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Effect of Aqueous Solvation upon the Electronic Excitation Spectrum of the Glycine Zwitterion: A Theoretical CI Study Using a Fractional Charge Model[†]

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Abstract: Ab initio configuration interaction calculations have been carried out for the lower electronic states of the glycine zwitterion in both the gas phase and in dilute aqueous solution. The solution calculations employ a fractional charge model for the water molecules. The calculated gas phase and solution spectra differ sharply. While excited electronic states of marked Rydberg character are more strongly affected than are valence states, all transitions are shifted to higher energy in solution. We find good agreement with experimentally observed optical absorption spectrum of the glycine zwitterion in thin films.

When a molecule is photoexcited, one common result of the absorption of energy is an expanded electronic radial distribution. In the limit, the excited electron moves so far from the nuclear frame that it exhibits an atom-like spectrum and the term Rydberg state is appropriate, but some expansion almost always occurs. The degree of expansion varies from state to state in the same molecule, and it frequently happens that highly expanded Rydberg type states lie lower in energy than more contracted valence excited states. The 3s Rydberg state of ethylene provides a well-known example of this phenomenon—it lies lower in energy than does the intense π–π^* (N → V) transition.[1]

It has commonly been asserted[1] that some estimate of the radial extent of an excited state, or of the excited electron in such a state, can be arrived at by comparing the absorption spectrum of a molecule in the gas phase to that in a solid film or in solution. This is based upon the physically appealing argument that radially expanded electrons will, because of the size of their probability distribution, interact with nearby solvent molecules or neighboring molecules in a film, i.e., that they will be "crowded" so that the excitation energy of such a state will rise or the absorption intensity will be spread out to such an extent that the transition will either be strongly blue-shifted or will no longer be seen in condensed phases. There are many examples of this effect.

This difference between the properties of gaseous molecules and those in condensed phases is exacerbated in the case of molecular states involving some separation of charge. A common and important example is a molecular zwitterion. Here the gaseous molecule contains positive and negative charge centers which interact through space without the intervention of any dielectric medium. Such systems, however, commonly exist only in the presence of such a medium, and it is the neutral molecule, not the zwitterion, which is most stable in the gas phase. Attempts to carry out ab initio quantum mechanical calculations on the electronic excited states of such systems are bound to meet with failure; the medium, be it a solvent or a solid film, makes a fundamental contribution to the stability and energy of these states. This contribution varies from state to state and attempts to carry out calculations without explicit inclusion of the medium will lead to numerical results which do not bear detailed comparison with experiment.

In this paper we report and compare large scale ab initio configuration interaction calculations on the lower excited states of the glycine zwitterion in the gas phase and in aqueous solution. The results bear little resemblance to each other, but the aqueous results compare favorably with the experimental glycine zwitterion spectrum taken from a solid film. As expected, all the static effects of "crowding" are observed; Rydberg type states which exist in the gas phase are shifted to the extent that the gas phase results are useless as a guide to understanding this molecule. Dynamic broadening is, of course, missing from our calculations.

The introduction of a statistically meaningful representation of a solvent into an ab initio calculation is not entirely trivial. We have chosen the simplest possible approach, the fractional charge model originally suggested by Noell and Morokuma.[2] A zwitterion exerts powerful coulombic forces upon polar solvent molecules. The result is that the fluctuations within the first solvation sphere are relatively small at room temperature, and one can get away with using but one set of solvent coordinates rather than being forced to average over a large number of possible configurations to gain meaningful results. Our coordinates and the methods we have used are described in the next section.

Method of Calculation

Ab initio self-consistent field (SCF) calculations were performed on the glycine zwitterion, $NH_3^+CH_2COO^-$, by using a modified version of HONDO76, a Gaussian-based program for closed-shell SCF computations employing the methodology[3] of King, Dupuis, and Rys. The following molecular parameters[4] were used

bond lengths (Å)	bond angles (deg)
C–C = 1.53	∠NCC = 109.47
C–O = 1.25	∠CCO = 117.5
C–N = 1.48	∠CCH = 109.47
C–H = 1.10	∠CNH = 109.47
N–H = 1.03	

The atomic orbital basis set employed was Dunning's (9s5p/3s2p) contraction centered on the two oxygens, the two carbons, and the nitrogen and the (5s/1s) contraction centered on each hydrogen.[6] This was augmented by a set of ten diffuse functions, formed by s-, p-, and d-type Cartesian Gaussians with exponents set equal to 0.02, centered at the midpoint of a line joining the two oxygen atoms. The same glycine geometry and basis set was used in both the gas and solution phase calculations.

The atomic coordinates for hydrated glycine zwitterion were obtained from the results of the Monte Carlo simulation performed by Mezei, Mehrotra, and Beveridge,[5,7] which represents a dilute aqueous solution of the glycine zwitterion at 25 °C. We used two different, but equally representative, sets of coordinates,[5] G26 and G28, corresponding to solvation of the zwitterion by 26 and 28

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(1) Robin, M. B. *Higher Excited States of Polyatomic Molecules*; Academic Press: New York, 1975.

(2) Noell, J. O.; Morokuma, K. *J. Phys. Chem.* **1976**, *80*, 2675. Noell, J. O.; Morokuma, K. *Chem. Phys. Lett.* **1975**, *36*, 465.

(3) King, H. F.; Dupuis, M. *J. Comput. Phys.* **1976**, *21*, 144. Dupuis, M.; Rys, J.; King, H. F. *J. Chem. Phys.* **1976**, *65*, 111.

(4) Carozzo, L.; Corongiu, G.; Petrongolo, C.; Clementi, E. *J. Chem. Phys.* **1978**, *68*, 787. Romano, S.; Clementi, E. *Inter. J. Quantum Chem.* **1978**, *14*, 839.

(5) Beveridge, D. L.; Mezei, M; private communications.

(6) Dunning, T. H., Jr. *J. Chem. Phys.* **1970**, *53*, 2823. Dunning, T. H., Jr.; Hay, P. J. *Modern Theoretical Chemistry* Schaefer, H. F., III, Ed.; Plenum Press: New York, 1976.

0002-7863/86/1508-6880$01.50/0

Table I. Atomic Coordinates (Å)

Glycine Zwitterion

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
O	1.1161	−0.7062	0.2717	H	−0.6428	−1.7038	0.4122
O	1.0345	1.4324	−0.3105	H	−1.9713	−1.5275	−0.6054
C	0.5002	0.3320	−0.0530	H	2.0895	−1.0909	1.0147
C	−1.0250	0.2495	−0.1420	H	−1.3469	0.4971	−1.1645
N	−1.4651	−1.1221	0.1955	H	−1.4731	0.9633	0.5653

Water Coordinates

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
O(1)	−0.0828	−0.5425	−3.3382	O(14)	1.6057	−5.3182	1.1042
H(1)	0.5874	0.3197	−3.9843	H(14)	1.1680	−6.0882	0.7412
H(1)	0.0025	−1.4886	−3.2204	H(14)	1.9819	−4.8752	0.3436
O(2)	3.2319	2.2829	3.5321	O(15)	1.9660	−3.0011	−0.4632
H(2)	4.0272	1.9129	3.9152	H(15)	1.4969	−2.2038	−0.2172
H(2)	2.6576	2.4444	4.2806	H(15)	2.8776	−2.7243	−0.5554
O(3)	−3.8205	1.0493	−0.4186	O(16)	2.7765	−0.7278	2.3507
H(3)	−3.3749	0.2425	−0.6770	H(16)	3.1661	0.1084	2.0953
H(3)	−4.5068	1.1654	−1.0756	H(16)	2.1293	−0.9091	1.6692
O(4)	−3.1632	−0.8377	2.2492	O(17)	−3.2332	−1.4543	−1.6298
H(4)	−4.0754	−0.8448	1.9595	H(17)	−3.9618	−1.2133	−2.2019
H(4)	−3.1341	−1.4713	2.9661	H(17)	−2.9993	−2.3422	−1.9002
O(5)	−2.0668	−3.8753	−0.3275	O(18)	4.4815	−2.5904	−0.4101
H(5)	−1.7926	−4.7904	−0.2666	H(18)	4.9851	−3.0117	0.2864
H(5)	−1.6064	−3.4386	0.3891	H(18)	4.9620	−2.7962	−1.2119
O(6)	−2.0985	0.5294	−4.6645	O(19)	1.0236	−4.1371	−2.7652
H(6)	−1.5425	1.1217	−5.1706	H(19)	1.4295	−3.6900	−2.0226
H(6)	−1.5670	0.2919	−3.9047	H(19)	0.3757	−4.7200	−2.3695
O(7)	−5.3805	2.1271	1.7921	O(20)	0.4555	5.4014	−2.5998
H(7)	−5.0638	1.2771	1.4864	H(20)	0.6835	4.4747	−2.6743
H(7)	−4.6060	2.6894	1.7824	H(20)	−0.4138	5.4617	−2.9951
O(8)	−0.1267	−2.9087	1.6964	O(21)	5.6581	0.2353	−0.4516
H(8)	0.0415	−2.2899	2.4071	H(21)	5.5893	−0.5304	0.1186
H(8)	0.6566	−3.4581	1.6662	H(21)	5.0564	0.8741	−0.0693
O(9)	1.8037	2.9592	−2.4925	O(22)	3.4547	1.8793	0.7629
H(9)	1.9282	2.1137	−2.9236	H(22)	3.3554	2.2220	1.6511
H(9)	1.5140	2.7371	−1.6076	H(22)	2.5586	1.7921	0.4378
O(10)	−3.2447	3.7608	−2.6062	O(23)	0.0307	3.6133	0.4997
H(10)	−2.6823	4.0892	−3.3076	H(23)	0.0566	2.6976	0.2220
H(10)	−2.8030	4.0269	−1.7998	H(23)	0.7823	3.7081	1.0847
O(11)	2.7156	0.1225	−2.4885	O(24)	1.0932	3.7319	4.4780
H(11)	1.8705	−0.1407	−2.1242	H(24)	0.3457	3.2816	4.8712
H(11)	3.3080	0.1338	−1.7368	H(24)	0.7034	4.3451	3.8548
O(12)	−3.0015	3.6469	0.4092	O(25)	0.1501	−0.5773	3.3668
H(12)	−2.9019	2.7554	0.0753	H(25)	−0.3608	0.1899	3.1090
H(12)	−2.1287	3.8848	0.7223	H(25)	1.0434	−0.2482	3.4669
O(13)	−1.6192	1.4769	2.6670	O(26)	−2.8215	−2.8146	3.9683
H(13)	−1.8795	2.3879	2.8032	H(26)	−2.4377	−2.5704	4.8105
H(13)	−2.4415	0.9872	2.6848	H(26)	−3.5410	−3.4040	4.1944

water molecules, respectively. Coordinates for the more important of these, G26, are in Table I. Note that the immediate solvation environment of the glycine zwitterion was found by Mezei et al.[7] to contain, on the average, 14.4 water molecules.

In an attempt to obtain an economical, yet qualitatively correct, inclusion of solvent effects, we represented the solvent water molecules by fractional point charges[2] situated at the locations of the solvent atomic centers. Neither electrons nor atomic basis functions are explicitly associated with such centers. As pointed out by Noell and Morokuma,[2] the Hamiltonian for this solvated system is thus identical in form with that for the solute itself, and no new types of integrals are introduced in the calculation, the only change being the addition of the nuclear attraction and repulsion integrals arising from the solvent sites.

The principal cause of a Rydberg state's shift to higher energy upon solvation is often thought to be the "overlap" of these distributions with those of the solvent molecules or their "crowding". This is a physically attractive picture, but is is only another way of phrasing a change in the coulombic and exchange potential felt by the electrons in these states relative to that in the gas phase. The exchange portion of this difference is expected to be small, but only the coulombic difference is modelled by the fractional point change model.

Noell and Morokuma[2] determined that, for solvents such as water, an excellent initial choice of the fractional charges are those which reproduce the dipole moment of the solvent molecule. For a typical water molecule with coordinates as in Table I, the experimental dipole moment of 1.85 D can be reproduced by placing a fractional charge of −0.6570 at the location of the oxygen atom and fractional charges of +0.3285 at the locations of each of the two hydrogen atoms. We used these fractional charges to represent all the water molecules in the G26 configuration of Mezei, et al.[5] This yields a value of −95.64 kcal/mol for the energy of solvation of glycine zwitterion by 26 water molecules (calculated by subtracting the total energy of the glycine zwitterion and the total electrostatic energy of the fractional charges representing the 26 water molecules in the G26 configuration from the total energy of the hydrated glycine zwitterion), as compared to the statistical thermodynamic Monte Carlo value of −99.28 kcal/mol reported by Mezei, et al.[7] the study from which this particular solvent configuration is abstracted. Our calculation does not, of course, represent an attempt to estimate the solvation energy of glycine, but the calculated energy indicates that the model is physically reasonable.

Changing the fractional charges to $g_O = -0.931$ on the oxygen and $g_H = +0.4655$ on the hydrogens (corresponding to a monomer

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(7) Mezei, M.; Mehrotra, P. K.; Beveridge, D. L. *J. Biomol. Struct. Dyn.* **1984**, *2*, 1.

Table II. Some Ground-State Properties and SCF Orbital Energies of Glycine Zwitterion[a]

property	Glyz±	$\mathrm{Glyz(H_2O)^{\pm 26}}$ G26 confgrtn	$\mathrm{Glyz(H_2O)^{\pm 28}}$ G28 confgrtn
tot. SCF energy	−282.690289 hartrees		
solvtn energy (SCF)		−95.64 kcal/mol	−85.56 kcal/mol
tot. CI energy	−283.156569 hartrees		
	Orbital Energies (in hartrees)		
MO			
17	−0.516820	−0.565401	−0.568037
18	−0.391226	−0.450170	−0.453312
19	−0.370711	−0.441771	−0.434306
20	−0.347484	−0.423500	−0.419879
21	0.001632	0.023882	0.024200
22	0.045368	0.048960	0.061775
23	0.052780	0.064464	0.064823
24	0.061387	0.068502	0.079828
25	0.084288	0.086604	0.087648
26	0.086692	0.088356	0.094746
27	0.096597	0.096432	0.102389
28	0.098760	0.106824	0.103312
29	0.105772	0.120712	0.112519
30	0.159722	0.142291	0.146125
31	0.244669	0.190140	0.191745
32	0.245134	0.241790	0.244266
33	0.297099	0.296393	0.292304

[a] Unsolvated [Glyz±], solvated by 26 water molecules [$\mathrm{Glyz(H_2O)^{26}}$], and by 28 water molecules [$\mathrm{Glyz(H_2O)^{28}}$].

Table III. Electronic Excitation Spectrum of Gas-Phase Glycine Zwitterion

main compnnt (excttn from ground states)	excttn energy (eV)	wavenumber ($\mathrm{cm^{-1}}$)	oscilltr strength
21 ← 20	5.017	40 468	0.0005
21 ← 19	5.066	40 863	0.0200
21 ← 18	5.441	43 885	0.0205
23 ← 20	6.474	52 217	0.0013
24 ← 20	6.964	56 170	0.0049
31 ← 20	7.838	63 217	0.1940
30 ← 19	8.205	66 176	0.4949
30 ← 20	8.379	67 578	0.0043

Table IV. Electronic Excitation Spectrum of Glycine Zwitterion Solvated by 26 Water Molecules

main compnnt (excttn from ground state)	excttn energy (eV)	wavenumber ($\mathrm{cm^{-1}}$)	oscilltr strength
21 ← 19	7.535	60 777	0.0057
21 ← 18	7.701	62 116	0.0182
21 ← 20	7.716	62 235	0.0003
23 ← 20	8.764	70 682	0.0049
31 ← 20	8.955	72 230	0.2267
24 ← 20	8.981	72 436	0.0005
30 ← 19	9.503	76 643	0.4698
30 ← 20	9.753	78 660	0.0007
30 ← 18	9.904	79 884	0.3644
22 ← 19	16.053	129 475	0.0662
23 ← 18	16.678	134 518	0.0446

dipole moment of 2.6D) yields a solvation energy of −140.46 kcal/mol for the same system. In all subsequent calculations, therefore, we used the fractional point charges which reproduce the experimental dipole moment on all the water molecules

$$g_O = -0.657 \qquad g_H = +0.3285$$

With these fractional charges and the G28 atomic coordinates of Mezei et al.,[5] we obtain an energy of solvation for glycine zwitterion by 28 water molecules of −85.56 kcal/mol. In all our SCF calculations, 60 molecular orbitals were generated (including the diffuse, Rydberg-type orbitals). The 1s carbon, oxygen, and nitrogen molecular orbitals were then frozen, as were the three highest (unoccupied) molecuar orbitals, leaving a total of 52 molecular orbitals available for transformation. We worked with the G26 coordinates (26 water molecules) in all subsequent CI calculations.

The configuration interaction method used in the next stage of the calculation was the program PEPCI developed by Diamond, Segal, and Wetmore.[8] This program partitions the CI space into two subspaces: (a) the core space, consisting of the reference configurations (typically about half a dozen) and those configurations most strongly interacting with them, and (b) the tail space, which is the large number of remaining configurations. the method utilizes second-order Brillouin–Wigner perturbation theory within this large multireference configuration space, with neglect of the off-diagonal Hamiltonian matrix elements in the tail space.

The results of initial CI calculations were used to identify significant contributors to each eigenvector. In our CI calculations, all single and double excitations from the reference configurations were generated. The full core size, in all cases, was 128 configurations. For each root, the core vector comprised between 79.2 and 86.1% of the final vector. One is well within the limits of perturbation theory, however, since the weight of the tail results from the combined weight of many very small numbers.

Separate CI calculations were performed on the unsolvated, gas phase glycine zwitterion and on the glycine zwitterion solvated by 26 water molecules. All excitation energies were determined relative to the CI ground state of the system under consideration.

Results and Discussion

In Table II we present some ground state properties of the gas-phase glycine zwitterion and the energies of solvation for 26 water molecules and for 28 water molecules. Also listed are the orbital energies of some of the interesting orbitals in the three calculations. Molecular orbital 18 is an orbital that is largely localized on one of the oxygen atoms, while orbital 19 is mainly localized on the other oxygen atom. Orbital 20, the highest occupied molecular orbital in the ground state, is delocalized strictly within the carboxylate group and has the characteristics of the nonbonding π orbital of that group (node at the position of the carboxylate carbon atom). Orbitals 21 through 30 are essentially diffuse, Rydberg-type orbitals (although orbital 30 has significant valence mixing). Molecular orbital 31 is again delocalized within the carboxylate group and has the characteristics of the corresponding antibonding π orbital (a nodal plane bisecting each C–O bond). These qualitative characteristics of the molecular orbitals remain unchanged upon solvation of the glycine zwitterion. However, as is evident from Table II, solvation has a very significant effect on the orbital energies. The occupied valence orbitals are strongly stabilized, while the low-lying Rydberg orbitals are correspondingly destabilized. The unoccupied valence orbitals are, in general, only weakly stabilized with respect to the parent gas-phase zwitterion.

The stabilization of the valence orbitals upon solvation is easy to understand by using electrostatic considerations. The solvent dipoles polarize the valence electron charge distributions; the resulting dipole–induced dipole attraction leads to stabilization of the valence orbitals. The Rydberg orbitals, however, are so large and diffuse that there is considerable interpenetration between these orbitals and the solvent charge distributions. (For instance, the s-type Rydberg function used in our calculations still has a magnitude over 40% of its maximum value, at the location of the nearest solvent oxygen). Thus the destabilization of the Rydberg orbitals also admits of a simple electrostatic interpretation.

Finally, we note that the energy of solvation is moderately sensitive to the detailed configuration (G26 or G28) of solvent molecules around the central glycine zwitterion, whereas the

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(8) Diamond, J. J.; Segal, G.A.; Wetmore, R. W. *J. Phys. Chem.* **1984**, *88*, 3532.

Table V. Percent Contributions of a Few Leading Configurations to the Norms of Several Excited States of Gaseous Glycine Zwitterion

	main compnnt of CI vector	percent contribution to norm of CI vector from configuration								
		A					B			
		21 ← 19	21 ← 18	31 ← 20	30 ← 19	30 ← 18	21 ← 20	23 ← 20	24 ← 20	30 ← 20
A	21 ← 19	77	2.6	0	2.2	0				
A	21 ← 18	2.6	77	0.5	0	2.2				
A	31 ← 20	0.5	0	69	8.3	0.3				
A	30 ← 19	1.7	0	8.6	69	1.9				
B	21 ← 20						80	0.2	0.2	2.3
B	23 ← 20						0	82	0.2	1.0
B	24 ← 20						0	0	76	6.8
B	30 ← 20						2.6	1.1	6.4	73

Table VI. Percent Contributions of a Few Leading Configurations to the Norms of Several Excited States of Solvated Glycine Zwitterion

	main compnnt of CI vector	percent contribution to norm of CI vector from configuration								
		A					B			
		21 ← 19	21 ← 18	31 ← 20	30 ← 19	30 ← 18	21 ← 20	23 ← 20	24 ← 20	30 ← 20
A	21 ← 19	53	21	0.1	5.7	2.3				
A	21 ← 18	21	55	0.5	1.8	4.7				
A	31 ← 20	1.9	0	69	4.8	3.5				
A	30 ← 19	5.1	1.2	9.0	57	8.1				
A	30 ← 18	1.0	5.7	0.6	11	63				
B	21 ← 20	0.5	1.1	0	0	0	73	0	0	8.5
B	23 ← 20						0.8	63	13	6.1
B	24 ← 20						0.6	8.4	69	5.5
B	30 ← 20						8.4	0.2	0	74

valence orbitals energies are relatively insensitive to the solvent configuration. The difference in solvation energy between the two configurations calculated is thus probably due to the cumulative effect of several small differences in the corresponding orbital energies of the occupied valence orbitals.

From the large stabilization of the occupied valence orbitals upon solvation and the corresponding destabilization of the low-lying Rydberg orbitals discussed earlier, it is at once obvious that we should expect the lines in the electronic spectrum of solvated glycine zwitterion which arise from transitions to these Rydberg orbitls to be enormously blue-shifted with respect to the gas-phase zwitterion. Our CI calculations completely justify such an expectation, as can be seen by a comparison of the data in Tables III and IV, where we present the calculated electronic spectra of the gas-phase glycine zwitterion and the glycine zwitterion solvated by 26 water molecules, respectively. Indeed, the valence-to-Rydberg transitions in the solvated zwitterion suffer a hypsochromic shift of nearly 20 000 wavenumbers, while the valence-to-valence transitions suffer a hypsochromic shift of around 10 000 wavenumbers. The latter blue-shift results from the fact that the occupied valence orbitals are stabilized to a much greater degree upon solvation than are the unoccupied ones.

In Tables V and VI we list the percent contributions of a few leading configurations to the norms of several CI states, for gas phase and solvated glycine zwitterions, respectively. We see from these data, and from Tables III and IV, that the excitation spectra of both gas-phase and solvated glycine zwitterions seem to neatly block out into a set of strongly allowed transitions (class A) and a set of weakly allowed transitions (class B). The configurations contributing to the transitions of class A are strongly mixed among themselves; likewise those contributing to the class B transitions are again strongly mixed among themselves. But there is negligible mixing between the strongly allowed and the weakly allowed transitions. Referring to the orbital characteristics discussed earlier in this section, we note that the transitions 21 ← 19, 21 ← 18, 30 ← 19, and 30 ← 18 of class A result from excitation of an electron in an atomic-type function localized on one of the two oxygen atoms. The same is also true of the transitions labeled 22 ← 19 and 23 ← 18 in Table IV. The only other transition belonging to class A is the one labeled 31 ← 20, the main component of which is the $\pi_3 \leftarrow \pi_2$ transition (alternatively labeled $\pi^* \leftarrow n_\pi$) of the COO$^-$ group. On the other hand, all the transitions of class B (21 ← 20, 23 ← 20, 24 ← 20, and 30 ← 20) originate in the π_2 orbital of the carboxylate group (the HOMO) which is of roughly d local symmetry within the COO moiety. These transitions are only weakly allowed.

Our calculated spectrum for glycine zwitterion solvated by 26 water molecules shares some common features with the experimental spectrum[1,9] of solid glycine zwitterion. The experimental spectrum of the solid shows[1,9] a strong band at 62 500 cm^{-1}, a second band at 68 000 cm^{-1}, and an intense band at 82 000 cm^{-1}. In our calculated spectrum for the solvated zwitterion, absorption begins only beyond 60 000 cm^{-1} (contrasted with about 41 000 cm^{-1} for the gas-phase zwitterion), with a peak at around 62 000 cm^{-1} due to valence-Rydberg excitation. The valence–valence absorption begins only around 72 000 cm^{-1} (contrasted with about 63 000 cm^{-1} for the gas-phase zwitterion). The intense absorption between 76 000 and 80 000 cm^{-1} is again due to predominantly valence-Rydberg excitation. It is obvious that the electronic excitation spectrum of solvated glycine zwitterion has more in common with the solid-state spectrum than with that of the gas-phase zwitterion.

Conclusions

This study is far from exhaustive, but it is clear that the fractional charge approach has provided a reasonable model for the solvent in this case. While the solvation energy appears to be somewhat sensitive to the precise details of the solvent molecule positions and charges, the excitation energies seem to be less so. A well-chosen solvent description has produced a description of the electronic excited states of this molecule which seems to be in good agreement with experiment and which is vastly different from that of the gas-phase molecule.

The expectation that states of significant Rydberg character will be severely blue-shifted is well borne out and this effect seems to be well modelled. The degree to which this modelling is sensitive to the details of the solvent distribution remains an open question. Our models G26 and G28 involve completely different sets of solvent coordinates and, hence, a completely different solvent distribution. Table II, however, shows an encouraging insensitivity of the shifts in orbital energies to the details of the two solvent models.

Spectroscopic properties like the circular dichroism spectrum of amino acids are often used to gain information about the configuration of such species. These spectra are almost always

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(9) Vinogradov, I. P.; Dodovna, N. Ya. *Opt. Spektrosk.* **1971**, *30*, 27.

obtained from condensed phases and our results would seem to indicate that their interpretation through quantum mechanical calculations which do not explicitly the perturbation due to the solvent is fraught with danger. It is worth noting in this regard, that, consistent with our opening remarks with respect to the ubiquity of radial expansion of the electronic distribution upon excitation, even valence excitations like 31 ← 20 are shifted by 10 000 cm^{-1} in solution relative to the gas phase. Such large perturbations almost certainly have a significant effect upon the optical rotatory strength.

Registry No. Glycine, 56-40-6.

Small-Ring Cyclic Alkynes: Ab Initio Molecular Orbital Study of Cyclopentyne

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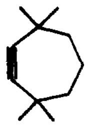
Abstract: The structure of the lowest energy singlet and triplet electronic states of cyclopentyne has been determined by ab initio MO theory at the GVB and ROHF levels, respectively, with the split-valence 3-21G basis set. Both electronic states prefer a C_s nonplanar structure, but the planarization energies are very small, indicating easy inversion. Harmonic force constant calculations on the optimized structures demonstrate that both singlet ($^1A'$) and triplet ($^3A''$) cyclopentyne are relative minima on the corresponding C_5H_6 potential-energy hypersurface. The triplet state is predicted to lie about 25 kcal/mol above the ground-state singlet. Harmonic vibrational frequencies are predicted for both electronic states. The triple-bond harmonic stretching frequency for singlet cyclopentyne is predicted to be 1828 cm^{-1}, whereas the analogous stretching frequency for the triplet state is 1622 cm^{-1}. These predictions should assist in the identification of cyclopentyne from matrix-isolation infrared spectroscopy.



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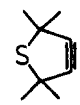

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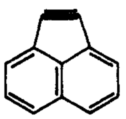

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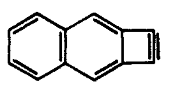

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Cyclic alkynes have been in recent times the subject of considerable interest, from either the theoretical or experimental point of view.[2–5] The integration of a triple bond into a small- or a medium-sized carbocycle is only possible through deviation of the C–C≡C–C moiety from the linear geometry, and this provokes an increasing destabilization of the system as the ring size decreases. The intriguing question is for the minimum ring size able to accommodate a triple bond, even for a transient existence. From an experimental point of view, cyclooctyne is readily available by dehalogenation of 1,2-dibromocyclooctene and exhibits a moderate stability.[6] The same is true for 3,3,7,7-tetramethylcycloheptyne (**1**),[7] but the parent compound, although easily generated, cannot be isolated.[6,8] No derivative of cyclohexyne has been reported with an appreciable lifetime in solution.[9] However, even the unsubstituted compound can be efficiently trapped as transition-metal complexes[10] and as Diels–Alder adducts.[11] Some five-membered ring cycloalkynes, like norbornyne (**2**),[12] 2,2,5,5-tetramethyl-1-thiacyclopentyne (**3**),[13] acenaphthyne (**4**),[14] and cyclopentyne (**5**),[15] have been generated. All of them have very short lifetimes in solution, but **4** has successfully been generated in an argon matrix at 15 K, and its UV and IR spectra have been recorded.[14] Indirect evidences on the generation of five-membered ring cycloalkynes include the isolation of the cyclotrimers of **2** and **4**[12,14] and the formation of the Diels–Alder adduct of **3** with 2,5-dimethylfuran and of the 1,3-dipolar cycloadduct of **3** with phenyl azide,[13] as well as the 2 + 2 cycloadducts of **5** with a variety of olefins.[15,16] All attempts to generate four-membered ring cycloalkynes have been up to now unsuccessful. The generation of cyclobutyne has never been substantiated,[17] and even the attempted synthesis of naphthocyclobutyne (**6**), postulated by similitude with **4** as a good candidate for a detectable cyclobutyne derivative, has not been confirmed.

It appears, therefore, that five-membered rings are the smallest able to accommodate a carbon–carbon triple bond in their structures and that, behind this limit, the energy cost of distorting the C—C≡C bond angles up to near 90° prevents the generation of cyclobutynes.

From the theoretical point of view, the problem of cyclic alkynes has been attacked in the opposite direction. Thus, Schaefer and co-workers have been interested in determining the smallest cycloalkyne whose singlet electronic state has a stable equilibrium

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(1) (a) Departament de Química Orgànica. (b) Departament de Quimica Física.

(2) Hoffman, R. W. *Dehydrobenzene and Cycloalkynes*; Academic: New York, 1967.

(3) Krebs, A. *Chemistry of Acetylenes*; Viehe, H. G., Ed.; Marcel Dekker: New York, 1969; pp 987–1062.

(4) Nakagawa, M. *The Chemistry of the Carbon–Carbon Triple Bond*; Patai, S., Ed.; Wiley: Chichester, England, 1978; pp 635–712.

(5) Greenberg, A.; Liebmann, J. F. *Strained Organic Compounds*; Academic: New York, 1978; pp 133–138.

(6) Blomquist, A. T.; Liu, L. H. *J. Am. Chem. Soc.* **1953**, *75*, 2153. Wittig, G.; Dorsch, H. L. *Ann.* **1968**, *711*, 46.

(7) Krebs, A.; Kimling, H. *Angew. Chem.* **1971**, *83*, 540.

(8) Krebs, A. *Tetrahedron Lett.* **1968**, 4511.

(9) Applequist, D. E.; Gebauer, P. A.; Gwynn, D. E.; O'Connor, L. H. *J. Am. Chem. Soc.* **1972**, *94*, 4272.

(10) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 750.

(11) Wittig, G.; Pohlke, R. *Chem. Ber.* **1961**, *94*, 3276. Wittig, G.; Meske-Schüller, I. *Ann.* **1968**, *711*, 65. Willey, F. G.; *Angew. Chem.* **1964**, *76*, 144. Wittig, G.; Krebs, A. *Chem. Ber.* **1961**, *94*, 3260. Wittig, G.; Mayer, U. *Chem. Ber.* **1963**, *96*, 342.

(12) Gassman, P. G.; Valcho, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4768. Gassman, P. G.; Gennick, I. *J. Am. Chem. Soc.* **1980**, *102*, 6863.

(13) Bolster, J. M.; Kellogg, R. M. *J. Am. Chem. Soc.* **1981**, *103*, 2868.

(14) Chapman, O. L.; Gano, J.; West, P. R.; Regitz, M.; Maas, G. *J. Am. Chem. Soc.* **1981**, *103*, 7033.

(15) Fitjer, L.; Kliebisch, V.; Wehle, D.; Modaressi, S. *Tetrahedron Lett.* **1982**, *23*, 1661. Fitjer, L.; Modaressi, S. *Tetrahedron Lett.* **1983**, *24*, 5495. Gilbert, J. C.; Baze, M. E. *J. Am. Chem. Soc.* **1983**, *105*, 664.

(16) Gilbert, J. C.; Baze, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 1885.

(17) Montgomery, L. K.; Roberts, J. D. *J. Am. Chem. Soc.* **1960**, *82*, 4750. Wittig, G.; Wilson, E. R. *Chem. Ber.* **1965**, *98*, 451.