1})$ of HCl, MeCN, and the MeCN-HCl complex calculated using PBE/aug-TZV2P. Absorbsion intensities are given in parenthesis.



Figure S7: A histogram of the population as function of the N-Cl distance of the 55 picoseconds until the cluster decomposes. Harmonic HCl stretch wavenumbers (green), harmonic HCl stretch absorption intensities (blue), and potential energies (black) of optimized structures with fixed N-Cl distances at the PBE/aug-cc-pV(T+d)Z level of theory. The corresponding molecular structures are shown in Fig. S10.



Figure S8: A histogram of the population as function of the C-N-H angle of the 55 picoseconds until the cluster decomposes. Harmonic HCl stretch wavenumbers (green), harmonic HCl stretch absorption intensities (blue), and potential energies (black) of optimized structures with fixed C-N-H angles at the PBE/aug-cc-pV(T+d)Z level of theory. The corresponding molecular structures are shown in Fig. S11.



Figure S9: Dependence of ν_{HCl} and I_{HCl} on the three geometrical parameters under investigation for 22 geometries from the molecular dynamics simulation with 2.5 ps spacing, i.e. the geometry at 2.5 ps, 5 ps, ..., and 55 ps. Although significant scatter is seen in the case of the N-H-Cl angle and even more so in the C-N-H angle, the trends resemble those of Figures 3, S7 and S8 (included as connected hollow points). Generally, the structures from the MD simulation have lower absorption intensities and higher H-Cl stretch wavenumbers than the constrained optimizations which is as expected since the hydrogen bond, generally, is strengthened during the constrained optimization. For all structures, the H-Cl distance is optimized prior to the vibrational analysis with all atoms but the H atom fixed in space. The effect of this optimization, on the value of the three investigated parameters is negligible.



Figure S10: Optimized geometries of the MeCN-HCl molecular complex at fixed N-Cl distances, at the PBE/aug-cc-pV(T+d)Z level of theory. Cl is green, H is white, N is blue and C is grey. The Cl-H-N-C-C atoms are essentially perfectly aligned. These geometries are used for calculating the wavenumbers, absorption intensities, and potential energy surface of the harmonic HCl stretch, shown in Fig. S7.



Figure S11: Optimized geometries of the MeCN-HCl molecular complex at fixed C-N-H angles, at the PBE/aug-cc-pV(T+d)Z level of theory. Cl is green, H is white, N is blue and C is grey. These geometries are used for calculating the wavenumbers, absorption intensities, and potential energy surface of the harmonic HCl stretch, shown in Fig. S8.



Figure S12: Comparison of the experimental FTIR spectrum and the simulated spectrum using the N-Cl distance as the only variable degree of freedom. The simulated spectrum is vertically scaled.



Figure S13: Comparison of the experimental FTIR spectrum and the simulated spectrum using the C-N-H angle as the only variable degree of freedom. The simulated spectrum is blue-shifted 180 cm^{-1} and vertically scaled.