Appendix A

Derivation of the rate constant of the stepwise mechanism of the proton transfer reaction in porphycene.
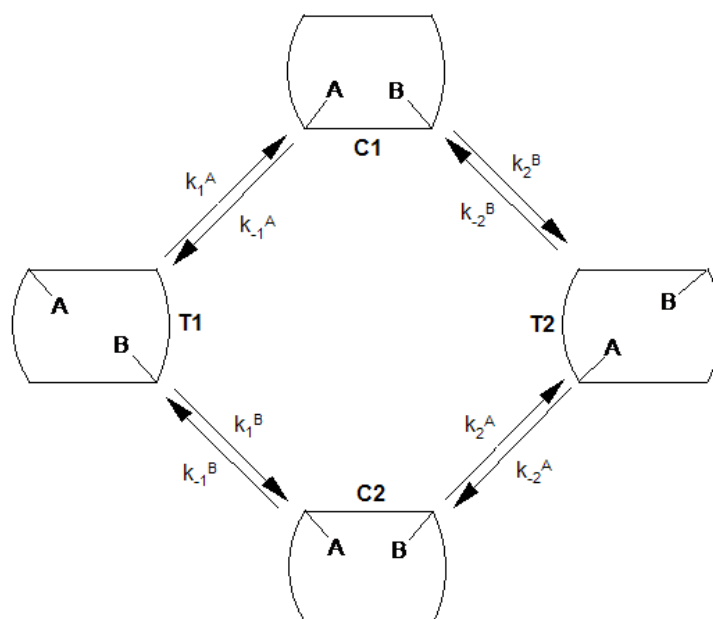

Figure A.1: Scheme representing the stepwise mechanism of the proton transfer reaction in porphycene. A,B = H or D

In this appendix we will provide a step-by-step derivation of Eq. (3.7). For the stepwise mechanism shown in Scheme A.1 one can use the traditional kinetic analysis and write the rate law for the interconversion between the two trans tau-

tomers (T1 and T2) as follows:

$$\frac{d[T1]}{dt} = -k_1^A[T1] - k_1^B[T1] + k_{-1}^A[C1] + k_{-1}^B[C2], \tag{A.1}$$

where C1 and C2 are the cis tautomers of porphycene and k's are the rate coefficients shown in Scheme A.1. Since C1 and C2 are considered as intermediates for the stepwise mechanism, the steady state approximation can be applied.

$$\frac{d[C1]}{dt} = k_1^A[T1] - k_2^B[C1] - k_{-1}^A[C1] + k_{-2}^B[T2] = 0, \tag{A.2}$$

and

$$\frac{d[C2]}{dt} = k_1^B[T1] - k_2^A[C2] - k_{-1}^B[C2] + k_{-2}^A[C2] = 0. \tag{A.3}$$

Therefore:

$$[C1] = \frac{k_1^A[T1] + k_{-2}^B[T2]}{k_2^B + k_{-1}^A}, \tag{A.4}$$

and

$$[C2] = \frac{k_1^B[T1] + k_{-2}^A[C2]}{k_2^A + k_{-1}^B}. \tag{A.5}$$

It follows from Eqns. (A.1), (A.4) and (A.5) that:

$$\begin{aligned}
\frac{d[T1]}{dt} = {} & -k_1^A[T1] - k_1^B[T1] \\
& + k_{-1}^A \frac{k_1^A[T1] + k_{-2}^B[T2]}{k_2^B + k_{-1}^A} \\
& + k_{-1}^B \frac{k_1^B[T1] + k_{-2}^A[C2]}{k_2^A + k_{-1}^B}.
\end{aligned} \tag{A.6}$$

On rearranging Eq. (A.6), one gets:

$$\begin{aligned}
\frac{d[T1]}{dt} = {} & \frac{-k_1^A k_{-1}^A - k_1^A k_2^B + k_{-1}^A k_1^A}{k_{-1}^A + k_2^B}[T1] \\
& + \frac{-k_1^B k_{-1}^B - k_1^B k_2^A + k_{-1}^B k_1^B}{k_{-1}^B + k_2^A}[T1] \\
& + \left(\frac{k_{-1}^A k_{-2}^B}{k_{-1}^A + k_2^B} + \frac{k_{-1}^B k_{-2}^A}{k_{-1}^B + k_2^A} \right)[T2].
\end{aligned} \tag{A.7}$$

Accordingly,

$$\begin{aligned}
\frac{d[T1]}{dt} = {} & -\left(\frac{k_1^A k_2^B}{k_{-1}^A + k_2^B} + \frac{k_1^B k_2^A}{k_{-1}^B + k_2^A} \right)[T1] \\
& + \left(\frac{k_{-1}^A k_{-2}^B}{k_{-1}^A + k_2^B} + \frac{k_{-1}^B k_{-2}^A}{k_{-1}^B + k_2^A} \right)[T2].
\end{aligned} \tag{A.8}$$

Finally one can write the rate of reaction as follows:

$$\frac{d[T1]}{dt} = -k_{SM}^{AB}[T1] + k_{SM}^{AB}[T2], \tag{A.9}$$

where index SM stands for stepwise mechanism. Therefore,

$$k_{SM}^{AB} = \frac{k_1^A k_2^B}{k_{-1}^A + k_2^B} + \frac{k_1^B k_2^A}{k_{-1}^B + k_2^A}. \tag{A.10}$$

Consider the symmetric case of porphycene (i.e. A = B = H), then Eq. (A.10) becomes

$$k_{SM}^{HH/DD} = k_1^{H/D}. \tag{A.11}$$

Furthermore, the asymmetric case of porphycene (i.e. A = H and B = D) results in

$$k_{SM}^{HD} = \frac{k_1^H k_2^D + k_1^D k_2^H}{2(k_2^H + k_2^D)}. \tag{A.12}$$

Appendix B

Empirical q_1/q_2 approach.

The values of q_1 and q_2 cannot be obtained directly from the NMR experiment. However, one can correlate the NMR chemical shifts of the deuterated and normal species with the geometrical parameters q_1 and q_2. According to the valence bond order concept of Pauling [171] and Brown [172], one can define the valency p_{ij} (ij = AH) as follows:

$$p_{ij} = exp(-(r_i - r_i^o)/b_i),\qquad\qquad(B.1)$$

where b_i is the bond decay parameter and r_i^o is the distance when $p_1 = 1$. p_i becomes zero at infinite distance. The distances r_1 and r_2 are shown in Fig. 1.8. Dunitz extended the valence bond order to cover the hydrogen bonded systems [173]:

$$p_1 + p_2 = exp(-(r_1 - r_1^o)/b_1) + exp(-(r_2 - r_2^o)/b_2) = 1.\qquad(B.2)$$

Hence, the two bond distances r_1 and r_2 can not be varied independently since one can use Eq. (B.2) to express r_1 as a function of r_2 or q_1 as a function of q_2. For the symmetric case A-H$\cdots$A, where $b_1 = b_2 = b$ and $r_1^o = r_2^0 = r^o$ it follows that [28]

$$q_2 = r_1 + r_2 = 2r^o + 2q_1 + 2b \cdot ln(1 + exp(-2q_1/b)).\qquad(B.3)$$

Steiner et al. obtained an experimental correlation between q_1 and q_2 based on neutron diffraction data for various N-H$\cdots$N hydrogen bonds [22, 174]. Limbach et al. modified this correlation (using the anharmonic correction of the ground state vibrations of the hydrogen or deuterium) and obtained a better fit to experimental data (NMR and neutron diffraction), especially in the region of symmetric and quasi-symmetric hydrogen bonds (where q_1 is close to 0) [42, 43]. An empir-

ical correction for the valence bond order has been proposed by Limbach [42, 43]:

$$p_{NH}^{L} = p_{NH} - c^{L}(p_{NH} - p_{HN})^{f}(p_{NH} - p_{HN}) - d^{L}(p_{NH}p_{HN^g}) \qquad \text{(B.4)}$$

$$p_{HN}^{L} = p_{HN} - c^{L}(p_{NH} - p_{HN})^{f}(p_{NH} - p_{HN}) - d^{L}(p_{NH}p_{HN^g}), \qquad \text{(B.5)}$$

where c, d, f and g are isotope sensitive empirical parameters. The chemical shifts can be written as a function of the valence bond orders as follows: [175, 176]

$$\delta(^{1}H) = \Delta_{H}(4p_1p_2)^{m} + \delta_{1}^{o}p_1 + \delta_{2}^{o}p_2, \qquad \text{(B.6)}$$

where, Δ_{H} is the excess chemical shift of the quasi symmetric complex and δ_{1}^{o} and δ_{2}^{o} are the limiting chemical shifts for distances r_{1}^{o} and r_{2}^{o} respectively. m is an empirical fitting parameter with value close to 1. For the N-H...N case, Eq. (B.6) can be simplified, as $\delta_{1}^{o} = \delta_{2}^{o}$,

$$\delta(^{1}H) = \Delta_{H}(4p_1p_2)^{m} + \delta^{o}. \qquad \text{(B.7)}$$

Using this equation, the valence bond order and some systems with known geometries and similar core, one can establish a correlation between the experimentally measured chemical shifts and the geometrical changes q_1 and q_2. From the empirical q_1 and q_2, one can then calculate the primary and secondary geometric H/D isotope effects.

Appendix C

Input files for MCTDH.

The used relaxation input file (HH case) for the calculation of the ground state wave function.

end-init_wf-section

end-input

The used operator input (HH case) file for MCTDH calculations.

RUN-SECTION

name = file_name

relaxation

tfinal=100.0

tout= 10.

overwrite

update

output

psi

end-run-section

OPERATOR-SECTION

opname = op_file_name

end-operator-section

SBASIS-SECTION

q1,q2 = 4

q3,q4 = 4

end-sbasis-section

PBASIS-SECTION

q1 HO 64 xi-xf -0.56 0.56

q2 HO 64 xi-xf -0.56 0.56

q3 HO 128 xi-xf -6.5 6.5

q4 HO 64 xi-xf -1.5 1.5

end-pbasis-section

INTEGRATOR-SECTION

CMF/fix

BS/spf = 10 , 1.0d-8

SIL/A = 40 , 1.0d-8

end-integrator-section

INIT_WF-SECTION

build

q1 gauss 0.000 0.0 0.1

q2 gauss 0.000 0.0 0.1

q3 gauss 0.000 0.0 0.1

q4 gauss 0.000 0.0 0.1

end-build

OP_DEFINE-SECTION

title

4D system

end-title

end-op_define-section

PARAMETER-SECTION

mass_q1 = 1.0, AMU

mass_q2 = 1.0, AMU

mass_q3 = 1.0, AMU

mass_q4 = 1.0, AMU

B_00 = 7.9931978d-07

B_01 = 7.7293359d-06

B_10 = -3.5433424d-04

B_02 = 1.5984175d-01

B_11 = -1.4398189d-04

B_20 = 1.5973074d-01

B_03 = -8.1598779d-05

B_12 = 4.9461731d-01

B_21 = 1.8665123d-04

B_30 = 1.6605993d-01

B_04 = 9.1543319d-02

B_13 = 1.3718024d-03

B_22 = 5.1391203d-01

B_31 = 1.2697971d-03

B_40 = 8.8016621d-02

B_05 = 2.2341013d-04

B_14 = 2.4508811d-01

B_23 = -1.6313050d-03

B_32 = 4.7206428d-01

B_41 = -1.1472811d-03

B_50 = 4.4487777d-02

B_15 = -3.1575315d-03

B_24 = 2.4057259d-01

B_33 = -1.0786550d-02

B_42 = 2.5612118d-01

B_51 = -2.8569251d-03

B_25 = 3.5034979d-03

B_34 = -2.9169110d-01

B_43 = 1.1070784d-02

B_52 = -1.6425420d-01

B_35 = 2.2097963d-02

B_44 = 1.3973124d-01

B_53 = 2.2351428d-02

B_45 = -2.6136768d-02

B_54 = 1.1787250d+00

B_55 = -4.0642140d-02

C_00 = -2.2650727d-06

C_01 = -3.7847905d-05

C_10 = -3.2887795d-04

C_02 = 6.8344149d-04

C_11 = 4.6304580d-04

C_20 = 1.5968777d-01

C_03 = -3.2866822d-05

C_12 = 6.4528517d-04

C_21 = 1.6749939d-02

C_30 = 1.6909950d-01

C_04 = 3.1360993d-06

C_13 = -8.1750251d-05

C_22 = -5.7900864d-04

C_31 = 6.4529577d-03

C_40 = 8.8088825d-02

C_05 = -3.4328158d-07

C_14 = -4.1546759d-06

C_23 = 4.9147402d-05

C_32 = -1.7750873d-04

C_41 = 7.4013998d-03

C_50 = 3.1863647d-02

C_15 = 2.1952784d-06

C_24 = 1.7316971d-05

C_33 = 5.3656026d-04

C_42 = 8.1422455d-04

C_51 = 9.3004498d-03

C_25 = -3.6567606d-06

C_34 = -1.5143146d-05

C_43 = -3.6610023d-04

C_52 = 9.8114780d-05

C_35 = -1.6837232d-05

C_44 = -2.1172628d-05

C_53 = -1.4047898d-03

C_45 = 1.0491063d-05

C_54 = 6.4393302d-06

C_55 = 5.0687512d-05

D_00 = 5.5247855d-06

D_01 = -7.8402428d-05

D_10 = -7.1585523d-06

D_02 = 6.8415893d-04

D_11 = -1.0356638d-05

D_20 = 1.5965265d-01

D_03 = -2.7524981d-05

D_12 = -3.6908696d-07

D_21 = 1.5716953d-02

D_30 = 1.1170066d-04

D_04 = 3.1083738d-06

D_13 = 1.3367106d-06

D_22 = -6.9437147d-04

D_31 = 1.5124007d-04

D_40 = 9.2593109d-02

D_05 = -5.0340183d-07

D_14 = 3.1617117d-08

D_23 = 6.8821054d-05

D_32 = 5.3431909d-06

D_41 = 9.6246730d-03

D_50 = -3.4892401d-04

D_15 = -3.9751014d-08

D_24 = 2.4364829d-05

D_33 = -1.9424463d-05

D_42 = 8.5078288d-04

D_51 = -4.7542712d-04

D_25 = -3.8044434d-06

D_34 = -4.5875548d-07

D_43 = -5.6650714d-04

D_52 = -1.6799933d-05

D_35 = 5.7755402d-07

D_44 = -3.6613766d-05

D_53 = 6.1084772d-05

D_45 = 1.5782332d-05

D_54 = 1.4425556d-06

D_55 = -1.8162746d-06

#

K_4_4 = .339373253d-01

K_4_4_4 = -.502823646d-05

K_4_4_1 = .365091798d-03

K_4_4_2 = .189111447d-04

K_4_4_3 = .116589069d-03

K_1_1_4 = -.598802311d-05

K_2_2_4 = .449574615d-04

K_3_3_4 = .377082201d-05

K_1_2_4 = -.688581443d-01

K_1_3_4 = .190291849d-04

K_2_3_4 = -.298190256d-02

end-parameter-section

HAMILTONIAN-SECTION

modes | q1 | q2 | q3 | q4

1.0 |1 KE

1.0 |2 KE

1.0 |3 KE

1.0 |4 KE

#

B_00 | xq0 | xq0 | xq0

B_11 | xq1 | xq1 | xq0

B_12 | xq1 | xq2 | xq0

B_21 | xq2 | xq1 | xq0

B_13 | xq1 | xq3 | xq0

B_22 | xq2 | xq2 | xq0

B_31 | xq3 | xq1 | xq0
B_14 | xq1 | xq4 | xq0
B_23 | xq2 | xq3 | xq0
B_32 | xq3 | xq2 | xq0
B_41 | xq4 | xq1 | xq0
B_15 | xq1 | xq5 | xq0
B_24 | xq2 | xq4 | xq0
B_33 | xq3 | xq3 | xq0
B_42 | xq4 | xq2 | xq0
B_51 | xq5 | xq1 | xq0
B_25 | xq2 | xq5 | xq0
B_34 | xq3 | xq4 | xq0
B_43 | xq4 | xq3 | xq0
B_52 | xq5 | xq2 | xq0
B_35 | xq3 | xq5 | xq0
B_44 | xq4 | xq4 | xq0
B_53 | xq5 | xq3 | xq0
B_45 | xq4 | xq5 | xq0
B_54 | xq5 | xq4 | xq0
B_55 | xq5 | xq5 | xq0
C_10 | xq1 | xq0 | xq0
C_11 | xq1 | xq0 | xq1
C_20 | xq2 | xq0 | xq0
C_12 | xq1 | xq0 | xq2
C_21 | xq2 | xq0 | xq1
C_30 | xq3 | xq0 | xq0
C_13 | xq1 | xq0 | xq3
C_22 | xq2 | xq0 | xq2
C_31 | xq3 | xq0 | xq1
C_40 | xq4 | xq0 | xq0
C_14 | xq1 | xq0 | xq4
C_23 | xq2 | xq0 | xq3
C_32 | xq3 | xq0 | xq2
C_41 | xq4 | xq0 | xq1
C_50 | xq5 | xq0 | xq0
C_15 | xq1 | xq0 | xq5
C_24 | xq2 | xq0 | xq4
C_33 | xq3 | xq0 | xq3
C_42 | xq4 | xq0 | xq2
C_51 | xq5 | xq0 | xq1
C_25 | xq2 | xq0 | xq5
C_34 | xq3 | xq0 | xq4
C_43 | xq4 | xq0 | xq3
C_52 | xq5 | xq0 | xq2
C_35 | xq3 | xq0 | xq5
C_44 | xq4 | xq0 | xq4
C_53 | xq5 | xq0 | xq3
C_45 | xq4 | xq0 | xq5
C_54 | xq5 | xq0 | xq4
C_55 | xq5 | xq0 | xq5
D_00 | xq0 | xq0 | xq0
D_01 | xq0 | xq0 | xq1
D_10 | xq0 | xq1 | xq0
D_02 | xq0 | xq0 | xq2
D_11 | xq0 | xq1 | xq1

D_20 | xq0 | xq2 | xq0
D_03 | xq0 | xq0 | xq3
D_12 | xq0 | xq1 | xq2
D_21 | xq0 | xq2 | xq1
D_30 | xq0 | xq3 | xq0
D_04 | xq0 | xq0 | xq4
D_13 | xq0 | xq1 | xq3
D_22 | xq0 | xq2 | xq2
D_31 | xq0 | xq3 | xq1
D_40 | xq0 | xq4 | xq0
D_05 | xq0 | xq0 | xq5
D_14 | xq0 | xq1 | xq4
D_23 | xq0 | xq2 | xq3
D_32 | xq0 | xq3 | xq2
D_41 | xq0 | xq4 | xq1
D_50 | xq0 | xq5 | xq0
D_15 | xq0 | xq1 | xq5
D_24 | xq0 | xq2 | xq4
D_33 | xq0 | xq3 | xq3
D_42 | xq0 | xq4 | xq2
D_51 | xq0 | xq5 | xq1
D_25 | xq0 | xq2 | xq5
D_34 | xq0 | xq3 | xq4
D_43 | xq0 | xq4 | xq3
D_52 | xq0 | xq5 | xq2
D_35 | xq0 | xq3 | xq5
D_44 | xq0 | xq4 | xq4
D_53 | xq0 | xq5 | xq3
D_45 | xq0 | xq4 | xq5
D_54 | xq0 | xq5 | xq4
D_55 | xq0 | xq5 | xq5
#
K_4_4/2. |4 q$\hat{2}$
K_4_4_4/6. |4 q$\hat{3}$
K_4_4_1/2. |1 q |4 q$\hat{2}$
K_4_4_2/2. |2 q |4 q$\hat{2}$
K_1_1_4/2. |1 q$\hat{2}$ |4 q
K_2_2_4/2. |2 q$\hat{2}$ |4 q
K_1_2_4 |1 q |2 q |4 q
K_4_4_3/2. |3 q |4 q$\hat{2}$
K_3_3_4/2. |3 q$\hat{2}$ |4 q
K_1_3_4 |1 q |3 q |4 q
K_2_3_4 |2 q |3 q |4 q
end-hamiltonian-section
LABELS-SECTION
#
xq0 = 1
xq1 = q
xq2 = q^2
xq3 = q^3
xq4 = q^4
xq5 = q^5
end-labels-section
end-operator

Appendix D

Coordinate transformation from old "molecule" to new "laboratory" frames.

In this Appendix an expression that relates the original coordinates r and ϕ to new r' and ϕ' ones is derived. We recall that r and ϕ describe the P-S bond length and the dihedral angle defined by the atoms OPSD, corresponding to the torsional angle of the SD versus OPH_2 fragments around the S-P bond, respectively (Fig. D.1), whereas r' and ϕ' are defined as the distance between the c.o.m's of the SD and OPH_2 fragments and the torsion of SD versus OPH_2 fragments around the line connecting the c.o.m's of the SD and OPH_2 fragments, see Figure D.1. It is assumed that the line (r') is oriented along the Z-axis, and the atoms O and P remain in the X-Z-plane.

First, consider the situation where $\phi' = \phi'$, the vector describing the S-D bond, $\vec{r}_{SD}$, can be defined as

$$\vec{r}_{SD} = \vec{r}_D - \vec{r}_S, \tag{D.1}$$

where the vectors $\vec{r}_D$ and $\vec{r}_S$ for the "old" coordinates are

$$\vec{r}_D = \begin{pmatrix} 1.34 \\ 0.00 \\ 2.19 \end{pmatrix}, \tag{D.2}$$

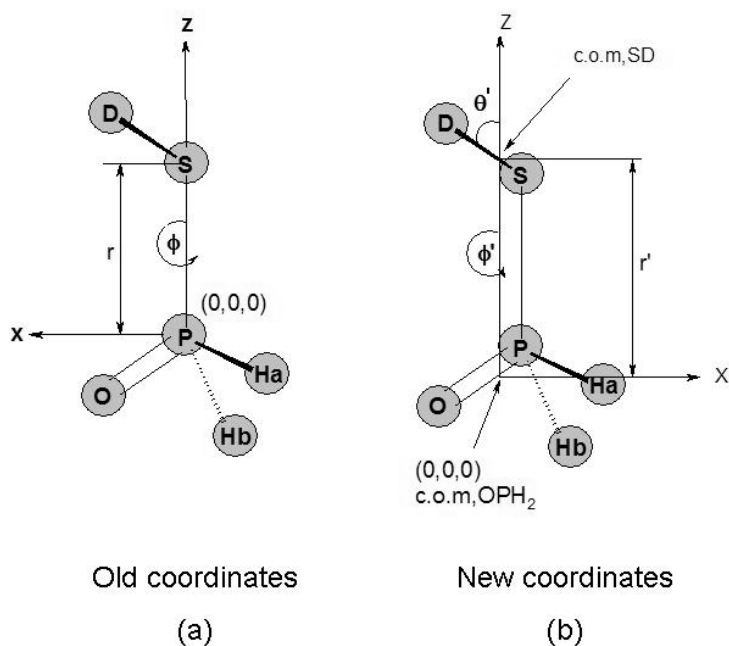$$\vec{r}_S = \begin{pmatrix} 0.00 \\ 0.00 \\ 2.12 \end{pmatrix}. \tag{D.3}$$

Figure D.1: Schematic diagram showing the old (a) as well as the new (b) coordinates. The polar angle θ and the different origins are also shown.

The center of mass of the fragment SD is defined as

$$\vec{r}_{c.o.m,SD} = c_D \vec{r}_D + c_S \vec{r}_S, \tag{D.4}$$

with

$$c_D = \frac{m_D}{m_D + m_S} \qquad \& \qquad c_S = \frac{m_S}{m_D + m_S}. \tag{D.5}$$

Likewise, the center of mass of the fragment H_2PO is defined as

$$\vec{r}_{c.o.m,H_2POSD} = c_O \vec{r}_O + c_P \vec{r}_P + c_{H_a} \vec{r}_{H_a} + c_{H_b} \vec{r}_{H_b}, \tag{D.6}$$

with

$$c_O = \frac{m_O}{m_O + m_P + m_{H_a} + m_{H_b}},$$
$$c_P = \frac{m_P}{m_O + m_P + m_{H_a} + m_{H_b}},$$
$$c_{H_a} = \frac{m_{H_a}}{m_O + m_P + m_{H_a} + m_{H_b}},$$
$$c_{H_b} = \frac{m_{H_b}}{m_O + m_P + m_{H_a} + m_{H_b}},$$

$$\tag{D.7}$$

and, again in terms of the "old" coordinates

$$\vec{r}_O = \begin{pmatrix} 1.30 \\ 0.00 \\ -0.71 \end{pmatrix}, \tag{D.8}$$

$$\vec{r}_P = \begin{pmatrix} 0.00 \\ 0.00 \\ 0.00 \end{pmatrix}, \tag{D.9}$$

$$\vec{r}_{H_a} = \begin{pmatrix} -0.84 \\ 1.09 \\ -0.24 \end{pmatrix}, \tag{D.10}$$

$$\vec{r}_{H_b} = \begin{pmatrix} -0.84 \\ -1.09 \\ -0.24 \end{pmatrix}. \tag{D.11}$$

Using Eqns. (D.4) and (D.6), one can calculate $\vec{r}'$ as

$$\vec{r}' = \vec{r}_{c.o.m,SD} - \vec{r}_{c.o.m,H_2POSD}. \tag{D.12}$$

Equations (D.1) and (D.12) are then used to calculate the angle θ'

$$\theta' = arc\,cos\left(\frac{\vec{r}' \cdot \vec{r}'_{SD}}{|\vec{r}'| \cdot |\vec{r}_{SD}|}\right) = 0.52\pi. \tag{D.13}$$

In the following, it is assumed that the angle θ' is fixed. Let the c.o.m of the (non-rotating) OPH_2 fragment be now the origin of the new coordinates, i.e. $\vec{r}'_{c.o.m,OPH_2} = \vec{0}$. Then the vectors $\vec{r}'_P$, $\vec{r}'_O$ and $\vec{r}'_{OP}$ can be calculated as shown in section D (in a_0) to be

$$\vec{r}'_P = \begin{pmatrix} 0.74 \\ 0.00 \\ 0.45 \end{pmatrix}, \tag{D.14}$$

$$\vec{r}'_O = \begin{pmatrix} -1.72 \\ 0.00 \\ -0.87 \end{pmatrix}, \tag{D.15}$$

$$\vec{r}'_{OP} = \begin{pmatrix} 2.46 \\ 0.00 \\ 1.32 \end{pmatrix}, \tag{D.16}$$

and

$$\vec{r}' = \vec{r}'_{c.o.m,SD} - \vec{r}'_{c.o.m,OPH_2} = \vec{r}'_{c.o.m,SD} = c_D\vec{r}'_D + c_S\vec{r}'_S. \tag{D.17}$$

Also

$$\vec{r}'_{SD} = \vec{r}'_D - \vec{r}'_S. \tag{D.18}$$

From the matrix representation of eqns. (D.17) and (D.18)

$$\begin{pmatrix} \vec{r}' \\ \vec{r}'_{SD} \end{pmatrix} = \begin{pmatrix} c_D & c_S \\ 1 & -1 \end{pmatrix} \begin{pmatrix} \vec{r}'_D \\ \vec{r}'_S \end{pmatrix}, \tag{D.19}$$

one can obtain

$$\begin{pmatrix} \vec{r}'_D \\ \vec{r}'_S \end{pmatrix} = \begin{pmatrix} 1 & c_S \\ 1 & -c_D \end{pmatrix} \begin{pmatrix} \vec{r}' \\ \vec{r}'_{SD} \end{pmatrix}$$

$$= \begin{pmatrix} \left\{ \begin{pmatrix} 0 \\ 0 \\ \vec{r}' \end{pmatrix} + c_S \vec{r}'_{SD} \begin{pmatrix} sin\theta' cos\phi' \\ sin\theta' sin\phi' \\ cos\theta' \end{pmatrix} \right\} \\ \left\{ \begin{pmatrix} 0 \\ 0 \\ \vec{r}' \end{pmatrix} - c_D \vec{r}'_{SD} \begin{pmatrix} sin\theta' cos\phi' \\ sin\theta' sin\phi' \\ cos\theta' \end{pmatrix} \right\} \end{pmatrix}, \tag{D.20}$$

where θ' is the polar angle defined by the Z-axis and the $\vec{r}'_{SD}$, fixed to $0.52\,\pi$, see Eq. D.13. The bond length, $|\vec{r}'_{SD}|$, is fixed to 2.53 a_0. Eqns. (D.14) and (D.20) allow to calculate

$$\vec{r}'_{PS} = \vec{r}'_S - \vec{r}'_P \tag{D.21}$$

and finally to express r in terms of r' and ϕ',

$$r = r_{SP} = |\vec{r}'_S - \vec{r}'_P|$$
$$= \sqrt{(\vec{r}'_{S_X} - \vec{r}'_{P_X})^2 + (\vec{r}'_{S_Y} - \vec{r}'_{P_Y})^2 + (\vec{r}'_{S_Z} - \vec{r}'_{P_Z})^2}. \tag{D.22}$$

Next, an expression for ϕ in terms of r' and ϕ' is derived. For this purpose, one notes from Fig. D.2 that ϕ is the angle between the OPS- and DPS-planes, i.e. ϕ is also the angle between two vectors $\vec{a}'$ and $\vec{b}'$ perpendicular to these planes,

$$\phi = arc\ cos \left(\frac{\vec{a}' \cdot \vec{b}'}{|\vec{a}'| \cdot |\vec{b}'|} \right). \tag{D.23}$$

Using eqns. (D.16), (D.18) and (D.21) one obtains

$$\vec{a}' = \frac{\vec{r}'_{OP} \times \vec{r}'_{PS}}{|\vec{r}'_{OP} \times \vec{r}'_{PS}|}, \tag{D.24}$$

and

$$\vec{b}' = \frac{\vec{r}'_{PS} \times \vec{r}'_{SD}}{|\vec{r}'_{PS} \times \vec{r}'_{SD}|}. \tag{D.25}$$
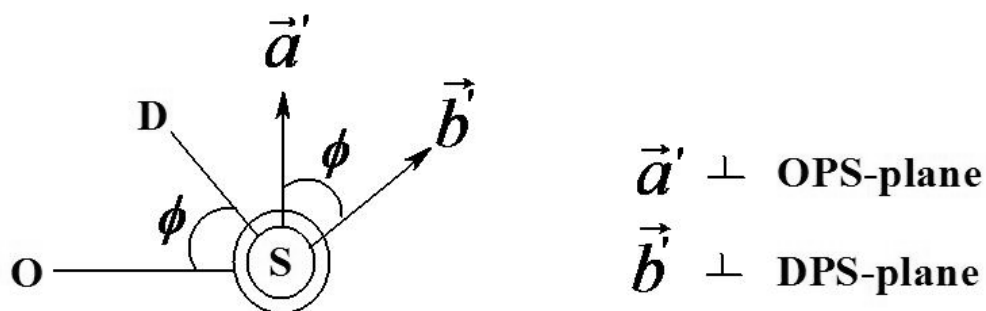
Figure D.2: The torsional angle is represented as the angle between OPS- and DPS-planes as well as the angle between the two vectors $\vec{a}'$ and $\vec{b}'$ perpendicular to these planes.

Equations (D.17), (D.20) and (D.23)-(D.25) then allow to calculate ϕ in terms of r' and ϕ'.

This transformation from r and ϕ to corresponding values of r' and ϕ' yields e.g. the potential energy surface in the new coordinates:

$$V'(r', \phi') = V(r(r', \phi'), \phi(r', \phi')),$$
(D.26)

The transformed potential $V'(r', \phi')$ is then splined on a grid of ca. 74700 points (415×180), which is written in a grid representation as:

$$V'(r_i', \phi_j') = V(r\{r_i', \phi_j'\}, \phi\{r_i', \phi_j'\}).$$
(D.27)

Appendix E

Calculation of the reduced moment of inertia of H_2POSD.

In this appendix, the reduced moment of inertia I'_{SD,OPH_2} (Eqn. (4.4)), which appears in the 2D-Hamiltonian is calculated. As mentioned in the previous section the origin is considered to be the center of mass of the fragment H_2PO, see Fig. D.1. The acute angles created by the Z-axis and the line connecting each atom with the corresponding center of mass, as shown in Fig. E.1,
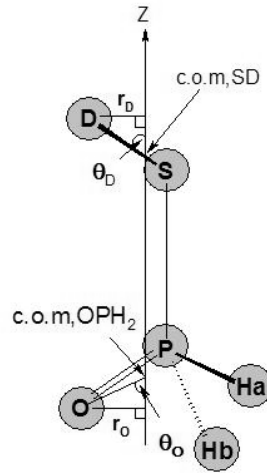

Figure E.1: Scheme representing the different θ's that are used to calculate the moment of inertia for the center of masses of the two fragments SD and H_2PO that is exploited in the 2D-Hamiltonian.

can be calculated as:

$$\theta_D = arc\ cos\left(\frac{\vec{r}_D \cdot \vec{r}_{c.o.m,SD}}{|\vec{r}_D| \cdot |\vec{r}_{c.o.m,SD}|}\right),\qquad\text{(E.1)}$$

$$\theta_S = 180 - arc\ cos\left(\frac{\vec{r}_S \cdot \vec{r}_{c.o.m,SD}}{|\vec{r}_S| \cdot |\vec{r}_{c.o.m,SD}|}\right), \qquad (E.2)$$

$$\theta_P = arc\ cos\left(\frac{\vec{r}_P \cdot \vec{r}_{c.o.m,OPH_2}}{|\vec{r}_P| \cdot |\vec{r}_{c.o.m,OPH_2}|}\right), \qquad (E.3)$$

$$\theta_O = 180 - arc\ cos\left(\frac{\vec{r}_O \cdot \vec{r}_{c.o.m,OPH_2}}{|\vec{r}_O| \cdot |\vec{r}_{c.o.m,OPH_2}|}\right), \qquad (E.4)$$

and

$$\theta_{H_{a/b}} = 180 - arc\ cos\left(\frac{\vec{r}_{H_{a/b}} \cdot \vec{r}_{c.o.m,OPH_2}}{|\vec{r}_{H_{a/b}}| \cdot |\vec{r}_{c.o.m,OPH_2}|}\right). \qquad (E.5)$$

The normal line from each atom to the Z-axis are defined as

$$r_D = c_S \cdot r_{SD} \cdot sin(\theta_D), \qquad (E.6)$$

$$r_S = c_D \cdot r_{SD} \cdot sin(\theta_S), \qquad (E.7)$$

$$r_P = |\vec{P}| \cdot sin(\theta_P), \qquad (E.8)$$

$$r_O = |\vec{O}| \cdot sin(\theta_O), \qquad (E.9)$$

and

$$r_{H_{a/b}} = |\vec{H_{a/b}}| \cdot sin(\theta_{H_{a/b}}). \qquad (E.10)$$

Using Eqns. (E.6) and (E.7), one can calculate the moment of inertia of SD fragment

$$I_{SD} = m_D r_D^2 + m_S r_S^2. \qquad (E.11)$$

Equations (E.8) to (E.10) allows us to calculate the moment of inertia of the fragment H_2PO

$$I_{OPH_2} = m_O r_O^2 + m_P r_P^2 + m_{H_a} r_{H_a}^2 + m_{H_b} r_{H_b}^2. \qquad (E.12)$$

Therefore, the reduced moment of inertia can be calculated as

$$I'_{SD,OPH_2} = \frac{I_{SD} I_{OPH_2}}{I_{SD} + I_{OPH_2}}. \qquad (E.13)$$