Electronic supplementary information (ESI)

Infrared spectroscopy of nucleotides in the gas phase
2. The protonated cyclic 3',5'-adenosine monophosphate

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- **Reference of Gaussian 03.** Any additional computational detail and material (cartesian coordinate xyz files, calculated vibrational frequencies for all structures, etc.) is available upon request.

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Table S1 Vibrational assignment of [*c*AMP+H]$^+$ in the 3200-3700 cm^{-1} region. Experimental and calculated (scaling factor value: 0.955) wavenumbers are given in cm^{-1} for structures **N3-s'**, **N3-a**, **N1-s'**, and **N7-a**; calculated intensities (in parentheses) are given in km mol^{-1}.

Exp	Mode	N3_s'	N1_s'	Mode	N3_a	Mode	N7_a
-	-	-	-	N^+H	3258 (473)		
3404 (sh)	N^+H	3390 (362)	3405 (201)	NH_2 s str	3405 (257)	NH_2 s str	3426 (206)
3420	NH_2 s str	3406 (170)	3412 (185)		-		
						N^+H	3460 (182)
3527	NH_2 s str	3525 (109)	3520 (117)	NH_2 s str	3525 (109)		
				Sugar OH	3585 (145)	NH_2 s str	3554 (73)
3618	Sugar OH	3618 (103)	3617 (91)	-		Sugar OH	3621 (101)
3647	Phosphate OH	3645 (269)	3650 (246)	Phosphate OH	3647 (236)	Phosphate OH	3649 (220)

Table S2 Vibrational assignment of [*c*AMP+H]$^+$ in the 800-1800 cm^{-1} region. Experimental and calculated (scaling factor value: 0.98) wavenumbers are given in cm^{-1} for structures **N3-s'** and **N1-s'**; calculated intensities (in parentheses) are given in km mol^{-1}.

	Exp	**N3-s'**	exp/raw	**N1-s'**	exp/raw
P-OC stretches	857	810 (208)	1.04	816 (212)	1.03
P-OH stretch (equatorial)	941	906 (378)	1.02	904 (386)	1.02
Ribose CO and Phosphate CO stretch	1035	1018 (304)	1.00	994 (97)	1.02
Ribose CC stretch	1124	1119 (215)	0.98	1122 (102)	0.98
Sugar OH bend					
Stretch P=O (axial)	1321	1276 (150)	1.01	1266 (152)	1.02
Adenine ring def		1468 (113)		1463 (42)	
N^+-H stretch (+Adenine ring def)		1619 (192)		1616 (42)	
NH2 scissoring	1658	1656 (917)	0.98	1681 (878)	0.97

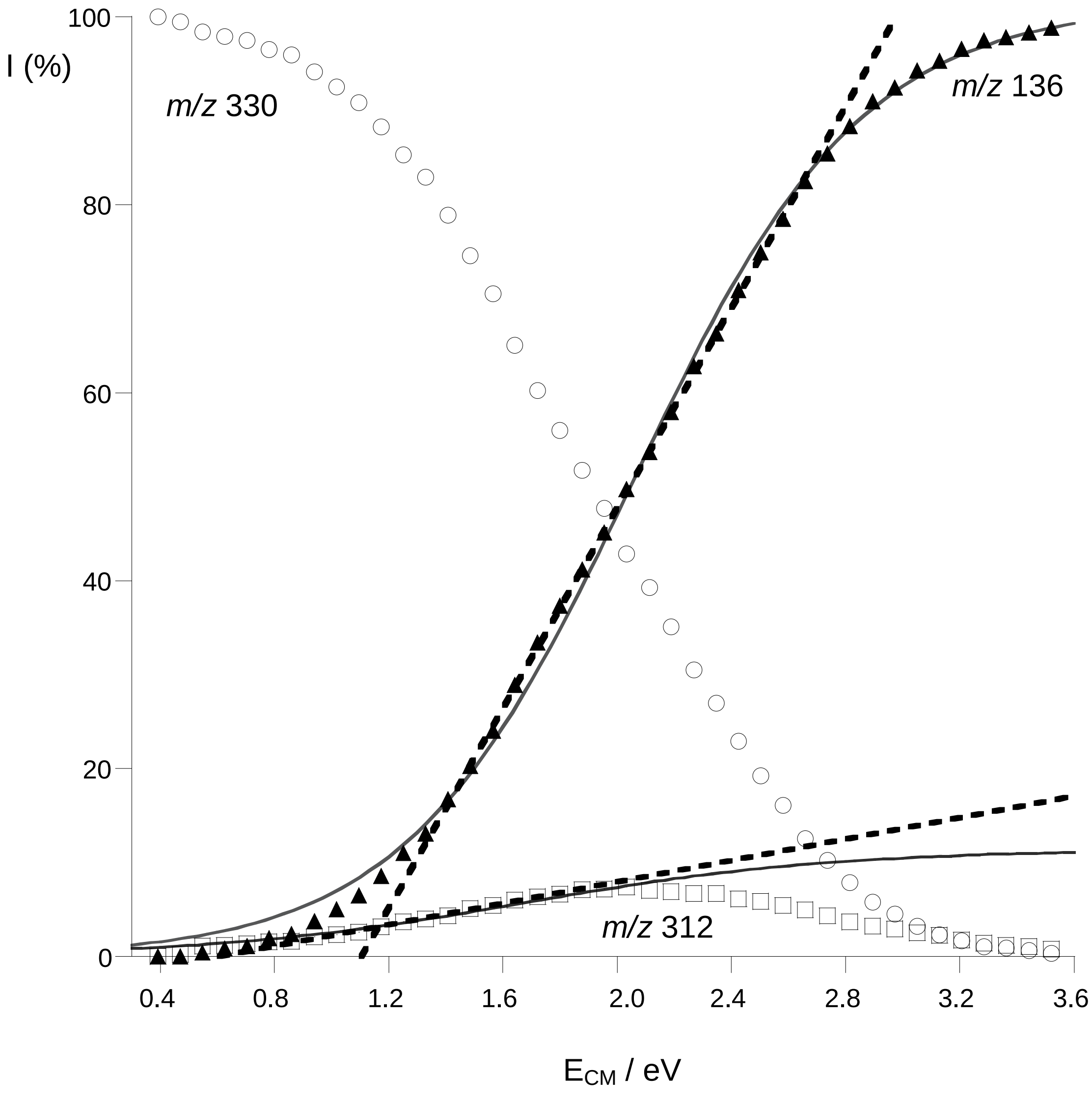


Fig. S1. Relative abundance of the precursor and fragment ions as a function of the center of mass collision energy (E_{CM}) associated with the CID of mass-selected [*c*AMP+H]$^+$ ions (○, *m/z* 330) to afford ions at *m/z* 312 (□) and 136 (▲).

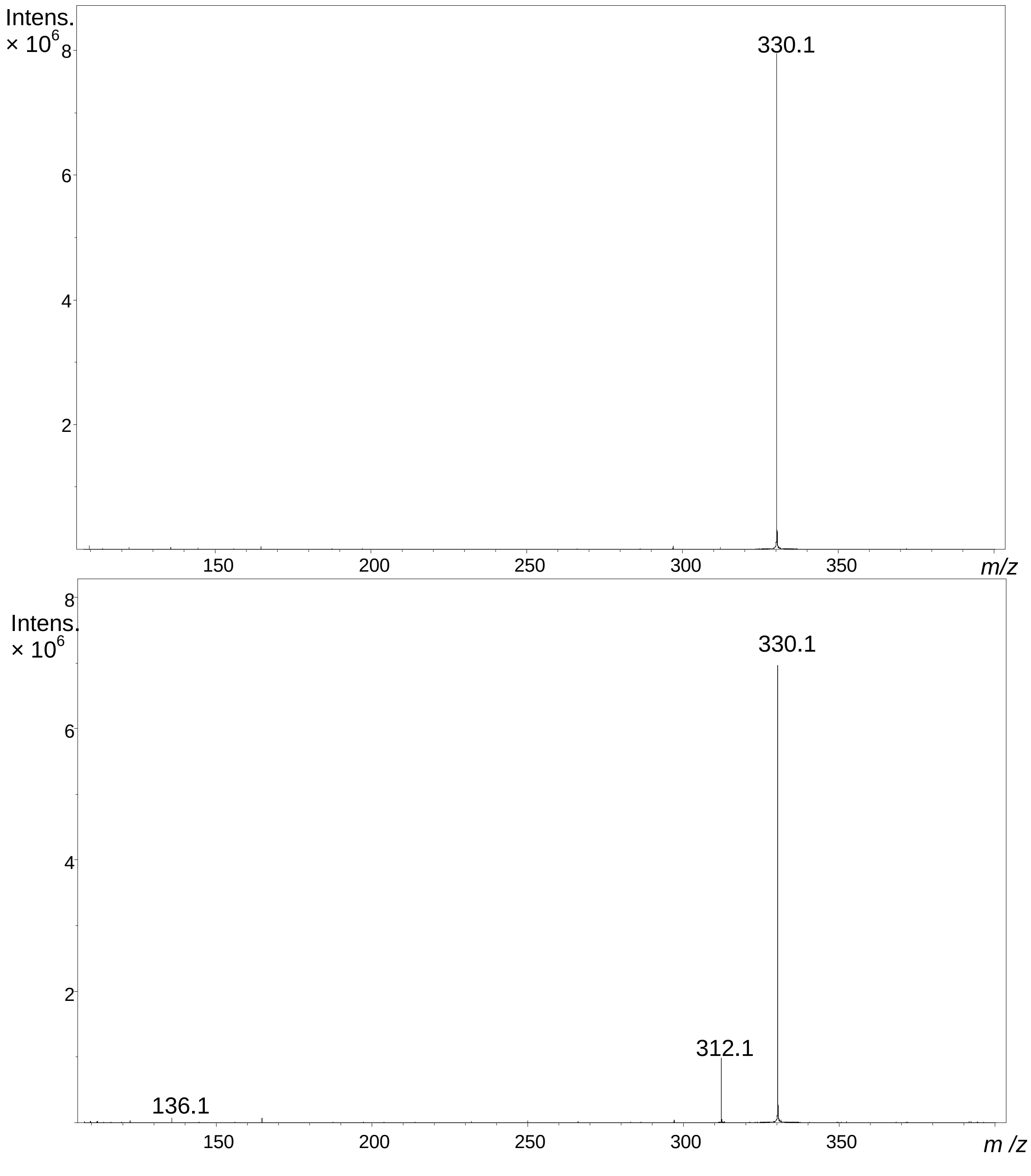
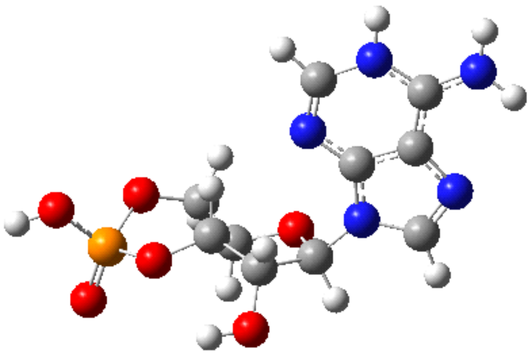
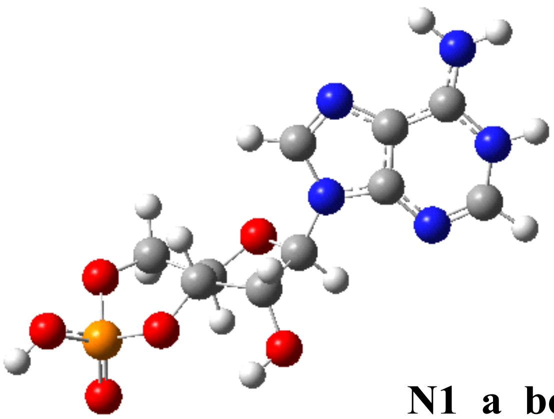


Fig. S2. MS/MS mass spectra recorded after irradiation of mass selected [*c*AMP+H]$^+$ (*m/z* 330) when the laser is turned off resonance (upper trace) and on resonance (lower trace) with an IR active mode (1660 cm^{-1}).



N1_s_boat
+3.2



N1_a_boat
+4.5

Fig. S3. Optimized structures for low energy conformers of N1 protonated structures of [*c*AMP+H]$^+$ with a twist-boat cyclic phosphate. Relative energies (ΔH(0K) B3LYP/6-311+G(d,p)) are given in units of kJ.mol^{-1}.

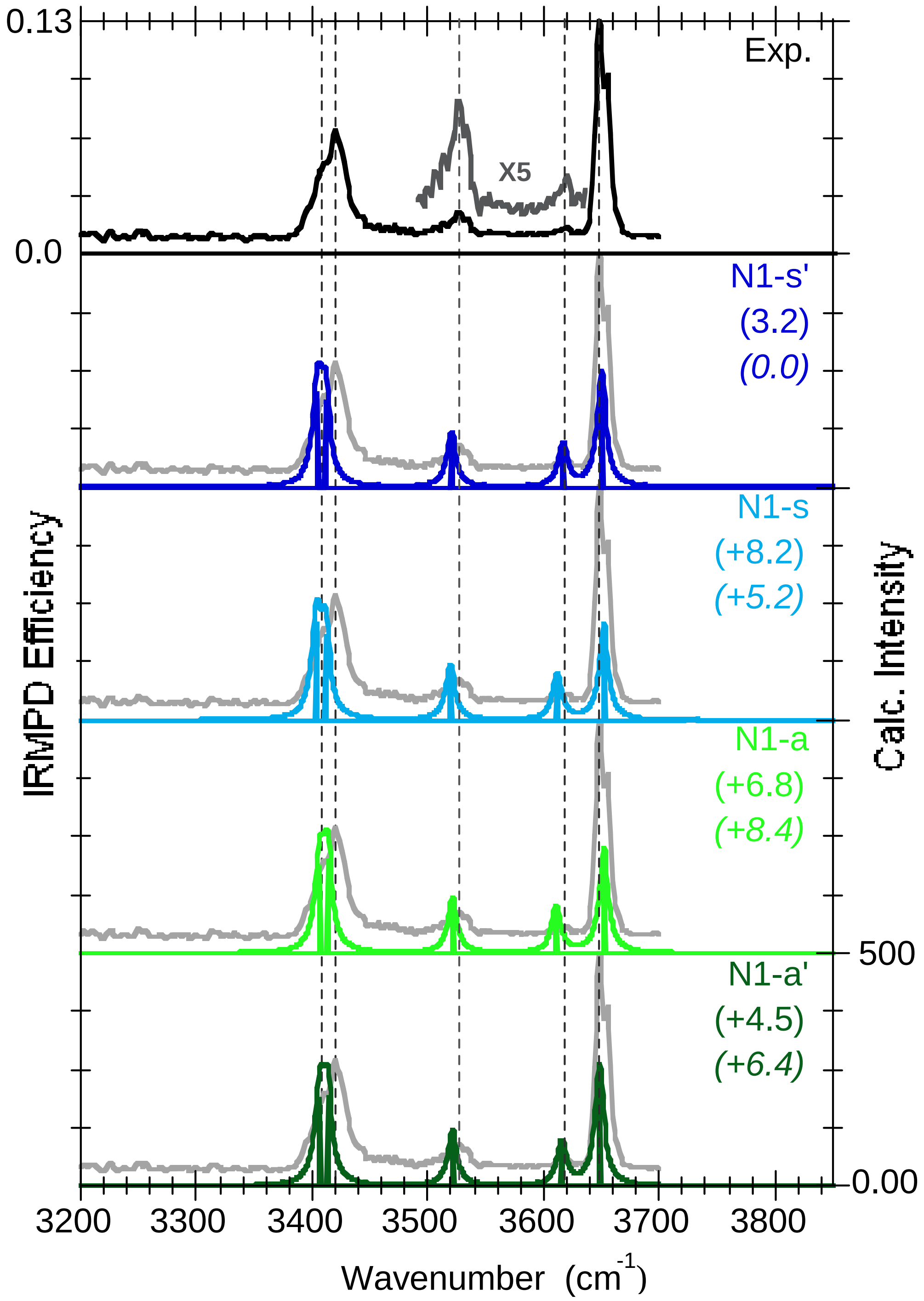


Fig. S4. Experimental IRMPD spectrum of $[c\text{AMP+H}]^+$ (upper trace) in the 3200-3700 cm^{-1} range and calculated IR absorption spectra of N1 protonated structures (see Fig. 3 for the labels); calculated intensities are given in $km.mol^{-1}$ on the right scale, each band is convoluted by a lorentzian profile (fwhm=10 cm^{-1}); relative ΔH(0K) computed at the B3LYP/B2 (upper values) and at the MP2/B2//B3LYP/B2 level are given in units of $kJ.mol^{-1}$.

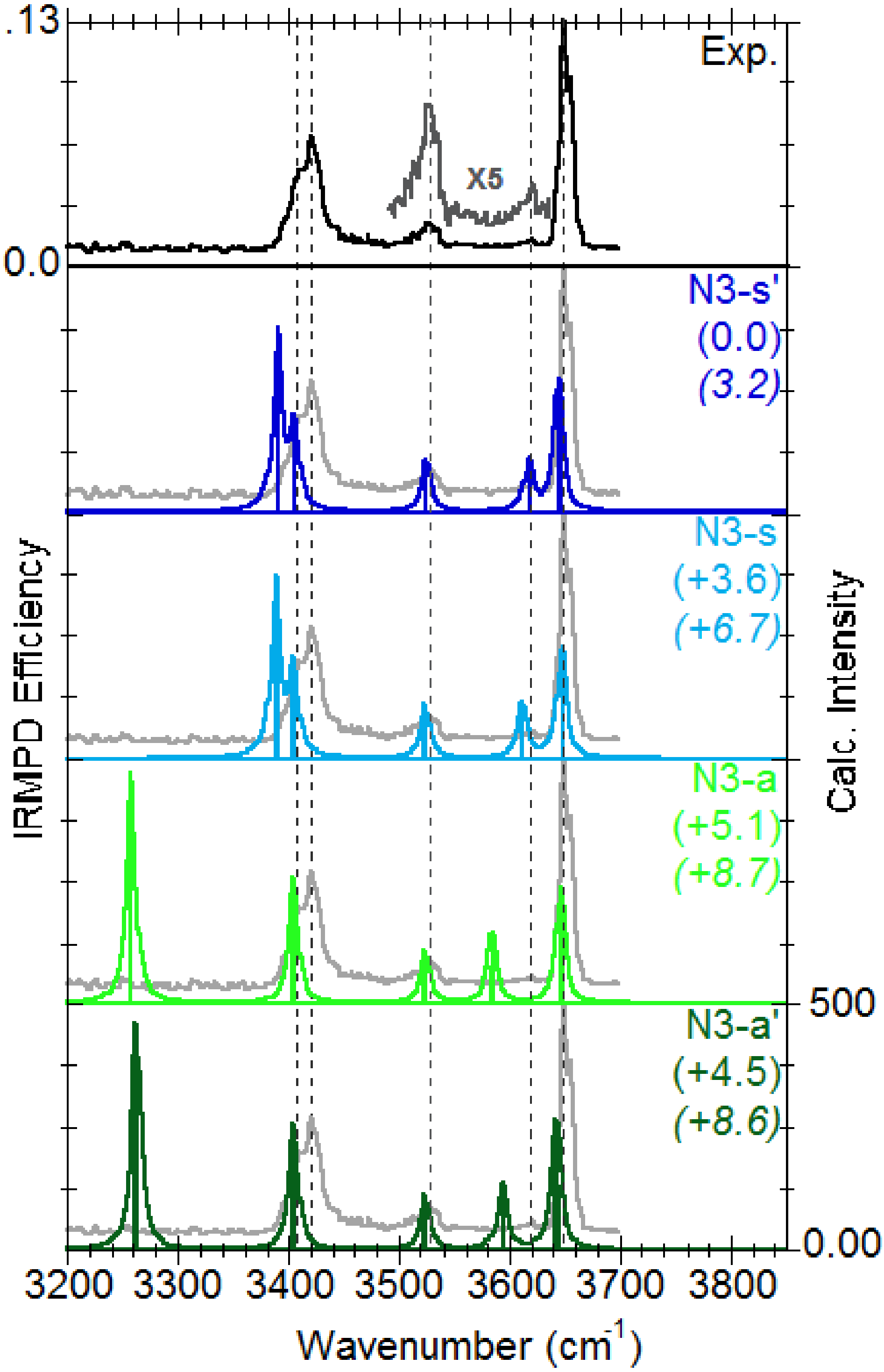


Fig. S5. Experimental IRMPD spectrum of [*c*AMP+H]$^+$ (upper trace) in the 3200-3700 cm^{-1} range and calculated IR absorption spectra of N3 protonated structures (see Fig. 3 for the labels); calculated intensities are given in km.mol^{-1} on the right scale, each band is convoluted by a lorentzian profile (fwhm=10 cm^{-1}); relative ΔH(0K) computed at the B3LYP/B2 (upper values) and at the MP2/B2//B3LYP/B2 level are given in units of kJ.mol^{-1}.

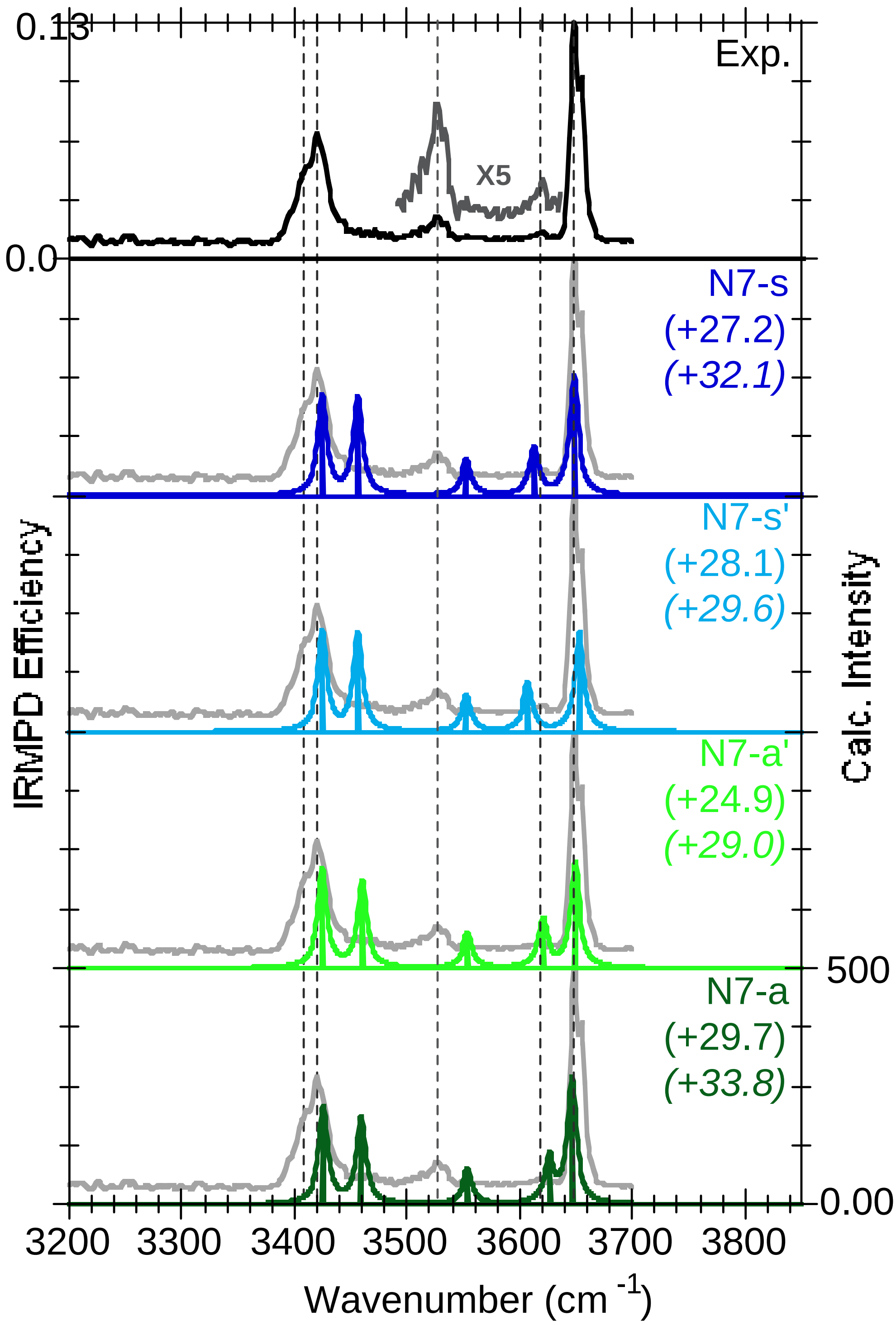


Fig. S6. Experimental IRMPD spectrum of [*c*AMP+H]$^+$ (upper trace) in the 3200-3700 cm^{-1} range and calculated IR absorption spectra of N7 protonated structures (see Fig. 3 for the labels); calculated intensities are given in km.mol^{-1} on the right scale, each band is convoluted by a lorentzian profile (fwhm=10 cm^{-1}); relative ΔH(0K) computed at the B3LYP/B2 (upper values) and at the MP2/B2//B3LYP/B2 level are given in units of kJ.mol^{-1}.

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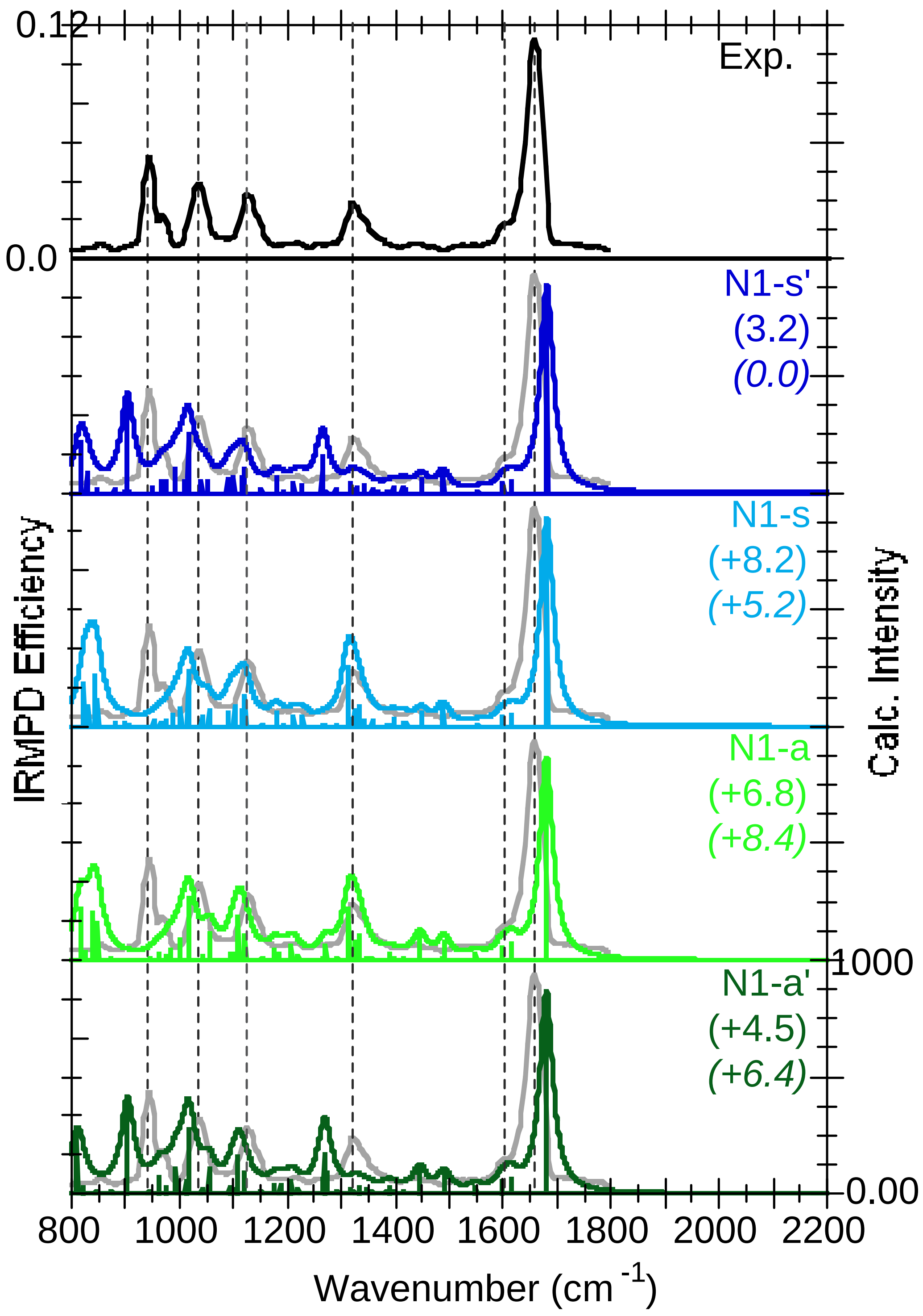

Fig. S7. Experimental IRMPD spectrum of [*c*AMP+H]$^+$ (upper trace) in the 800-1800 cm^{-1} range and calculated IR absorption spectra of N1 protonated structures (see Fig. 3 for the labels); calculated intensities are given in km.mol^{-1} on the right scale, each band is convoluted by a lorentzian profile (fwhm=30 cm^{-1}); relative ΔH(0K) computed at the B3LYP/B2 (upper values) and at the MP2/B2//B3LYP/B2 level are given in units of kJ.mol^{-1}.

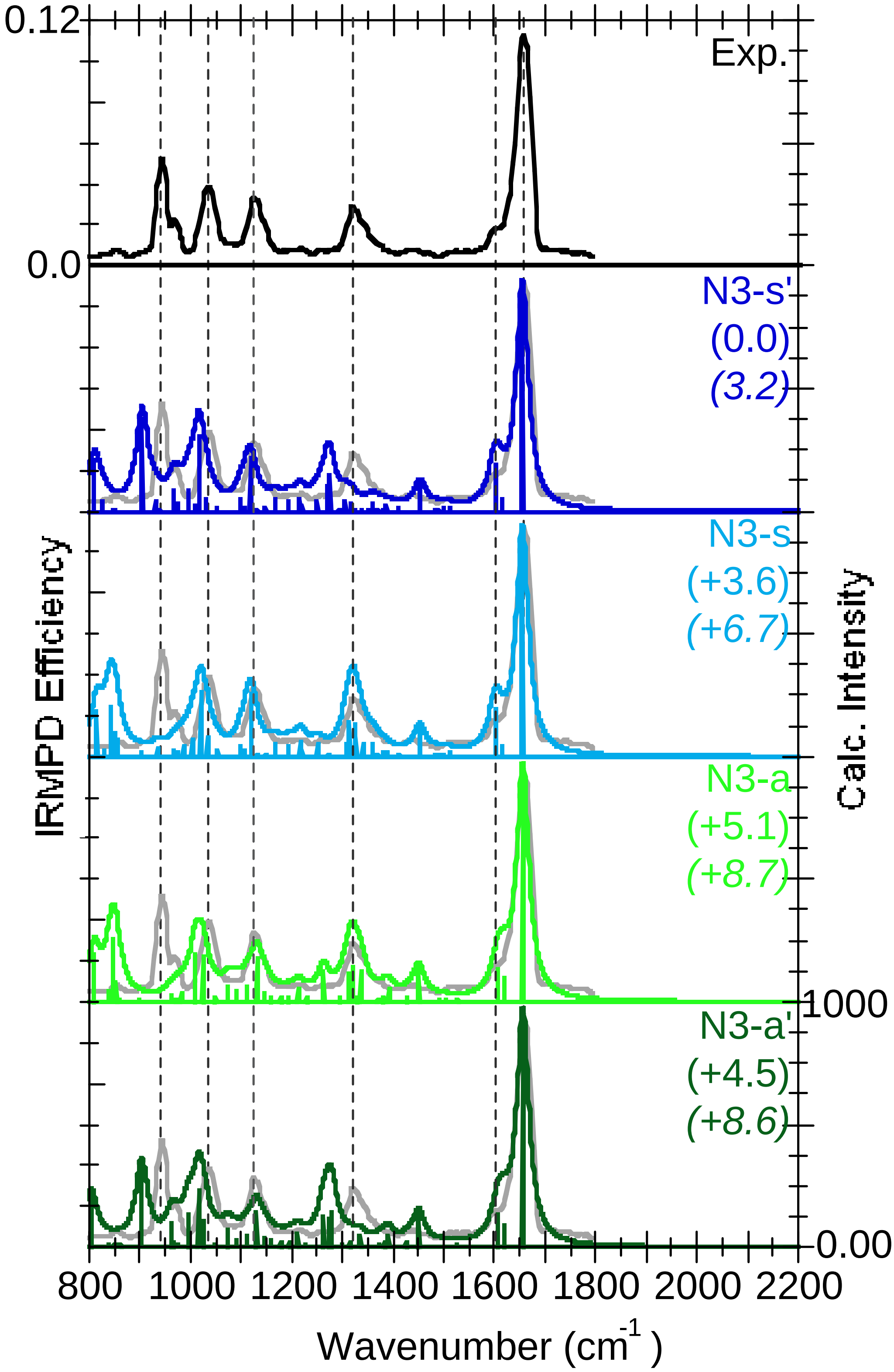

Fig. S8. Experimental IRMPD spectrum of [*c*AMP+H]$^+$ (upper trace) in the 800-1800 cm^{-1} range and calculated IR absorption spectra of N3 protonated structures (see Fig. 3 for the labels); calculated intensities are given in km.mol^{-1} on the right scale, each band is convoluted by a lorentzian profile (fwhm=30 cm^{-1}); relative ΔH(0K) computed at the B3LYP/B2 (upper values) and at the MP2/B2//B3LYP/B2 level are given in units of kJ.mol^{-1}.

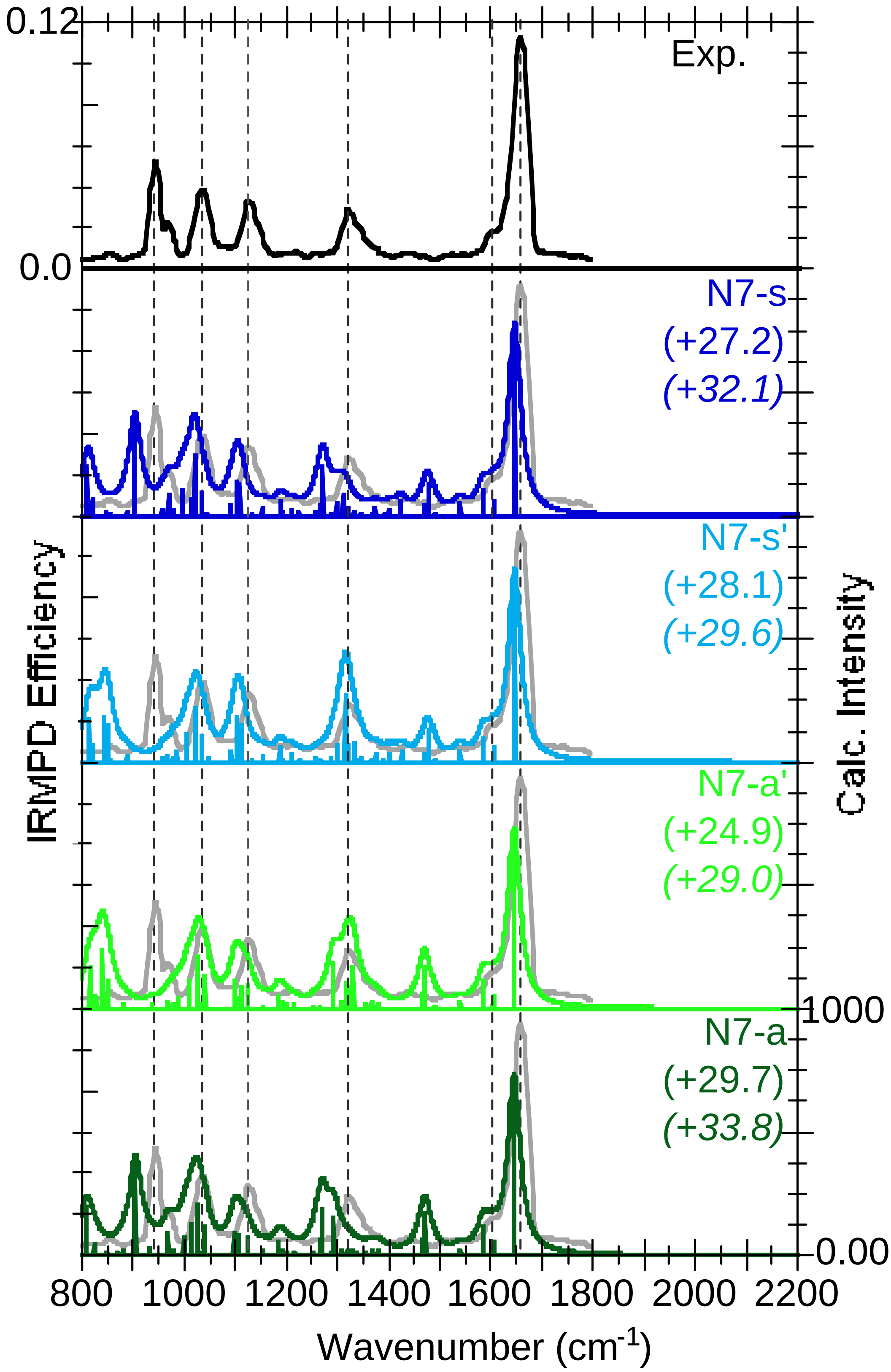

Fig. S9. Experimental IRMPD spectrum of [*c*AMP+H]$^+$ (upper trace) in the 800-1800 cm^{-1} range and calculated IR absorption spectra of N7 protonated structures (see Fig. 3 for the labels); calculated intensities are given in km.mol^{-1} on the right scale, each band is convoluted by a lorentzian profile (fwhm=30 cm^{-1}); relative ΔH(0K) computed at the B3LYP/B2 (upper values) and at the MP2/B2//B3LYP/B2 level are given in units of kJ.mol^{-1}.

Reference Gaussian 03, Revision C.02

Reference Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.