THEORETICAL STUDY OF THE S_0 AND S_1 STATES OF PROTONATED SCHIFF BASES

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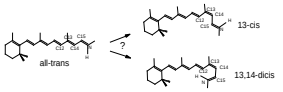
INTRODUCTION

The chromophore of the light-driven proton pump *Bacteriorhodopsin* is a retinal molecule which is linked to the protein *via* a protonated Schiff base (PSB). During the photocycle, which is induced by light absorption, the chromophore undergoes isomerization reactions and changes its protonation state. The fast primary step takes place on the potential energy surface (PES) of the first electronically excited state S_1. Two different mechanisms have been proposed for this primary step [1,2]:



In order to get more insight into the mechanism of this reaction we have carried out MRCI calculations [3] of the S_0 and S_1 states of a PSB model molecule. The calculated PES together with results from recent molecular dynamics simulations [4] reveal important information for the discussion of the mechanism of the primary step. The presented calculations are restricted to a two dimensional PES as a function of the two dihedrals τ_3 and τ_4. We have chosen this restricted set of variables in order to compare the results of different levels of theory and also in order to compare our calculated PES to the model PES applied in molecular dynamics simulations [4].

IR spectroscopy is an important tool for the structural investigation of intermediates during the photocycle. A reliable quantum chemical method for the prediction of the vibrational spectra of protonated Schiff bases would, therefore, be very helpful for the interpretation of experimental FTIR data. Experimentally, a blue shift of the C=N stretching vibration has been observed after protonation of the retinal Schiff base. Semiempirical quantum chemical methods could not reproduce this behavior. It is an interesting and important task to test whether density functional methods are useful for the description of protonated Schiff bases. On the basis of GVB calculations on a small model molecule [5], this blue shift was explained with an increased C=N force constant after protonation due to a rehybridization of the nitrogen. Our calculations on various model molecules at different levels of theory demonstrate, that this explanation is at least questionable in the model molecule and even very unlikely in the retinal Schiff base.

METHODS

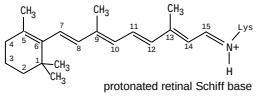
Part A:

MRCI calculations with single and double excitations have been carried out with the COLUMBUS[6,7] package of programs, using the standard 6-31G* basis set. After optimization of the all-trans conformation, the PES was calculated with all geometrical parameters fixed except the two torsional angles τ_3 and τ_4, which have been changed stepwise between 0° and 180° in order to generate the grid for the PES. The MRCI/6-31G* single point energy calculations used 10 reference states, 12 core and 12 frozen virtual MO's from a total of 100 basis functions, giving an active space of 3'766'784 CSF's.

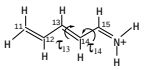
Part B:

HF, DFT, MP, CISD, and CCSD calculations were carried out with the program GAUSSIAN94[8]. CASSCF and MRCI calculations with single and double excitations and with different reference configurations have been carried out with the COLUMBUS package. The 6-31G** basis set was applied in all calculations.

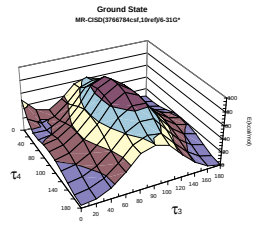
PART A: Potential Energy Surfaces of Ground and Excited States

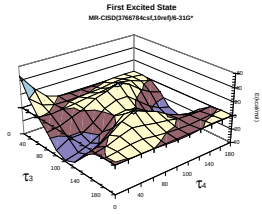


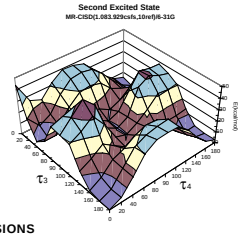
protonated retinal Schiff base



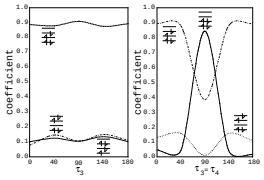
model molecule

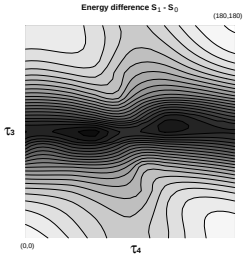






Coefficients of the most important configurations in the S_1state





CONCLUSIONS

In combination with the molecular dynamics simulations of Humphrey et al. [4], our calculated PES supports the all-trans -> 13-cis model. This is, however, largely based on the heights of rotational barriers which are shown to depend on the method.

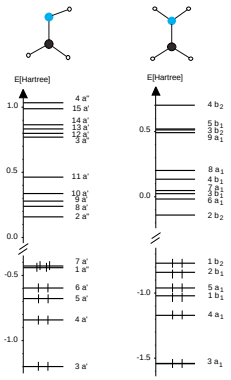
We can note some additional interesting results:

- in contrast to earlier semiempirical calculations, our study does not predict any significant contributions of higher excited states.
- in contrast to an earlier semiempirical study [9], we do not find any curve crossing with the ground state along the τ_3 coordinate.
- a transition S_1 -> S_0 has most likely to occur in the region where both dihedral angles are close to 90°. This implies that simultaneous rotations around τ_3 and τ_4 have to be expected on the excited PES.
- the decision about the conformation with respect to τ_4 has most likely to be made in the excited state

Additional degrees of freedom like the out of plane vibration of the proton at C14 [10] might also play an important role in the isomerization process and has to be considered in future work.

PART B: Force Constant Calculations of Methylimin and the Methyleniumion

MO-Schemes

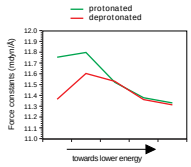


Selection of active orbitals for MRCI-calculations

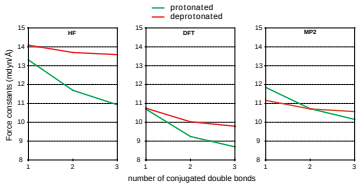
protonated molecule		
MRCI	active space	reference configurations
MRCI-1	$(1b_2)$ -> $(2b_2),(4b_2)$	4
MRCI-2	$(1b_1),(5a_1),(2b_1),(1b_2)$ -> $(2b_2)$, $(6a_1),(3b_1),(7a_1)$	48
MRCI-3	$(3a_1),(4a_1),(5a_1),(2b_1),(1b_2)$ -> $(2b_2),(4b_2),(5b_1),(3b_1),(8a_1),(11a_1),(7b_1)$	9
MRCI-4	$(5a_1),(2b_1),(1b_2)$ -> $(2b_2),(4b_2),(2b_1),(8a_1),(5b_1)$	26
MRCI-5	$(5a_1),(2b_1),(1b_2)$ -> $(2b_2),(4b_2),(8a_1),(3b_2),(5b_1),(4b_2)$	26

unprotonated molecule		
MRCI	active space	reference configurations
MRCI-1	$(1a'')$ -> $(2a''),(4a'')$	4
MRCI-2	$(5a'),(8a'),(1a''),(7a')$ -> $(2a'')$, $(8a'),(9a'),(10a')$	87
MRCI-3	$(6a'),(7a'),(4a'),(1a'')$ -> $(2a''),(9a'),(9a'),(3a''),(11a'),(15a'),(4a'')$	9
MRCI-4	$(4a'),(7a'),(6a')(1a'')$ -> $(2a''),(8a'),(15a'),(4a'')$	47
MRCI-5	$(4a'),(5a'),(7a'),(8a')(1a'')$ -> $(2a''),(8a'),(11a'),(3a''),(15a'),(4a'')$	98

Force constants (mdyn/Å) for different MRCI calculations



Force constants (mdyn/Å) v.s. number of double bonds



Force constants (mdyn/Å) and bond lengths (Å) of C=N bonds at different levels of theory

	HF	DFT	MP2	MP3	MP4	CISD	CCSD	CCSD(T)	CAS(8,8)	MRCI-1	MRCI-2	MRCI-3	MRCI-4	MRCI-5	GVB
fprot	13.31	10.69	11.85	12.40	11.40	12.38	11.87	11.38	12.71	11.80	11.76	11.53	11.38	11.33	11.65
fdeprot	14.09	10.74	11.16	12.04	10.85	12.36	11.59	11.00	10.72	11.37	11.37	11.61	11.53	11.32	11.14
Δf	-0.78	-0.05	0.69	0.36	0.55	0.02	0.28	0.38	1.99	0.44	0.39	-0.08	-0.15	0.02	0.51
CN-prot	1.263	1.289	1.282	1.277	1.286	1.276	1.281	1.286	1.272	1.282	1.283	1.2845	1.285	1.285	1.282
CN-deprot	1.250	1.282	1.281	1.274	1.284	1.270	1.278	1.284	1.291	1.281	1.280	1.2814	1.282	1.283	1.289
Δr	0.013	0.007	0.001	0.003	0.002	0.006	0.003	0.002	-0.019	0.001	0.003	0.0031	0.003	0.002	-0.007

RESULTS AND CONCLUSIONS

- our calculations clearly show, that the GVB result is not reproduced by the DFT method, i.e. no increase of the C=N force constant is found after protonation.
- most of the applied quantum chemical 'standard' methods except the CISD calculation are qualitatively in agreement with the GVB results.
- non of our calculations (except CAS(8,8)), however, could reproduce the result that the C=N bond length of the protonated molecule should be shorter than that of the unprotonated molecule.
- on the basis of CISD calculations we have searched for configurations which contribute significantly to the CI wave function
- we have found that several configurations which are formed after excitation into MO's of high energy are important.
- on the basis of this data we have carried out MRCI calculations with different sets of reference configurations.
- our data shows that the lower the energy of the MRCI calculations are (i.e. the better the CI wave function is) the smaller the difference between the two force constants becomes.
- due to limitations of the programs a real 'benchmark calculation' could not yet be performed.
- our investigation on the behavior of the C=N force constant as a function of the length of the conjugated system makes clear that even if the GVB result should be correct in the case of the system with one double bond, this effect will most likely be lost in the case of the retinal Schiff base.
- the blue shift found in the retinal Schiff base has, thus, to be caused by other effects.

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