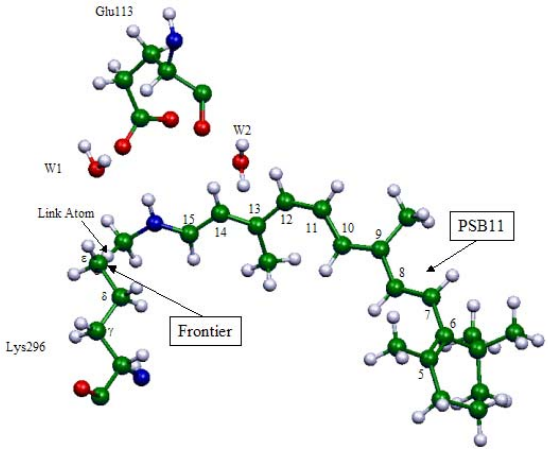
1. The QM/MM Scheme

The QM/MM force-field is defined by the following Hamiltonian:

$$\widehat{H} = \widehat{H}_{QM} + \widehat{H}_{MM} + \sum_{i=1}^{n}\sum_{j=1}^{Q} -\frac{q_j}{r_{ij}} + \sum_{i=1}^{N}\sum_{j=1}^{Q} \frac{Z_i q_i}{r_{ij}} + E_{vdW} + E_{bonded}$$

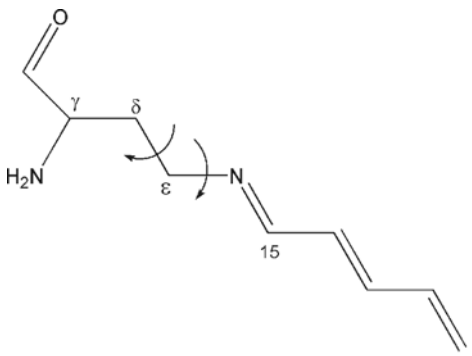
where $\widehat{H}_{QM}$ describes the QM segment in the vacuum, $\widehat{H}_{MM}$ represents the MM segment and the remaining terms describe the interactions between the QM and MM segments. These include:

- *(i)* the electrostatic interaction of QM electrons and nuclei with the MM point charges (q_j),
- *(ii)* the short-range van der Waals interactions (E_{vdW}) and
- *(iii)* additional parametrized potentials (E_{bonded}) required to correctly describe the QM/MM frontier geometry (see Scheme 2).



Scheme 2.

Notice that the QM wavefunction is polarized by the MM point charges. In contrast, the MM point charges remain constant during the calculation. On the other hand, the charges of the chosen Amber96 force-field (1) take into account the polarization effect in a mean-field way.



Scheme 3.

The QM/MM frontier is set at the C_ε-C_δ bond of the Lys-296 side-chain (see Schemes 2 and 3). This choice ensures a QM segment (comprising the retinal model and the last bond of the Lys-296 side-chain) of a moderate size and far enough from the QM segment "reactive part" (i.e. the π-backbone). The simplest and more widely used hydrogen link atom (HLA) scheme is used to cap the pending valence on the QM C_ε atom. The link hydrogen atom is fixed at 1 Å from C_ε and kept along the C_ε-C_δ axis.

As documented elsewhere (2), to correctly describe the frontier the HLA may interact with all the MM point charges, but cannot be involved in other MM potentials. Few MM potentials involving the frontier atoms have been reparameterized. First, the values of the point charges residing on the Lys-296 atoms have been changed to reflect its QM/MM status. In fact, in Amber96 any aminoacid residue has a net charge. The lysine residue has a net charge of +1 (i.e. protonated lysine). In our QM/MM framework, the MM part of Lys-296 residue must have a null charge and this requires changes in the MM point charges of this residue (Table 2).

Table 2. The values of the reparametrized QM/MM point charges for Lys-296.

Atom	N	C_α	$C_{carbonyl}$	H_N	$O_{carbonyl}$	H_α
Charge	-0.3981	-0.2400	0.6840	0.2246	-0.6396	0.1426
Atom	C_β	H_β	C_γ	H_γ	C_δ	H_δ
Charge	-0.0094	0.0362	0.0187	0.0103	0.0000	0.0621

The charge of the frontier MM carbon atom C_δ is set to 0 to ensure that the QM wavefunction is not overpolarized by the close HLA. This procedure is allowed by the little value of the original Amber96 point charge and makes possible the use of the standard MM bonded potentials (stretching, bending, etc.) for the description of the geometry of the frontier. Second, the van der Waals atomic parameters for retinal (i.e. for a conjugated hydrocarbon chain containing sp^2 carbon atoms) are not defined in the Amber96 force-field. Similarly, the C_{15}-N-C_ε-C_δ torsion potential does not exist in Amber96.
These missing parameters have been determined in such a way to reproduce the ground state (S_0) and first excited state (S_1) CASSCF torsional energy profiles relative to the N-C_ε-C_δ-C_γ and C_{15}-N-C_ε-C_δ dihedral angles of the model system given in Scheme 3 (3). The resulting van der Waals parameters are (R*=1.87 Å, ε=0.0860 kcal·mol^{-1}) for an sp^2 carbon atom of the retinal π-system, (R*=1.87 Å, ε=0.1094 kcal·mol^{-1}) for a sp^3 carbon atom of retinal (i.e. the methyl substituents in position 9 ad 12 in Scheme 2) and (R*=0.92 Å, ε=0.0157 kcal.mol^{-1}) for the hydrogen atom of retinal. The C_{15}-N-C_ε-C_δ torsion potential is given by: $0.750\,[1 + \cos(\phi - 0)]$.

2. The Protein Model

The recent refinement (4) at 2.8 Å of the bovine rhodopsin crystal structure (1HZX in the Protein Data Bank archive) was used as a basis to build our Rh model. In particular, we selected the higher resolution monomer A. In this monomer some residues located far from the retinal chromophore region are missing (236-240 and 331-333). Since we are interested in a correct description of the retinal region only we

did not try to add these residues. For the same reason, the ionization status of the potentially charged carboxylic residues of the protein has been defined with a simple choice: since the majority of the carboxylic residues are located in the region near the cytoplasmic side these are deprotonated (i.e. negatively charged) whenever a counterion is found in its vicinity. If not, we assume a protonated (i.e. neutral) state. The same strategy is used for the residues in the extracellular region.

Close to the retinal, there are few potentially charged ionic residues such as Glu-113 (i.e. the retinal PSB counterion), Asp-83 and Glu-181. While Glu-113 is defined as deprotonated and forming a salt bridge with the protonated Schiff base (5), the Asp-83 and Glu-181 residues are kept neutral since no counterion can be identified in their vicinity. Indeed, experimental evidence (6) has been reported that indicates that these residues are both protonated (i.e neutral). In the retinal region the Glu-122 residues could have His-211 as counterion, thus leading to an ion-pair. However, Fourier Transform IR (FTIR) experiments suggest that Glu-122 is protonated. Accordingly, His-211 and Glu-122 have been taken as protonated (i.e. neutral) in our model. Finally, all histidine residues have been defined as protonated residues with the only exception of His-195 that is in close contact with Glu-197.

Two water molecules have been introduced in the model. The first one, already present in the crystal structure, is located between the retinal and Glu-181 (W2 in Scheme 2). The second one (W1) has been placed between the retinal protonated Shiff base and its counterion Glu-113, as suggested by Kandori *et al*. (7). The other hetero atoms appearing in the crystal structure have been omitted because they are not in direct interaction with retinal. To get a globally neutral model, a chloride ion has been set close to Arg-147.

3. PSB11 in Explicit Solution

We have placed the PSB11 chromophore in a rectangular box of methanol molecules. The geometry of the solution was constructed by placing methanol molecules within 10 Å from any given atom of the chromophore by using the xleap module of the *AMBER* package (8); this procedure has generated 385 methanol molecules. To neutralize the system we added a chlorium ion. The resulting system consisted of 2365 atoms.

4. Optimized Structures

Shown are cartesian coordinates (Å) for the following optimized structures (optimized fragments only).

S_0-Rh. Optimized at the CASSCF/6-31G*/Amber level of theory with the active space comprising 12 electrons/12 orbitals. The atoms in bold indicate atoms that have been kept frozen during optimization procedure. Atom HLA denotes the hydrogen link atom.

Atom	*X*	*Y*	*Z*	Charge
N	1.115000	6.262998	-5.370998	-.51630

C	.802000	5.175998	-4.439998	.03970
C	1.938999	4.160999	-4.360998	.53660
O	2.402999	3.833999	-3.271999	-.58190
H	.490880	6.403988	-6.155218	.29360
H	.662240	5.589198	-3.441299	.11050
C	-.489000	4.469998	-4.870998	.05600
C	-1.315000	3.909999	-3.724999	.01360
C	-.537000	2.944999	-2.848999	.80540
O	.016000	1.955999	-3.390999	-.81880
O	-.486999	3.177999	-1.613999	-.81880
H	-.314450	3.720259	-5.641098	-.01730
H	-1.159730	5.222768	-5.250978	-.01730
H	-2.210399	3.425999	-4.109319	-.04250
H	-1.646269	4.758728	-3.123839	-.04250
N	1.944999	-1.515999	4.989998	-.39805
C	1.830999	-.073000	5.100998	-.24000
C	1.949999	.463000	6.510998	.68395
O	1.821999	1.661999	6.712998	-.63955
H	1.163730	-2.051989	4.638878	.22455
H	2.644289	.388350	4.539988	.14260
C	.562184	.471593	4.412214	-.00940
C	.647395	.228339	2.905479	.01870
C	-.679201	.455348	2.174548	.00000
C	-.708968	-.461944	.943648	
N	.291210	-.059143	-.057086	
H	.470702	1.539804	4.566224	.03620
H	-.334259	.047233	4.842267	.03620
H	.959465	-.797585	2.745855	.01030
H	1.413660	.875469	2.475668	.01030
H	-.787766	1.507093	1.895066	.06210
H	-1.513575	.182041	2.825106	.06210
H	-1.683488	-.416855	.485487	
H	-.483060	-1.472114	1.241346	
H	.072029	.761400	-.609640	
C	1.350744	-.740551	-.312793	
C	2.261938	-.426553	-1.383077	
C	3.409522	-1.137401	-1.614307	
C	4.226937	-.717263	-2.758500	
C	5.501593	-1.060244	-3.082862	
C	6.488897	-1.815909	-2.311867	
C	7.644302	-2.341877	-2.801413	
C	8.620835	-2.867257	-1.833984	
C	9.884947	-3.253504	-2.108414	
C	10.867027	-3.698740	-1.077738	
C	3.817233	-2.327584	-.768648	
C	7.991565	-2.385426	-4.269794	
H	1.507712	-1.588868	.327671	
H	2.022008	.432939	-1.991398	
H	3.735651	-.035300	-3.432174	
H	5.869230	-.620176	-3.991390	
H	6.352824	-1.861952	-1.248001	
H	8.298926	-2.874170	-.805891	
H	10.218396	-3.280674	-3.132515	
H	4.511171	-2.023172	.006920	
H	2.980531	-2.807926	-.280945	
H	4.303004	-3.078338	-1.373993	
H	8.848604	-1.758557	-4.486209	
H	8.238350	-3.398579	-4.572195	
H	7.179480	-2.037786	-4.893307	
C	11.168708	-2.940210	.005408	
C	12.112710	-3.411058	1.095387	

C	10.572190	-1.576746	.294799	
C	12.971140	-4.610722	.707356	
H	12.754464	-2.584176	1.388436	
H	11.507147	-3.645675	1.971969	
C	12.123882	-5.631464	-.039153	
H	13.812886	-4.290319	.102836	
H	13.385472	-5.060778	1.607585	
C	11.532018	-5.065845	-1.341825	
H	12.707358	-6.517567	-.273729	
H	11.309031	-5.957637	.606632	
C	12.644310	-4.909884	-2.396356	
C	10.494740	-6.077888	-1.863311	
H	12.251256	-4.497879	-3.322959	
H	13.453490	-4.276500	-2.051512	
H	13.071030	-5.881054	-2.633373	
H	10.107298	-5.805704	-2.839668	
H	10.950892	-7.058984	-1.956257	
H	9.652096	-6.164023	-1.181586	
H	11.346294	-.915013	.677607	
H	10.125919	-1.105259	-.569708	
H	9.808473	-1.647207	1.066035	
O	1.037522	-2.104677	-3.633396	-.83400
H	1.653329	-2.006463	-2.886779	.41700
H	1.253322	-1.269512	-4.093395	.41700
O	-2.065384	1.322998	-.787389	-.83400
H	-1.490912	2.093161	-1.054265	.41700
H	-2.842395	1.491924	-1.341554	.41700
HLA	-.685062	.138693	1.742812	

S_1-Rh. Optimized at the CASSCF/6-31G*/Amber level of theory with the active space comprising 12 electrons/12 orbitals. The atoms in bold indicate atoms that have been kept frozen during optimization procedure. Atom HLA denotes the hydrogen link atom.

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H	2.644289	.388350	4.539988	.14260
C	.560260	.469759	4.413709	-.00940
C	.637439	.215498	2.908273	.01870
C	-.697008	.430800	2.187310	.00000

C	-.729704	-.476793	.951634	
N	.262429	-.075353	-.037043	
H	.472075	1.539069	4.560412	.03620
H	-.335567	.049777	4.850037	.03620
H	.954448	-.808894	2.750545	.01030
H	1.396703	.864205	2.468480	.01030
H	-.814063	1.481916	1.910411	.06210
H	-1.525561	.151645	2.841774	.06210
H	-1.708358	-.428549	.501950	
H	-.499820	-1.486916	1.245199	
H	.050758	.731629	-.591373	
C	1.346265	-.786671	-.316893	
C	2.201289	-.496446	-1.354148	
C	3.436832	-1.243574	-1.646306	
C	4.183089	-.821224	-2.698347	
C	5.513090	-1.297182	-3.137986	
C	6.449705	-1.945409	-2.395006	
C	7.764865	-2.377237	-2.857023	
C	8.668109	-2.788308	-1.879412	
C	9.952191	-3.308960	-2.119105	
C	10.891498	-3.740309	-1.089246	
C	3.783707	-2.432753	-.776678	
C	8.111174	-2.412224	-4.325265	
H	1.503488	-1.616883	.339327	
H	1.985683	.376588	-1.947214	
H	3.783065	-.019873	-3.291442	
H	5.770727	-.995035	-4.137993	
H	6.263021	-2.103383	-1.351424	
H	8.337169	-2.726931	-.857399	
H	10.234086	-3.508421	-3.140445	
H	4.386271	-2.133163	.074702	
H	2.897369	-2.913541	-.385959	
H	4.327842	-3.183614	-1.327952	
H	8.884917	-1.691651	-4.563961	
H	8.464164	-3.396096	-4.616404	
H	7.256970	-2.176460	-4.943598	
C	11.122394	-3.014206	.049227	
C	12.061427	-3.492306	1.137992	
C	10.484659	-1.677325	.374125	
C	12.977331	-4.641434	.728619	
H	12.660356	-2.650354	1.475569	
H	11.447127	-3.781913	1.992241	
C	12.192239	-5.660485	-.083655	
H	13.825417	-4.268815	.163943	
H	13.379194	-5.111249	1.623559	
C	11.626671	-5.068168	-1.385640	
H	12.808634	-6.520455	-.327598	
H	11.367543	-6.035551	.522196	
C	12.766602	-4.835871	-2.394214	
C	10.650254	-6.105955	-1.975486	
H	12.392157	-4.401687	-3.318956	
H	13.548952	-4.195710	-2.001861	
H	13.229436	-5.784412	-2.651354	
H	10.285641	-5.826561	-2.958925	
H	11.152105	-7.062775	-2.080037	
H	9.789834	-6.254489	-1.327210	
H	11.233085	-1.023586	.814888	
H	10.066065	-1.166080	-.481435	
H	9.695320	-1.795801	1.114004	
O	1.040996	-2.126382	-3.657277	-.83400
H	1.525976	-2.035244	-2.817460	.41700

H	1.338649	-1.287133	-4.062139	.41700
O	-2.079398	1.326166	-.787390	-.83400
H	-1.467536	2.069761	-1.044687	.41700
H	-2.827350	1.505178	-1.373341	.41700
HLA	-.703744	.118129	1.754996	

S_1-$Rh_{stretch}$. Optimized at the CASSCF/6-31G*/Amber level of theory with the active space comprising 12 electrons/12 orbitals. The atoms in bold indicate atoms that have been kept frozen during optimization procedure. Atom HLA denotes the hydrogen link atom.

Atom	*X*	*Y*	*Z*	Charge
N	1.115000	6.263000	-5.371000	-.51630
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C	1.939000	4.161000	-4.361000	.53660
O	2.403000	3.834000	-3.272000	-.58190
H	.490880	6.403990	-6.155220	.29360
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C	-1.315000	3.910000	-3.725000	.01360
C	-.537000	2.945000	-2.849000	.80540
O	.016000	1.956000	-3.391000	-.81880
O	-.487000	3.178000	-1.614000	-.81880
H	-.314450	3.720260	-5.641100	-.01730
H	-1.159730	5.222770	-5.250980	-.01730
H	-2.210400	3.426000	-4.109320	-.04250
H	-1.646270	4.758730	-3.123840	-.04250
N	1.945000	-1.516000	4.990000	-.39805
C	1.831000	-.073000	5.101000	-.24000
C	1.950000	.463000	6.511000	.68395
O	1.822000	1.662000	6.713000	-.63955
H	1.163730	-2.051990	4.638880	.22455
H	2.644290	.388350	4.539990	.14260
C	.560590	.467900	4.409570	-.00940
C	.631370	.218170	2.902820	.01870
C	-.702510	.441070	2.182360	.00000
C	-.730630	-.450100	.934010	
N	.251890	-.034200	-.050020	
H	.471520	1.537190	4.556500	.03620
H	-.335570	.048910	4.845260	.03620
H	.943970	-.806710	2.740800	.01030
H	1.391420	.866990	2.464080	.01030
H	-.818290	1.495060	1.917910	.06210
H	-1.532460	.149920	2.828360	.06210
H	-1.718930	-.417050	.500140	
H	-.505450	-1.464920	1.225650	
H	.037000	.775680	-.600850	
C	1.355360	-.737260	-.309290	
C	2.241740	-.434823	-1.343889	
C	3.433741	-1.175216	-1.579281	
C	4.234590	-.765634	-2.694603	
C	5.551358	-1.118942	-3.027209	
C	6.509073	-1.845487	-2.274673	
C	7.705673	-2.382326	-2.773540	
C	8.647793	-2.881821	-1.836275	
C	9.934483	-3.268282	-2.111272	
C	10.896583	-3.703291	-1.098401	
C	3.839821	-2.360346	-.727187	

C	8.061096	-2.420903	-4.238585	
H	1.511577	-1.582334	.333376	
H	2.004948	.422937	-1.955000	
H	3.739298	-.090883	-3.372339	
H	5.920324	-.677185	-3.935732	
H	6.369976	-1.889067	-1.211217	
H	8.323502	-2.890050	-.809900	
H	10.267550	-3.300678	-3.134372	
H	4.488480	-2.070590	.095990	
H	2.981250	-2.838460	-.276630	
H	4.336470	-3.121340	-1.314820	
H	8.907780	-1.775220	-4.437320	
H	8.327770	-3.431570	-4.530110	
H	7.254660	-2.084120	-4.870110	
C	11.194370	-2.941042	-.009416	
C	12.129342	-3.409226	1.082317	
C	10.592796	-1.579261	.278199	
C	12.984900	-4.611630	.701200	
H	12.763380	-2.581770	1.383520	
H	11.503560	-3.645310	1.944850	
C	12.136360	-5.628570	-.048040	
H	13.836610	-4.298360	.105790	
H	13.377560	-5.061560	1.608520	
C	11.562696	-5.074517	-1.358820	
H	12.715100	-6.517660	-.276980	
H	11.309380	-5.944350	.585600	
C	12.677890	-4.922770	-2.408370	
C	10.513380	-6.078560	-1.876260	
H	12.285410	-4.508970	-3.334900	
H	13.490360	-4.294470	-2.060820	
H	13.099390	-5.895220	-2.646060	
H	10.126310	-5.807460	-2.854710	
H	10.955960	-7.064890	-1.967660	
H	9.673600	-6.155690	-1.190220	
H	11.364200	-.915540	.656100	
H	10.145040	-1.096610	-.580650	
H	9.836970	-1.662380	1.056670	
O	1.045260	-2.104770	-3.634140	-.83400
H	1.536040	-1.969400	-2.800280	.41700
H	1.223930	-1.228360	-4.027340	.41700
O	-2.117940	1.321130	-.811600	-.83400
H	-1.483650	2.048880	-1.047840	.41700
H	-2.858400	1.527490	-1.397690	.41700
HLA	-.706676	.136169	1.743772	

Rh-CI$_{90}$. Optimized at the CASSCF/6-31G*/Amber level of theory with the active space comprising 12 electrons/12 orbitals. The atoms in bold indicate atoms that have been kept frozen during optimization procedure. Atom HLA denotes the hydrogen link atom.

Atom	*X*	*Y*	*Z*	Charge
N	1.115000	6.263000	-5.371000	-.51630
C	.802000	5.176000	-4.440000	.03970
C	1.939000	4.161000	-4.361000	.53660
O	2.403000	3.834000	-3.272000	-.58190
H	.490880	6.403990	-6.155220	.29360
H	.662240	5.589200	-3.441300	.11050
C	-.489000	4.470000	-4.871000	.05600

C	-1.315000	3.910000	-3.725000	.01360
C	-.537000	2.945000	-2.849000	.80540
O	.016000	1.956000	-3.391000	-.81880
O	-.487000	3.178000	-1.614000	-.81880
H	-.314450	3.720260	-5.641100	-.01730
H	-1.159730	5.222770	-5.250980	-.01730
H	-2.210400	3.426000	-4.109320	-.04250
H	-1.646270	4.758730	-3.123840	-.04250
N	1.945000	-1.516000	4.990000	-.39805
C	1.831000	-.073000	5.101000	-.24000
C	1.950000	.463000	6.511000	.68395
O	1.822000	1.662000	6.713000	-.63955
H	1.163730	-2.051990	4.638880	.22455
H	2.644290	.388350	4.539990	.14260
C	.564676	.466355	4.401799	-.00940
C	.648657	.206123	2.895901	.01870
C	-.685469	.394102	2.166320	.00000
C	-.699998	-.520610	.935374	
N	.277826	-.112738	-.052912	
H	.475137	1.536559	4.543363	.03620
H	-.332882	.048285	4.835395	.03620
H	.984300	-.812850	2.743276	.01030
H	1.398635	.865620	2.456189	.01030
H	-.816183	1.440756	1.880194	.06210
H	-1.510987	.105856	2.819384	.06210
H	-1.682769	-.499085	.493784	
H	-.464496	-1.525445	1.237642	
H	.068630	.702148	-.577828	
C	1.324954	-.837932	-.421331	
C	2.145339	-.533732	-1.467314	
C	3.351023	-1.268386	-1.785110	
C	4.268442	-.719332	-2.619407	
C	5.441803	-1.438319	-3.147570	
C	6.651048	-1.457771	-2.509015	
C	7.785443	-2.208176	-2.928415	
C	8.725704	-2.551179	-1.927087	
C	9.949655	-3.134306	-2.153056	
C	10.908503	-3.434755	-1.084148	
C	3.594531	-2.584484	-1.075582	
C	7.995227	-2.581872	-4.374578	
H	1.494852	-1.699014	.190890	
H	1.957686	.379568	-1.994026	
H	4.066722	.239969	-3.049814	
H	5.309671	-1.970131	-4.085415	
H	6.692184	-.988708	-1.538064	
H	8.446479	-2.325455	-.911337	
H	10.220685	-3.435306	-3.156923	
H	3.898308	-2.400769	-.048324	
H	2.692078	-3.183886	-1.039027	
H	4.356661	-3.183825	-1.546339	
H	8.675784	-1.861888	-4.825182	
H	8.407739	-3.575980	-4.494196	
H	7.076167	-2.523870	-4.942351	
C	11.103664	-2.564415	-.048797	
C	11.994738	-2.910591	1.129409	
C	10.501023	-1.173868	.049012	
C	12.958292	-4.061280	.854619	
H	12.548355	-2.026439	1.435195	
H	11.336927	-3.152888	1.965545	
C	12.235337	-5.200218	.151328	
H	13.800759	-3.716467	.263245	

H	13.364461	-4.415615	1.798705	
C	11.641317	-4.792635	-1.209875	
H	12.911547	-6.035208	-.006925	
H	11.435179	-5.562006	.795833	
C	12.760508	-4.710584	-2.269258	
C	10.645710	-5.890253	-1.632161	
H	12.405295	-4.283228	-3.205990	
H	13.615245	-4.135653	-1.927761	
H	13.120745	-5.710659	-2.493852	
H	10.295411	-5.766254	-2.652789	
H	11.134000	-6.858540	-1.583385	
H	9.782103	-5.921865	-.972521	
H	11.255013	-.493724	.433252	
H	10.156189	-.761875	-.888584	
H	9.671175	-1.153170	.752901	
O	1.012854	-2.073951	-3.606484	-.83400
H	1.254838	-1.807542	-2.687599	.41700
H	1.441511	-1.296503	-4.023397	.41700
O	-2.063040	1.363916	-.756975	-.83400
H	-1.437154	2.080545	-1.039891	.41700
H	-2.778515	1.496744	-1.390275	.41700
HLA	-.685213	.081315	1.733789	

S_0-I. Optimized at the CASSCF/6-31G*/Amber level of theory with the active space comprising 12 electrons/12 orbitals. The atoms in bold indicate atoms that have been kept frozen during optimization procedure. Atom HLA denotes the hydrogen link atom.

Atom	*X*	*Y*	*Z*	Charge
N	1.115000	6.262998	-5.370998	-.51630
C	.802000	5.175998	-4.439998	.03970
C	1.938999	4.160999	-4.360998	.53660
O	2.402999	3.833999	-3.271999	-.58190
H	.490880	6.403988	-6.155218	.29360
H	.662240	5.589198	-3.441299	.11050
C	-.489000	4.469998	-4.870998	.05600
C	-1.315000	3.909999	-3.724999	.01360
C	-.537000	2.944999	-2.848999	.80540
O	.016000	1.955999	-3.390999	-.81880
O	-.487000	3.177999	-1.613999	-.81880
H	-.314450	3.720259	-5.641098	-.01730
H	-1.159730	5.222768	-5.250978	-.01730
H	-2.210399	3.425999	-4.109319	-.04250
H	-1.646269	4.758728	-3.123839	-.04250
N	1.944999	-1.515999	4.989998	-.39805
C	1.830999	-.073000	5.100998	-.24000
C	1.949999	.463000	6.510998	.68395
O	1.821999	1.661999	6.712998	-.63955
H	1.163730	-2.051989	4.638878	.22455
H	2.644289	.388350	4.539988	.14260
C	.539484	.471984	4.457270	-.00940
C	.520355	.188424	2.961083	.01870
C	-.830109	.502556	2.308465	.00000
C	-.953595	-.335885	1.032723	
N	.075275	.033385	.050714	
H	.477352	1.545853	4.579954	.03620
H	-.338573	.079379	4.953624	.03620
H	.736656	-.861790	2.817257	.01030
H	1.308515	.765898	2.474646	.01030

H	-.910024	1.571815	2.091159	.06210
H	-1.639667	.220847	2.986074	.06210
H	-1.931013	-.195416	.599051	
H	-.804815	-1.376962	1.268191	
H	-.032134	.923706	-.422019	
C	1.027101	-.759118	-.274720	
C	2.104243	-.436912	-1.169151	
C	3.055617	-1.379914	-1.433508	
C	4.398058	-.963092	-1.825783	
C	5.385307	-1.817328	-2.170898	
C	6.802155	-1.625020	-1.880676	
C	7.828852	-2.308726	-2.451678	
C	9.016268	-2.521422	-1.621410	
C	10.179184	-3.095270	-1.984819	
C	11.159879	-3.630059	-1.003859	
C	2.829408	-2.851460	-1.148505	
C	7.728559	-2.976646	-3.800131	
H	1.038936	-1.695927	.250558	
H	2.227625	.588721	-1.471359	
H	4.650751	.062051	-1.636729	
H	5.104302	-2.833001	-2.399382	
H	6.999301	-1.088144	-.967222	
H	8.849898	-2.341065	-.576788	
H	10.360423	-3.317201	-3.021187	
H	3.318777	-3.144675	-.223280	
H	1.781809	-3.111544	-1.080891	
H	3.241535	-3.460137	-1.943111	
H	8.584028	-2.705496	-4.412080	
H	7.727502	-4.067673	-3.725996	
H	6.842773	-2.645228	-4.340806	
C	11.501366	-2.984156	.138420	
C	12.398558	-3.605842	1.183451	
C	11.041028	-1.594627	.527450	
C	13.154333	-4.840054	.713302	
H	13.106622	-2.857284	1.528809	
H	11.772090	-3.853594	2.042505	
C	12.228750	-5.733438	-.096725	
H	14.018255	-4.545711	.126601	
H	13.527018	-5.379108	1.583558	
C	11.701033	-5.031505	-1.358073	
H	12.732876	-6.651295	-.386664	
H	11.382488	-6.027095	.524446	
C	12.826747	-4.889109	-2.398187	
C	10.589805	-5.925689	-1.944911	
H	12.460957	-4.402801	-3.298211	
H	13.663947	-4.319213	-2.016071	
H	13.197776	-5.867717	-2.693264	
H	10.248516	-5.587778	-2.916761	
H	10.964439	-6.936894	-2.071609	
H	9.729254	-5.967475	-1.282127	
H	11.867507	-1.061565	.991518	
H	10.681031	-1.001935	-.304494	
H	10.245617	-1.644651	1.269034	
O	1.026243	-2.066489	-3.677869	-.83400
H	1.569460	-1.872960	-2.900609	.41700
H	1.217461	-1.241975	-4.179501	.41700
O	-2.158805	1.333173	-.920688	-.83400
H	-1.565453	2.090237	-1.179010	.41700
H	-2.944214	1.535494	-1.456178	.41700
HLA	-.865198	.214455	1.862970	

S_0-PSB11 +Cl^-. Optimized at the CASSCF/6-31G*/Amber level of theory with the active space comprising 12 electrons/12 orbitals.

Atom	*X*	*Y*	*Z*	Charge
C	-6.523390	.894472	.637573	
H	-7.329653	1.123109	1.328226	
H	-5.693408	1.544258	.892303	
H	-6.857843	1.145143	-.365714	
C	-6.155413	-.599337	.744407	
C	-5.533412	-.839162	2.135085	
H	-4.601626	-.293392	2.244317	
H	-6.204115	-.499814	2.919850	
H	-5.316454	-1.891108	2.300475	
C	-7.461123	-1.404344	.594792	
H	-8.065209	-1.268111	1.488677	
H	-8.038119	-.993132	-.231299	
C	-7.223651	-2.885512	.328706	
H	-6.659129	-3.330592	1.146178	
H	-8.174069	-3.409659	.278392	
C	-6.452075	-3.050712	-.976375	
H	-6.084130	-4.071491	-1.074621	
H	-7.125709	-2.899553	-1.819997	
C	-5.283121	-2.093980	-1.123024	
C	-4.351608	-2.470929	-2.255224	
H	-3.673733	-1.676986	-2.533868	
H	-3.757397	-3.345102	-1.992947	
H	-4.929955	-2.742348	-3.134614	
C	-5.140127	-.993430	-.349200	
C	-3.986217	-.057584	-.506379	
H	-4.241122	.947116	-.795152	
C	-2.687853	-.356969	-.285591	
H	-2.430420	-1.363214	.007588	
C	-1.564744	.588439	-.417564	
C	-1.901259	2.023896	-.754092	
H	-2.595160	2.427292	-.022824	
H	-1.040195	2.673584	-.776040	
H	-2.382555	2.079289	-1.726074	
C	-.295748	.122582	-.239482	
H	-.190947	-.921882	-.014912	
C	.909241	.927138	-.375949	
H	.752698	1.966557	-.591337	
C	2.230236	.607341	-.303982	
H	2.895902	1.428458	-.503579	
C	2.947088	-.632735	-.006122	
C	2.211003	-1.873667	.449488	
H	2.867982	-2.680595	.749885	
H	1.565171	-1.640843	1.288554	
H	1.588427	-2.247238	-.358976	
C	4.303383	-.563521	-.173800	
H	4.750730	.335740	-.566920	
C	5.230550	-1.600549	.137954	
H	4.909575	-2.521719	.592830	
N	6.492661	-1.482161	-.069430	
H	6.813431	-.642680	-.537757	
C	7.468210	-2.518354	.285227	
H	8.442484	-2.060186	.367251	
H	7.198637	-2.967916	1.231423	
H	7.504496	-3.276049	-.487556	
Cl	6.865664	.978668	-2.026682	-1.00000

S_1-PSB11 +Cl^-. Optimized at the CASSCF/6-31G*/Amber level of theory with the active space comprising 12 electrons/12 orbitals.

Atom	*X*	*Y*	*Z*	Charge
C	-6.707572	1.201626	.769180	
H	-7.488240	1.400960	1.496797	
H	-5.880409	1.862641	1.002158	
H	-7.086144	1.467180	-.214728	
C	-6.304395	-.284787	.824699	
C	-5.621546	-.545828	2.182254	
H	-4.694582	.010775	2.266104	
H	-6.262065	-.235167	3.002432	
H	-5.383035	-1.597388	2.311987	
C	-7.594002	-1.119437	.706157	
H	-8.155721	-1.033231	1.633134	
H	-8.219991	-.696661	-.076204	
C	-7.331440	-2.581407	.369402	
H	-6.710295	-3.040231	1.136055	
H	-8.267042	-3.132424	.347999	
C	-6.628710	-2.671436	-.980174	
H	-6.244189	-3.677203	-1.141669	
H	-7.349105	-2.500672	-1.779640	
C	-5.489204	-1.683828	-1.139010	
C	-4.599687	-1.987738	-2.324123	
H	-3.948453	-1.168379	-2.590270	
H	-3.980367	-2.861444	-2.130653	
H	-5.210169	-2.226257	-3.190929	
C	-5.328417	-.619578	-.319347	
C	-4.180308	.324066	-.474457	
H	-4.429756	1.329511	-.764536	
C	-2.888902	.013732	-.239073	
H	-2.653684	-.996788	.055833	
C	-1.743303	.931074	-.364234	
C	-2.038665	2.378065	-.690433	
H	-2.763890	2.778084	.010409	
H	-1.166202	3.011959	-.648653	
H	-2.466953	2.463228	-1.684559	
C	-.488867	.426109	-.189573	
H	-.419079	-.621022	.036394	
C	.746473	1.178307	-.356132	
H	.632587	2.198496	-.667778	
C	2.050175	.812400	-.221985	
H	2.756145	1.576900	-.495814	
C	2.697493	-.426184	.224993	
C	1.908344	-1.505731	.926139	
H	2.540370	-2.230768	1.423179	
H	1.256666	-1.067406	1.670936	
H	1.291002	-2.045170	.216716	
C	4.037811	-.505185	-.015053	
H	4.526110	.290652	-.553111	
C	4.906016	-1.586277	.369829	
H	4.571436	-2.411450	.968400	
N	6.145369	-1.597473	.018876	
H	6.454796	-.826691	-.570962	
C	7.142843	-2.609060	.366661	
H	7.942725	-2.129920	.911138	
H	6.693006	-3.377364	.977124	
H	7.537569	-3.029967	-.545359	
Cl	6.592030	.813378	-2.106973	-1.00000

5. Excited-State Gradient

Excited-state (S_1) cartesian forces for the **PSB11** in **S_0-Rh**-optimized structure (see above). The forces are computed at the single root CASSCF/6-31G*/Amber level with a 12 electrons/12 orbitals active space. The Cartesian coordinates of the relevant fragment **(Å)** are also given.

Cartesian Coordinates of the Fragment

Atom	*X*	*Y*	*Z*
C	-.708968	-.461944	.943648
N	.291210	-.059143	-.057086
H	-1.683488	-.416855	.485487
H	-.483060	-1.472114	1.241346
H	.072029	.761400	-.609640
C	1.350744	-.740551	-.312793
C	2.261938	-.426553	-1.383077
C	3.409522	-1.137401	-1.614307
C	4.226937	-.717263	-2.758500
C	5.501593	-1.060244	-3.082862
C	6.488897	-1.815909	-2.311867
C	7.644302	-2.341877	-2.801413
C	8.620835	-2.867257	-1.833984
C	9.884947	-3.253504	-2.108414
C	10.867027	-3.698740	-1.077738
C	3.817233	-2.327584	-.768648
C	7.991565	-2.385426	-4.269794
H	1.507712	-1.588868	.327671
H	2.022008	.432939	-1.991398
H	3.735651	-.035300	-3.432174
H	5.869230	-.620176	-3.991390
H	6.352824	-1.861952	-1.248001
H	8.298926	-2.874170	-.805891
H	10.218396	-3.280674	-3.132515
H	4.511171	-2.023172	.006920
H	2.980531	-2.807926	-.280945
H	4.303004	-3.078338	-1.373993
H	8.848604	-1.758557	-4.486209
H	8.238350	-3.398579	-4.572195
H	7.179480	-2.037786	-4.893307
C	11.168708	-2.940210	.005408
C	12.112710	-3.411058	1.095387
C	10.572190	-1.576746	.294799
C	12.971140	-4.610722	.707356
H	12.754464	-2.584176	1.388436
H	11.507147	-3.645675	1.971969
C	12.123882	-5.631464	-.039153
H	13.812886	-4.290319	.102836
H	13.385472	-5.060778	1.607585
C	11.532018	-5.065845	-1.341825
H	12.707358	-6.517567	-.273729
H	11.309031	-5.957637	.606632
C	12.644310	-4.909884	-2.396356
C	10.494740	-6.077888	-1.863311
H	12.251256	-4.497879	-3.322959
H	13.453490	-4.276500	-2.051512
H	13.071030	-5.881054	-2.633373
H	10.107298	-5.805704	-2.839668

H	10.950892	-7.058984	-1.956257
H	9.652096	-6.164023	-1.181586
H	11.346294	-.915013	.677607
H	10.125919	-1.105259	-.569708
H	9.808473	-1.647207	1.066035

Cartesian Forces (a.u.)

Atom	*X*	*Y*	*Z*
C	.006722162	-.038202528	-.071552617
N	-.056316193	.037123194	.013864271
H	-.002119000	-.002404883	.003182531
H	-.001519193	-.000439069	.000677350
H	.000144628	-.007693712	.005948508
C	.062789804	-.023937913	-.032886462
C	-.042627676	.003238460	.032163630
C	.031133581	-.016366003	-.023096023
C	-.026663235	.001621925	.023894797
C	.038657892	-.012472691	-.004675930
C	-.048659143	.031253866	.007716354
C	.063020456	-.026514482	-.000882427
C	-.049714364	.024338827	-.007956440
C	.031313916	-.011089051	-.000954494
C	-.006324966	-.001717168	-.007037974
C	.000448095	.005098580	-.001124910
C	-.002883748	-.000764509	-.002018084
H	.001841468	.001664862	-.000364578
H	.000328426	-.000025724	.000117207
H	.001733188	.000521706	-.000705726
H	.001827130	-.003383131	-.001314139
H	-.002499786	-.004092210	-.000531945
H	.000426723	.000079040	-.000407246
H	-.001113252	-.002124847	.000211259
H	-.000096653	-.001621466	.003881956
H	.000644184	.000617066	-.000901908
H	.000537633	-.003285041	-.000517068
H	-.000739986	.000776721	.000434904
H	.000041076	.000186116	.000583246
H	.001051345	-.000209279	.001799923
C	-.003257873	.003560058	.007673584
C	.002108085	-.000303332	-.000422810
C	.000259215	-.000092225	-.000302252
C	.001075980	-.000663028	-.000301999
H	-.000741538	-.000055120	-.000508725
H	-.001061372	.000532372	-.001190673
C	-.001383026	.000461645	.002426789
H	.000035919	.000194049	.000055292
H	-.000591862	.000511514	-.000623251
C	.003229700	-.001790842	-.004489242
H	-.000383234	.000883876	-.000840370
H	.000180649	.000063724	-.000180726
C	.000259013	-.000139820	.000299205
C	-.000324384	.000292371	.001275811
H	.000306627	.000140792	-.000497579
H	.000201064	-.000075309	-.000101587
H	-.000530147	.000664145	-.000049460
H	-.000051329	-.000297574	-.001187122
H	-.000622004	.000778730	-.000223906
H	-.000028015	-.000477506	.000094866
H	-.001024872	-.000411422	-.000902526

H	.000031119	.001219808	-.000075753
H	.000597571	-.000461519	.000367837

Excited state (S_1) cartesian forces for the **PSB11** in **S_0-PSB11+Cl$^-$** optimized structure (see above). The forces are computed at the single root CASSCF/6-31G*/Amber level with a 12 electrons/12 orbitals active space. The Cartesian coordinates of the relevant fragment **(Å)** are also given.

Cartesian Coordinates of the Fragment

Atom	*X*	*Y*	*Z*
C	-6.523390	.894472	.637573
H	-7.329653	1.123109	1.328226
H	-5.693408	1.544258	.892303
H	-6.857843	1.145143	-.365714
C	-6.155413	-.599337	.744407
C	-5.533412	-.839162	2.135085
H	-4.601626	-.293392	2.244317
H	-6.204115	-.499814	2.919850
H	-5.316454	-1.891108	2.300475
C	-7.461123	-1.404344	.594792
H	-8.065209	-1.268111	1.488677
H	-8.038119	-.993132	-.231299
C	-7.223651	-2.885512	.328706
H	-6.659129	-3.330592	1.146178
H	-8.174069	-3.409659	.278392
C	-6.452075	-3.050712	-.976375
H	-6.084130	-4.071491	-1.074621
H	-7.125709	-2.899553	-1.819997
C	-5.283121	-2.093980	-1.123024
C	-4.351608	-2.470929	-2.255224
H	-3.673733	-1.676986	-2.533868
H	-3.757397	-3.345102	-1.992947
H	-4.929955	-2.742348	-3.134614
C	-5.140127	-.993430	-.349200
C	-3.986217	-.057584	-.506379
H	-4.241122	.947116	-.795152
C	-2.687853	-.356969	-.285591
H	-2.430420	-1.363214	.007588
C	-1.564744	.588439	-.417564
C	-1.901259	2.023896	-.754092
H	-2.595160	2.427292	-.022824
H	-1.040195	2.673584	-.776040
H	-2.382555	2.079289	-1.726074
C	-.295748	.122582	-.239482
H	-.190947	-.921882	-.014912
C	.909241	.927138	-.375949
H	.752698	1.966557	-.591337
C	2.230236	.607341	-.303982
H	2.895902	1.428458	-.503579
C	2.947088	-.632735	-.006122
C	2.211003	-1.873667	.449488
H	2.867982	-2.680595	.749885
H	1.565171	-1.640843	1.288554
H	1.588427	-2.247238	-.358976
C	4.303383	-.563521	-.173800
H	4.750730	.335740	-.566920
C	5.230550	-1.600549	.137954
H	4.909575	-2.521719	.592830

N	6.492661	-1.482161	-.069430
H	6.813431	-.642680	-.537757
C	7.468210	-2.518354	.285227
H	8.442484	-2.060186	.367251
H	7.198637	-2.967916	1.231423
H	7.504496	-3.276049	-.487556

Cartesian forces (a.u.)

Atom	*X*	*Y*	*Z*
C	0.000544625	-0.000494971	-0.000491127
H	0.000483584	0.000032847	-0.000225581
H	-0.000545558	0.000571005	0.000525737
H	-0.000380198	0.000100022	0.000207056
C	-0.001317448	0.002142078	0.000770719
C	0.000591065	-0.000432851	-0.000692829
H	-0.000471918	-0.000009044	0.001055359
H	0.000477382	-0.000028791	-0.000288039
H	-0.000253161	0.000635798	0.000110698
C	0.000155241	-0.000229815	-0.000581247
H	0.000554461	0.000098966	-0.000322238
H	-0.000003901	-0.000141944	0.000395638
C	0.000377951	0.000279329	0.000167761
H	-0.000450965	0.000104393	-0.000243056
H	0.000504991	0.000235586	-0.000074313
C	-0.000875144	-0.000231380	0.000421271
H	0.000076439	0.000690604	-0.000059218
H	0.000391911	0.000103621	0.000125001
C	0.001175952	-0.001870754	-0.000935959
C	0.001089636	0.000396969	0.000748124
H	-0.000072506	-0.000548811	-0.001136069
H	-0.000553678	0.000228670	-0.000064149
H	0.000213292	0.000309711	0.000075785
C	0.001086855	0.000932887	0.001769339
C	-0.021285826	0.003053680	-0.003788143
H	-0.000614578	0.001489891	0.000637563
C	0.041373312	0.006845884	0.001158045
H	0.000090629	-0.000488499	-0.000157784
C	-0.064278930	0.002069993	-0.004406074
C	-0.000185211	0.002162680	-0.000347183
H	0.000696384	-0.000016512	-0.000104541
H	-0.000218794	0.000314676	0.000052263
H	0.000841740	0.000110222	-0.000052556
C	0.067695213	0.002602414	0.001873702
H	0.001721812	-0.003315582	0.000986272
C	-0.061509941	0.004517325	-0.001280303
H	-0.001188143	-0.000393278	0.000274091
C	0.038035266	-0.031915691	0.006355849
H	0.001425557	0.002476085	-0.001401405
C	-0.037644292	0.010760829	0.001823067
C	-0.002193669	0.005914985	-0.004318737
H	0.000008339	0.003031556	-0.000726260
H	0.000701223	-0.001699825	0.000696120
H	0.001207898	-0.002196571	0.002160043
C	0.029232594	-0.010615173	0.002880794
H	-0.000329787	-0.002462626	0.000647837
C	-0.052123468	-0.005387329	0.008368773
H	0.001920883	0.007896044	-0.004264121
N	0.062343932	0.009699714	-0.008679652
H	-0.003475448	-0.011919572	0.004757231

C	-0.007662533	0.009998713	-0.004503925
H	-0.001649678	-0.000763954	0.000227091
H	0.000110171	0.000003448	-0.000810271
H	0.000901211	-0.000612455	0.001178051

Table 3. Energies relative to S_0 in kcal ·mol^{-1}

Structure	S_1		S_2	
	CASSCF	CASPT2	CASSCF	CASPT2
S_0-PSB11 +Cl^- (in CH_3OH)	95.30	67.27	108.05	83.49
S_1-PSB11 +Cl^- (in CH_3OH)	53.70	42.86	70.62	49.15
PSB11	87.71	62.83	104.56	87.38
PSB11+Glu113	99.17	80.24	113.23	80.78
S_0-Rh	91.91	59.72	109.23	87.23
S_1-Rh	48.56	37.29	66.94	51.30
S_1-$Rh_{stretch}$	75.53	49.58	81.69	67.87
Rh-CI	19.50	1.63	59.49	51.83
So-I	91.05	57.06	107.40	82.98

Table 4. Charge-transfer (Δq), change in dipole moments (Δμ) and oscillator strengths (f)

Structure	Δq[a]		Δμ (Debye)[b]		f[c]	
	S_0->S_1	S_0->S_2	S_0->S_1	S_0->S_2	S_0->S_1	S_0->S_2
S_0-PSB11 +Cl^- (in CH_3OH)	-0.212	-0.197	5.56	3.35	0.417	0.604
S_1-PSB11 +Cl^- (in CH_3OH)	-0.169	-0.273	3.41	8.51	0.318	0.654
PSB11	-0.370	-0.178	14.17	3.59	0.768	0.316
PSB11+Glu113	-0.187	-0.323	3.67	7.41	0.127	0.862
S_0-Rh	-0.343	-0.144	11.13	3.06	0.506	0.401
S_1-Rh	-0.272	-0.085	8.18	3.70	0.590	0.430
S_1-$Rh_{stretch}$	-0.346	-0.082	11.69	1.66	0.700	0.293
Rh-CI	-0.962	-0.002	22.74	0.01	0.0004	0.0006
So-I	-0.341	-0.176	10.89	3.88	0.426	0.447

(a) The magnitude of charge transfer induced by the vertical transition is evaluated as the change in the positive charge of the –NH=C_{15}- fragment. We use Mulliken charges as we only need to characterize the electronic transition and not to accurately fit point charges. Mulliken charges are calculated by using the CASPT2 functions.

(b) Dipoles are calculated by using first-order perturbated CASPT2 functions.

(c) Oscillator strenghts are calculated by using CASPT2 energies and CASSCF functions.

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