THE JOURNAL OF PHYSICAL CHEMISTRY A LETTERS

2008, *112,* 1854−1856
Published on Web 02/13/2008

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, Academy of Sciences of the Czech Republic, v.v.i., Flemingovo nám.2, 160 10 Prague 6, Czech Republic

Received: November 24, 2007; In Final Form: January 29, 2008

Using an adiabatic separation of the NH stretching vibration from the remaining vibrational molecular motions, the NH fundamental frequencies and absolute intensities of several keto/enol and 7/9NH tautomers of guanine are evaluated ab initio within the framework of a one-dimensional “semirigid” stretching Hamiltonian. The frequencies (calculated by means of the standard MP2, CCSD(T) and DFT procedures) are in a close one-to-one harmony with their experimental counterparts, thus evidencing the adequacy of the used separation for reliable assigning of the NH stretches in the vibrational spectra of very large molecular systems.

Introduction

Infrared (IR) gas-phase spectroscopy is one of the most powerful techniques for the structural characterization of molecular systems isolated in the gas phase. Mostly due to the experimental problems associated with volatilizing large, thermally labile, molecules, the technique is routinely used only for studying very small molecular systems. However, thanks to gradual progress in overcoming these problems and improvement of the available experimental setups over the last two decades (see, e.g., refs 1−6 and references therein), the experimental problems do appear surmountable and theory thus becomes more responsible for the application limits than experiment. The problems obviously arise from the strongly nonlinear dependence of the complexity of the molecular dynamical problems on the number of actual vibrational degrees of freedom. The problems are particularly enhanced by the conformational instabilities of the studied systems. The presence of surpassable barriers on the molecular potential energy surface prevents various theoretical treatments going beyond the harmonic approximation, such as the molecular dynamics (MD), perturbation theory (PT), and vibrational self-consistent (VSCF) techniques (see, e.g., refs 7−10 and references therein) from being used safely. A popular way of overcoming these limits is based on an empirical scaling of the calculated harmonic frequencies (see, e.g., refs 11 and 12). However, in the case of vibrational motions opposed by strongly anharmonic potentials (for instance, motions involved in hydrogen bondings, internal rotations, and ring deformations), the approach is no longer reliable[13] and, as these motions constitute very sensitive probes for structural assignments (see, e.g., refs 5 and 13 and references therein), a more realistic method is highly desirable. A possible way of meeting this requirement may lie in an adiabatic separation of the probing molecular modes from the “bath” of the remaining molecular motions while disregarding the nonadiabatic couplings (i.e., a Born−Oppenheimer-type approximation). Being only few-dimensional, the resulting dynamical problems are tractable in a numerically exact way for practically any shape of the corresponding effective potentials (see, e.g., ref 14). The approach is also very economical in terms of the ab initio calculations as it requires energy optimizations for only very few a molecular geometry points (see, e.g., ref 15). Apparently, it is ideally suited in the case of a single, highly characteristic molecular vibration, which is coupled to the remaining molecular motions only weakly. Although formally one-dimensional, the approach allows for all the important interaction terms from potential energy and even rotation−vibration interaction terms from kinetic energy by making it possible for the molecular valence coordinates to vary with the reference coordinate.[16,17] To gain insight into its prospects and reliability in the case of very large systems, we decided to probe it by performing model calculations on a suitable molecular model.

An excellent testing task is posed by the assignment of the NH stretches of the *keto*/*enol* and 7/9NH guanine tautomers (see Figure 1), which has been the subject of many discussions.[18−21] The main reason for the contradictory results of several groups is the close resemblance of the corresponding vibrational frequencies.[18−20] In addition, the tautomers are very close in their energy contents, four of them being within 5 kJ/mol. The assignment of the IR−UV double resonance spectra is further complicated by the very short lifetime of some of the tautomers because of ultrafast nonradiative decay.[22,23]

Despite being relatively large, guanine is still tractable by means of highly accurate ab initio procedures and thus allows for benchmark calculations. Moreover, the NH frequencies of the four lowest-energy tautomers are conclusively assigned by comparing experimental vibration transition moment angles (obtained using the helium nanodroplet isolation technique) with their ab initio counterparts.[21]

---

* Corresponding authors. E-mail: P.H., hobza@uochb.cas.cz; V.S., spirko@uochb.cas.cz.

10.1021/jp711151a CCC: $40.75

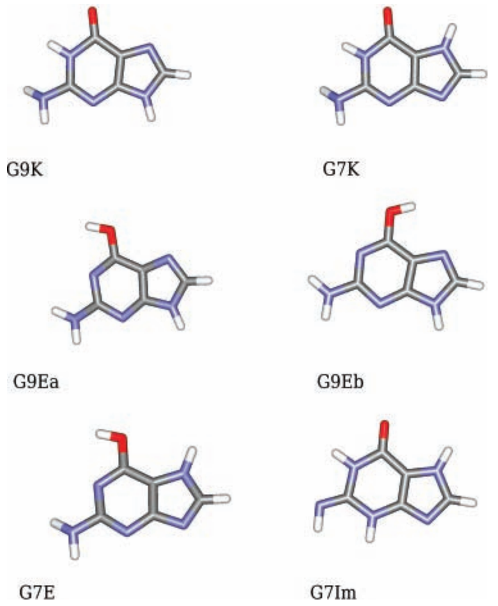

Figure 1. Chemical structures of the studied tautomers of guanine. C, N, O, and H atoms are represented in gray, blue, red, and white, respectively.

Computational Details

Ab Initio Calculations. For all tautomers, the geometry optimizations were performed using the MP2/cc-pVTZ method. A scan along a N−H bond with all the remaining structure parameters optimized was conducted at the same level of theory. The structures were subsequently used for the calculation of the scan using the CCSD(T)/cc-pVTZ method. The same calculations were also performed at the B3LYP/cc-pVTZ level.

Vibrational Calculations. The dynamical calculations were performed within the framework of the semirigid-bender formalism[17] using a nonrigid molecular reference closely following the NH stretching (r) motion. The appropriate Hamiltonian acquires the following form:

$$H = \frac{1}{2}\mu_{rr} J_r^{\,2} + \frac{1}{2}(J_r \mu_{rr}) J_r + \frac{1}{2}\mu^{1/4}\{J_r \mu_{rr} \mu^{-1/2}[J_r \mu^{1/4}]\} + V(r)$$

where $J_r = -i\hbar(\mathrm{d}/\mathrm{d}r)$, $\mu_{rr}(r)$ is the NH stretching component of the tensor that is the inverse of the 4×4 generalized HBJ[16] molecular inertia tensor, μ is the determinant of the matrix $[\mu_{\alpha,\beta}]$ ($\alpha,\beta = x,y,x,r$; x,y,z being Cartesian atomic coordinates in the molecular-fixed-axis system), and $V(r)$ is the NH stretching (energy minimum path) potential (for more details, see refs 16 and 17).

The eigenvalues and eigenvectors of **H** were obtained by means of the standard Numerov-Cooley integration technique.[24] The dynamical calculations were also performed at the standard harmonic and second-order perturbation theory levels.[8] For ab initio calculations, Molpro,[25] Gaussian03,[26] and Turbomole[27] program packages were used.

Results and Discussion

Complete documentation of the ab initio and dynamical calculations is available in the Supporting Information. The main outcome of the study, i.e., the comparison of the calculated and experimental HN and NH_2 fundamental frequencies, is provided in Table 1. As can be seen from this table, all the “adiabatic” frequencies are in very close agreement with their experimental counterparts and only very small linear shifts make this agreement practically perfect. This is especially true for CCSD(T) calculations where the vibrational frequencies for all tautomers are determined with “spectroscopic” accuracy and the sum of squares of the deviations (cf. Table 1) is less than 4 cm^{-1}. Despite deviating much more from the experiment than the “adiabatic” predictions, the harmonic approximants are still in one-to-one correspondence with the experiment, thus evidencing the reliability of the standard harmonic approach in the probed case. On the contrary, the frequencies evaluated using the standard second-order perturbation theory exhibit strong disharmony with the experiment. This approach is clearly not suitable for the purposes of assignment. The failure is not surprising: the standard polynomial quartic force field representation is inadequate for describing hydrogen containing stretching motions,[28] and moreover, the perturbation series in such cases strongly diverge and their correct summation requires an accounting for very high-order corrections.[29]

Importantly, the frequency differences resulting from fairly “cheap” MP2 and DFT procedures exhibit only slightly larger (theory vs experiment) dispersions than their “expensive” CCSD(T) counterparts. The former methods thus offer a promising potential for the adiabatic treatment of systems that are prohibitive even for the standard harmonic normal coordinate

TABLE 1: Differences between the Observed and Calculated Frequencies

		MP2[a]	MP2[b]		CCSD(T)[b]	B3LYP[b]		
	experiment	HA[c]	HA[c]	AS[d]	AS[d]	HA[c]	PT[e]	AS[d]
G7K	3504.8[f]	155.8	163.2	20.6	24.8	145.5	−34.3	1.1
G7Im	3505,[g] 3503[h]		161.6	19.8	24.2	144.6	−29.1	1.4
G9K	3506.9[f]	157.9	162.8	22.6	23.5	140.2	−22.9	−2.7
G9Eb	3509.6[f]	157.8	164.0	23.5	24.5	142.1	−14.4	−0.5
G9Ea	3511.3[f]	158.3	164.4	23.7	24.0	141.2	−22.5	−1.2
G7E	3516,[g] 3515[h]		166.0	24.1	26.0	146.3	−34.8	2.2
mvd[i]			*163.7*	*22.4*	*24.5*	*143.3*	*−26.3*	*0.1*
ssqd[j]			*11.3*	*15.8*	*3.7*	*31.0*	*311.7*	*17.0*
G9K:$^{\mathrm{as}}\nu_{\mathrm{NH}_2}$[k]	3544.5[f]	156.8		−43.7	−78.4	136.1	−22.3	
G9K:$^{\mathrm{sym}}\nu_{\mathrm{NH}_2}$[k]	3444.5[f]	143.2		−43.0	−74.1	127.9	−16.0	
G7K:$^{\mathrm{as}}\nu_{\mathrm{NH}_2}$[k]	3526.6[f]	160.5		−39.8	−74.1	140.7	−21.0	
G7K:$^{\mathrm{sym}}\nu_{\mathrm{NH}_2}$[k]	3430.5[f]	145.7		−38.7	−72.0	131.3	−14.6	
mvd[i]		*151.7*		*−41.4*	*−74.7*	*134.1*	*18.8*	
ssqd[j]		*211.7*		*17.7*	*21.4*	*93.8*	*42.6*	

[a] 6-311G* basis set.[21] [b] cc-pVTZ basis set. [c] Harmonic approximation. [d] Adiabatic separation. [e] Perturbation theory. [f] Referencd 21. [g] Reference 19. Assignment given in ref 22. [h] Reference 18. Assignment given in ref 22. [i] Mean value of the deviations. [j] Sum of the squares of the differences between the actual deviations and their mean value. [k] The dynamical calculations were simplified by using the leading (constant) terms of the standard **G** matrix.

approach. The reliability of the calculated vibrational energies also proves the reliability of the corresponding wavefunctions and their adequacy for the physically correct estimation of the NH stretching effects on the appropriate molecular properties. As can be seen in the case of the absolute infrared intensities (see Table 2 in Supporting informations), these effects may not be negligible.

Although generally penalised by a striking increase of the formal complexity of the kinetic energy operator, the non-rigid molecular reference adiabatic approach is easily extendable to multidimensional dynamical problems (see, e.g., ref 14). The extension is especially simple in the case of vibrational motions opposed by deep single-minimum potentials. In such cases, the kinetic energy operators exhibit only weak vibrational dependencies and can thus be safely represented by the standard Wilson-Decius **G** matrices.[30,31] The application potentials of this “simplified” approach are illustrated at the bottom of Table 1 by the results obtained for the NH_2 (two-dimensional) dynamical problem of the G7K and G9K tautomers. As arises from the table, the adiabatic approach provides a fairly quantitative reproduction of the ${}^{as}\nu_{NH_2}-{}^{sym}\nu_{NH_2}$ splittings, thus offering additional confirmation of the presented theoretical assignment of the probed guanine tautomers.

As with other approximate procedures, the adiabatic separation approach is beset by inaccuracy, which cannot be determined within its framework and should be thus used cautiously, and, if possible, in combination with other available approaches (both theoretical and experimental). Temporarily, the approach is being adopted for studying conformationally unstable molecular systems (hydrogen-bonded $X-H\cdots Y$ complexes,[14] torsionally flexible model peptides[32]), which cannot be described properly in terms of the standard harmonic approximation, and also tested as a tool for studying very large molecular systems (gramicidin[6]), which are too large to be treated in the full dimensionality even in the harmonic approximation.

Acknowledgment. This work was a part of the research project No. Z40550506) and supported by the Ministry of Education, Youth, and Sports of the Czech Republic (grant No. LC512) and by the Grant Agency of the Academy of Sciences of the Czech Republic (grant Nos. A400550511 and IAA400400504).

Supporting Information Available: Tables of relative energies and vibrational frequencies. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Rizzo, T. R.; Park, Y. D.; Levy, D. H. *J. Am. Chem. Soc.* **1985**, *107*, 277.

(2) Cable, J. R.; Tubergen, M. J.; Levy, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 6198.

(3) Karas, M.; Bachmann, D.; Bahr, U.; Hillenkamp, F. *Int. J. Mass. Spectrom. Ion Processes* **1987**, *78*, 53.

(4) Snoek, L. C.; Kroemer, R. T.; Hockridge, M. R.; Simons, J. P. *Phys. Chem. Chem. Phys.* **2001**, *3*, 1819.

(5) Bakker, J. M.; Plützer, C.; Hünig, I.; Hüber, T.; Compagnon, I.; von Helden, G.; Meijer, G. *Chem. Phys. Chem.* **2005**, *6*, 120.

(6) Abo-Riziq, A.; Crews, B. O.; Callahan, M. P.; Grace, L.; de Vries, M. S. *Angew. Chem., Int. Ed.* **2006**, *45*, 5166.

(7) Andreoni, W.; Curioni, A. *Parallel Comp.* **2000**, *26*, 819.

(8) Barone, V. *J. Chem. Phys.* **2005**, *122*, 014108.

(9) Pele, L.; Brauer, B.; Gerber, R. B. *Theor. Chem. Acc.* **2007**, *117*, 69.

(10) Benoit, D. M. *J. Chem. Phys.* **2006**, *125*, 244110.

(11) Scott, A. P.; Radom, L. *J. Phys. Chem. A* **1996**, *100*, 16502.

(12) Sinha, P.; Boesch, S. E.; Gu, C.; Wheeler, R. A.; Wilson, A. K. *J. Phys. Chem. A* **2004**, *108*, 9213.

(13) Giese, K.; Petkovic, M.; Naundorf, H.; Kuhn, O. *Phys. Rep. 2006* **2006**, *430*, 211.

(14) Kraemer, W. P.; Špirko, V.; Bludský, O. *J. Mol. Spectrosc*. **1994**, *164*, 500.

(15) Meuwly, M.; Bemish, R. J. *J. Chem. Phys.* **1997**, *106*, 8672.

(16) Hougen, J. T.; Bunker, P. R.; Johns, J. W. C. *J. Mol. Spectrosc.* **1970**, *34*, 136.

(17) Bunker, P. R.; Landsberg, B. M. *J. Mol. Spectrosc*. **1977**, *67*, 374.

(18) Mons, M.; Dimicoli, I.; Piuzzi, F.; Tardivel, B.; Elhanine, M. *J. Phys. Chem. A* **2002**, *106*, 5088.

(19) Nir, E.; Janzen, C.; Imhof, P.; Kleinermanns, K.; de Vries, M. S. *J. Chem. Phys.* **2001**, *115*, 4604.

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

(21) Choi, M. Y.; Miller, R. E. *J. Am. Chem. Soc.* **2006**, *128*, 7320.

(22) Mons, M.; Piuzzi, F.; Dimicoli, I.; Gorb, L.; Leszczynski, J. *J. Phys. Chem. A* **2006**, *110*, 10921.

(23) Chen, H.; Li, S. *J. Phys. Chem. A* **2006**, *110*, 12360.

(24) Cooley, J. W. *Math. Comput*. **1961**, *15*, 363.

(25) Werner, H.-J.; Knowles, P. J.; Schütz, M.; Lindh, R.; Celani, P.; Korona, T.; Rauhut, G.; Manby, F. R.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Lloyd, A. W.; McNicholas, S. J.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T. MOLPRO 2002.6, A Package of Ab initio Programs, University of Birmingham, U.K., 2002.

(26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian03*; Gaussian, Inc.: Wallingford, CT, 2004.

(27) Ahlrichs, R.; Bar, M.; Haser, M.; Horn, H.; Kolmel, C. *Chem. Phys. Lett* **1989**, *162*, 165.

(28) Dateo, C. E.; Lee, T. J.; Schwenke, D. W. *J. Chem. Phys.* **1994**, *101*, 5853.

(29) Čížek, J.; Špirko, V.; Bludský, O. *J. Chem. Phys.* **1993**, *99*, 7331.

(30) Wilson, E. B.; Decius, J. C.; Cross, P. C. *Molecular vibrations: The theory of infrared and Raman vibrational spectra*; McGraw-Hill: New York, 1955.

(31) Matanović, I.; Došlić, N. *J. Phys. Chem. A* **2005**, *109*, 4185.

(32) Chalupský, J.; Vondrášek, J.; Špirko, V. *J. Phys. Chem. A*, in press.