

**Assigning the NH stretches of the guanine tautomers using
adiabatic separation: CCSD(T) benchmark calculations**

Dana Nachtigallová, Pavel Hobza and Vladimír Špirko

Center for Biomolecules and Complex Molecular Systems

Institute of Organic Chemistry and Biochemistry, v.v.i.,

Academy of Sciences of the Czech Republic

Flemingovo nám. 2, 160 10 Prague 6, Czech Republic

TABLE I: Relative energies (in kJ/mol) of the guanine tautomers

	MP2/cc-pVTZ	CCSD(T) ^a	B3LYP/cc-pVTZ	CCSD(T)/aug-cc-pVDZ ^b
G7K	0.00	0.00	0.00	0.00
G9K	1.57	1.80	2.16	2.89
G9Eb	1.86	1.76	7.01	3.81
G9Ea	5.05	5.54	9.38	5.48
G7E	14.90	14.71	19.55	15.48
G7Im	30.30	27.65	24.24	

^a Optimized at the MP2/cc-pVTZ level ^b Optimized at the MP2/aug-cc-pVDZ level¹TABLE II: Observed and calculated NH vibrational frequencies^a

Experiment	MP2 ^b		MP2 ^c		CCSD(T) ^c		B3LYP ^c			
	Ref. ²	Ref. ³	Ref. ⁴	HA ^d	HA ^d	AS ^e	AS ^e	HA ^d	PT ^f	AS ^e
G7K	3504.8(120)	3504	3497	3660.6	3668.0	3525.4	3529.6(102)	3650.3(92)	3470.5	3505.9
G7Im		3505			3666.6	3524.8	3529.2(100)	3649.6(106)	3475.9	3506.4
G9K	3506.9(100)		3490	3664.8	3669.7	3529.4	3530.4(85)	3647.1(69)	3484.0	3504.2
G9Eb	3509.6(105)	3508		3667.4	3673.6	3533.1	3534.1(83)	3651.7(72)	3495.2	3509.1
G9Ea	3511.3(104)	3508	3516	3669.6	3675.7	3535.0	3535.3(84)	3652.5(73)	3488.8	3510.1
G7E		3516		3682.0	3540.1	3542.0(100)	3662.3(84)	3481.2		3518.2

^a Values given in parentheses are absolute IR intensities (in km/mol); the IR intensities taken from Ref.² were calculated using harmonic approximation. ^b6-311G* basis set², ^ccc-pVTZ basis set, ^dharmonic approximation, ^eadiabatic separation, ^fperturbation theory.

¹ Hanuš, M.; Ryjáček, F.; Kabeláč, M.; Kubař, T.; Bogdan, T. V.; Trygubenko, S. A.; Hobza, P. *J. Am. Chem. Soc.* **2003**, *125*, 7678-7688.

² Choi, M. Y.; Miller, R. E. *J. Am. Chem. Soc.* **2006**, *128*, 7320-7328.

³ Mons, M.; Dimicoli, I.; Piuzzi, F.; Tardivel, B.; Elhanine, M. *J. Phys. Chem. A* **2002**, *106*, 5088-5094.

⁴ Nir, E.; Plutzer, C.; Kleinermanns, K.; de Vries, M. S. *Eur. Phys. J. D* **2002**, *20*, 317-329.

TABLE III: Observed and calculated NH₂ vibrational frequencies of G7K and G9K^a

	Experiment	MP2 ^b	MP2 ^c	CCSD(T) ^c	B3LYP ^c	
	Ref ²	HA ^d	AS ^e	AS ^e	HA ^d	PT ^f
G9K: ^{as} ν _{NH₂}	3544.5	3701.3	3500.8	3466.1	3680.6	3522.2
G9K: ^{sym} ν _{NH₂}	3444.5	3587.7	3401.5	3370.4	3572.4	3428.5
G7K: ^{as} ν _{NH₂}	3526.6	3687.1	3486.8	3452.5	3667.3	3505.6
G7K: ^{sym} ν _{NH₂}	3430.5	3576.2	3391.8	3358.5	3561.8	3415.9

^a The dynamical calculations were simplified by using the leading (constant) terms of the standard **G** matrix. ^b6-311G* basis set,² ^ccc-pVTZ basis set, ^dharmonic approximation, ^eadiabatic separation, ^fperturbation theory.