Supporting Information

A protocol for the investigation of the IVR problem: The isomerization of HONO as a case of study

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1. Construction of the Potential Energy Surface.

The procedure used to construct the Potential Energy Surface as a function of the normal coordinates of vibration, exemplified in Figure S1, is as follows:

1. Calculation of the Intrinsic Reaction Coordinate (IRC): This step can be performed easily using any standard methodology in the commonly used computational chemistry software.
2. Extension of the IRC beyond the minimum points: As described in the main text, at the minimum point, the IRC coincides with one of the molecule normal modes (for HONO, the ν_{OH} mode). The identification of such normal mode, Q_1, is straightforward. The molecular geometry is displaced in the Q_1 direction in small steps (0.2 Å). The normal modes are recalculated at each new point and the molecule is again displaced in the Q_1 direction. This procedure is repeated until a point with an energy about that of the Transition State is found.
3. Calculation of the projected normal modes along the IRC: for each point of the curve obtained in the previous step, a projected frequency calculation is performed, and the molecular geometry is displaced in the positive and negative directions of a given normal coordinate, Q_i.
4. Recalculate the normal coordinates for each new point along Q_i: The normal coordinates are recalculated in each point of Q_i, and a new Q_i vector is found. The molecular geometry is displaced in the new Q_2 vector's direction, and the process is repeated.

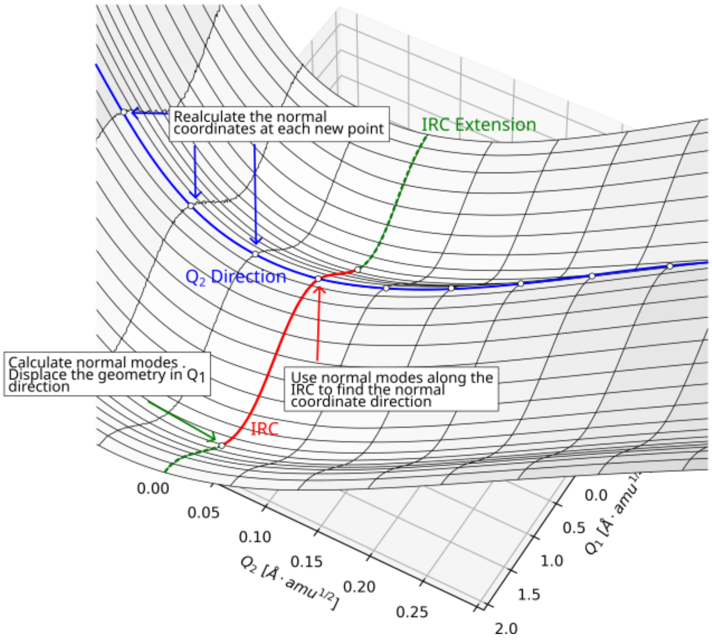

Figure S1: Procedure used to obtain the PES as a function of normal coordinates.

2. PES as a function of Q_1 and Q_3.

The contour plot for the PES in terms of Q_1 and Q_3 for HONO is given in **Figure S2** and the respective gradient vector field is shown in **Figure S3.**

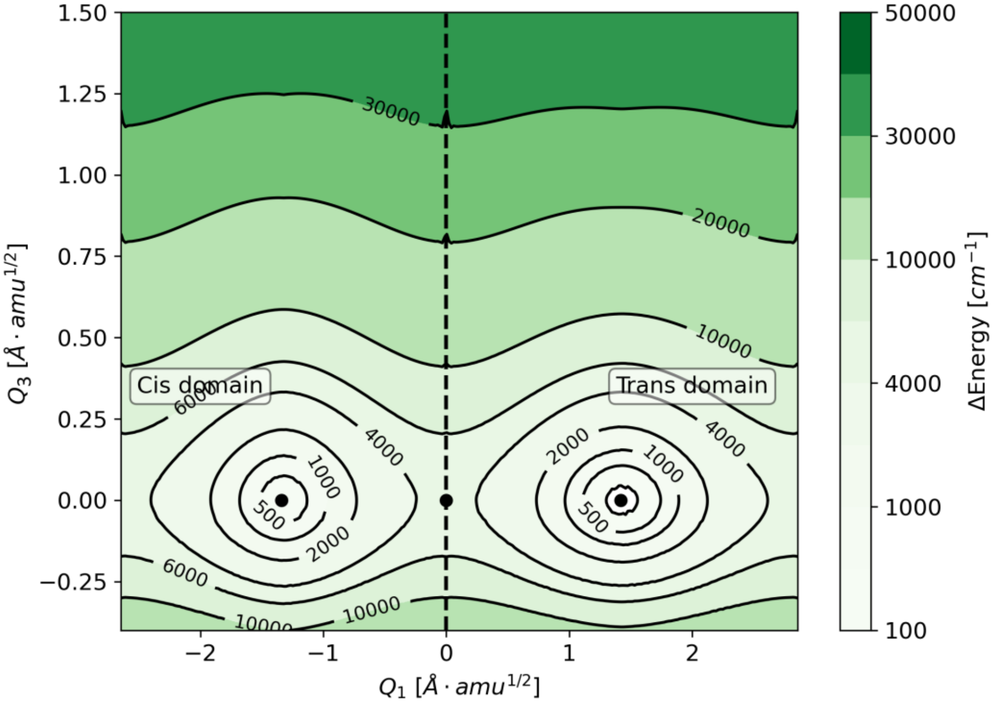

***Figure S2**: Potential energy surface V(Q_1, Q_3).*

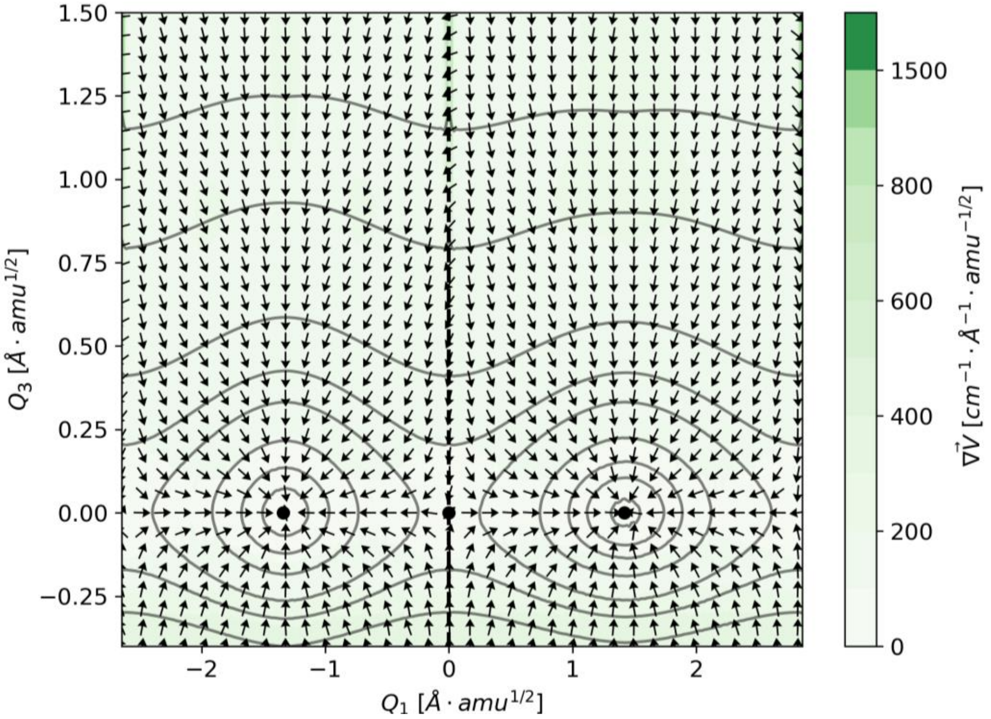

Figure S3: *Gradient vector field of $V(Q_1, Q_3)$. The three critical points, i.e. the cis minimum, the TSS and the trans minimum, are marked by black dots. The dotted line vertical line divides the surface into two domains, one for each isomer of HONO.*

3. Eigenspace of H(Q_1, Q_3).

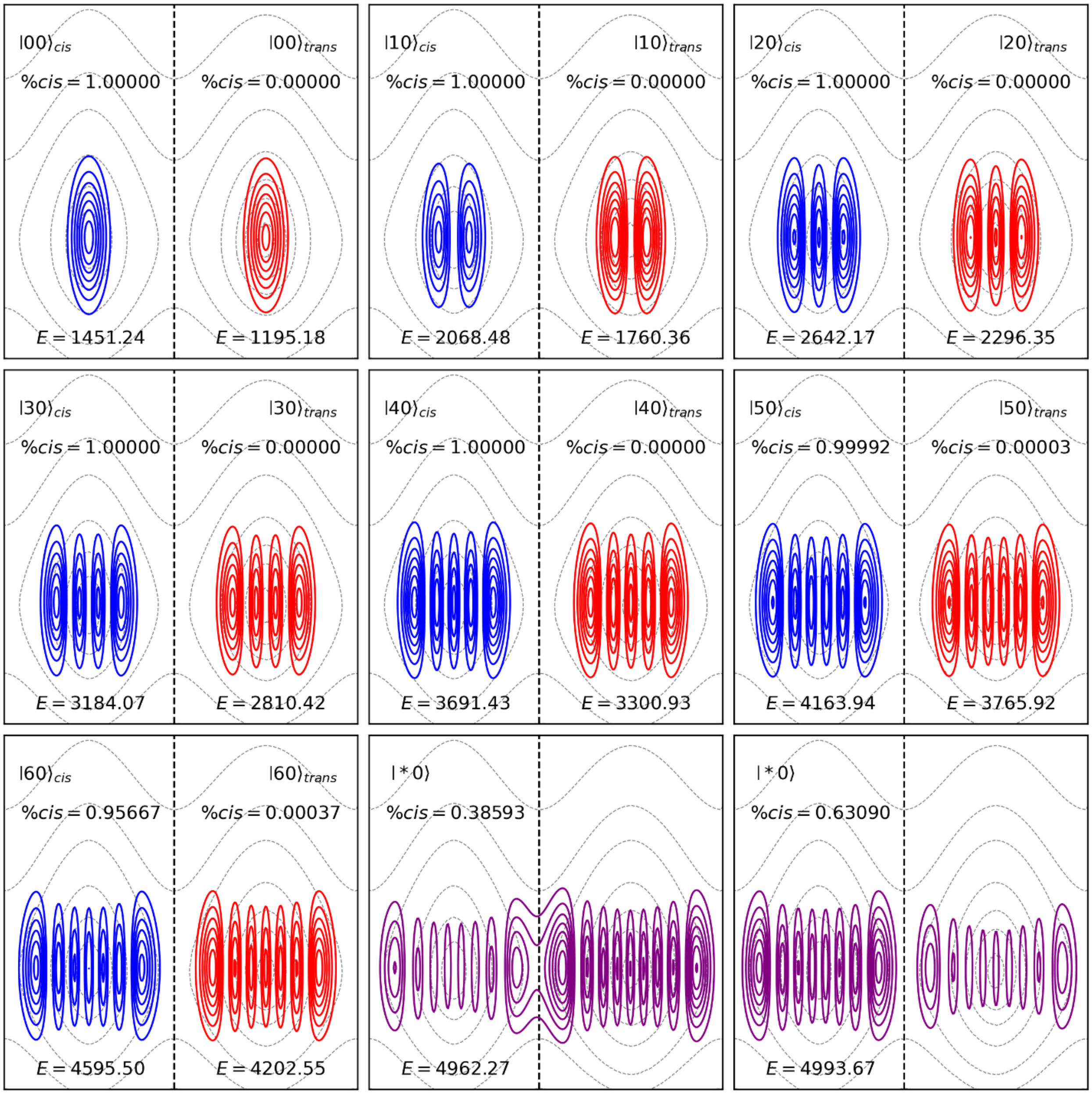

***Figure S4**: Probability density functions $(\Psi^{*}\Psi)$ $(|Q_1\ Q_3>)$ for the torsion mode of cis and trans isomers of HONO. High excited eigenstates become delocalized between the cis and trans domains.*

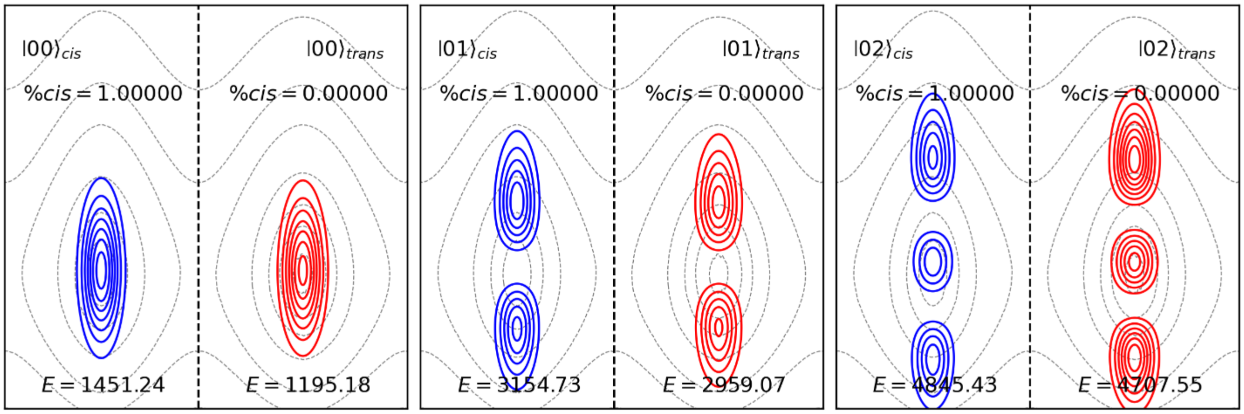

Figure S5: *Probability density functions* ($\Psi^*\Psi$) *(*$|Q_1\ Q_3>$*) for the* □$_{\mathrm{N=O}}$ *mode of cis and trans isomers of HONO. High excited eigenstates become delocalized between the cis and trans domains.*

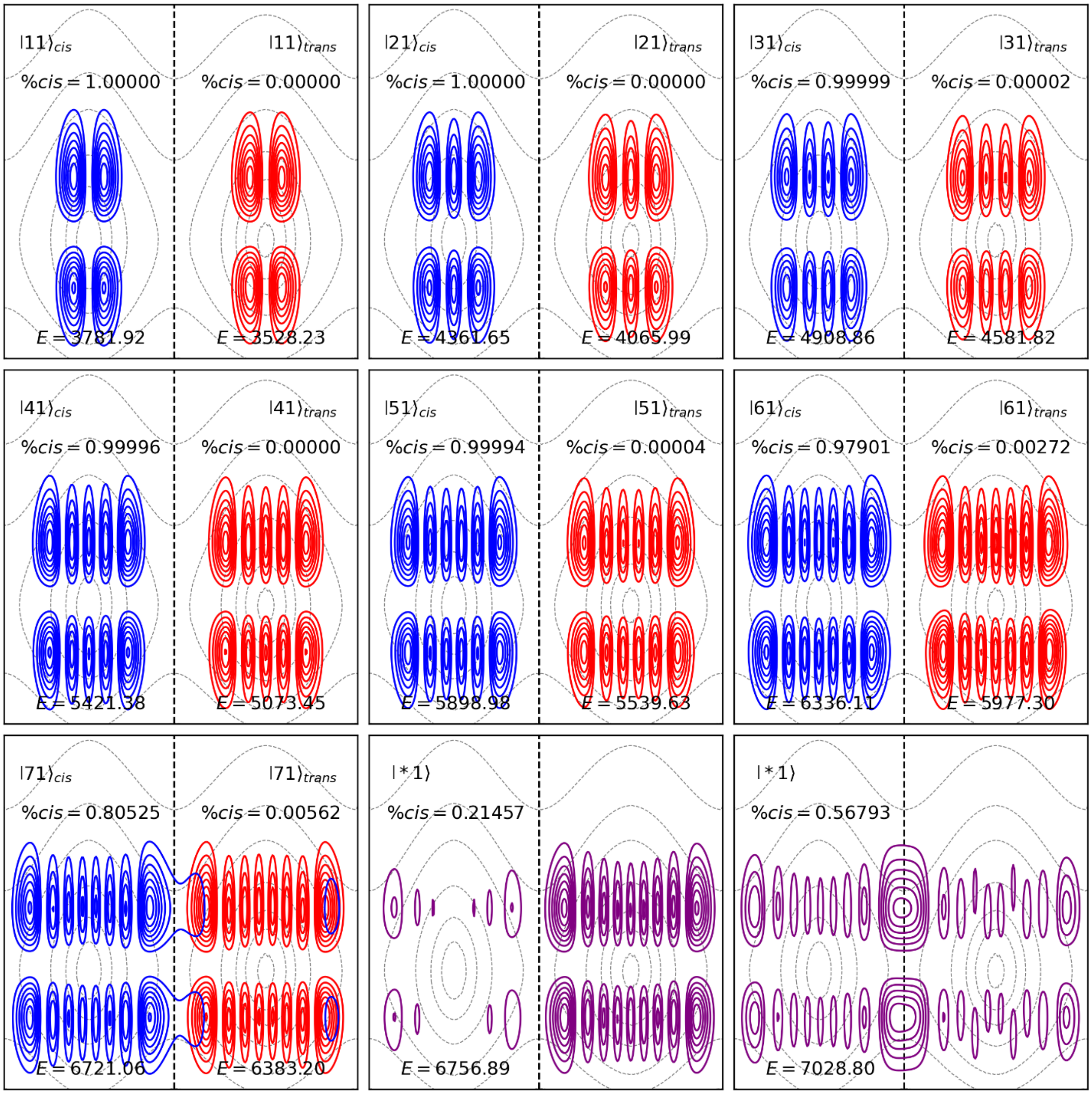

***Figure S6**: Probability density functions ($\Psi^*\Psi$) ($|Q_1\ Q_3>$) for the combination of torsion and* □$_{\text{N=O}}$ *mode of cis and trans isomers of HONO. High excited eigenstates become delocalized between the cis and trans domains.*

4. Dipole operator for Q_1 and Q_3.

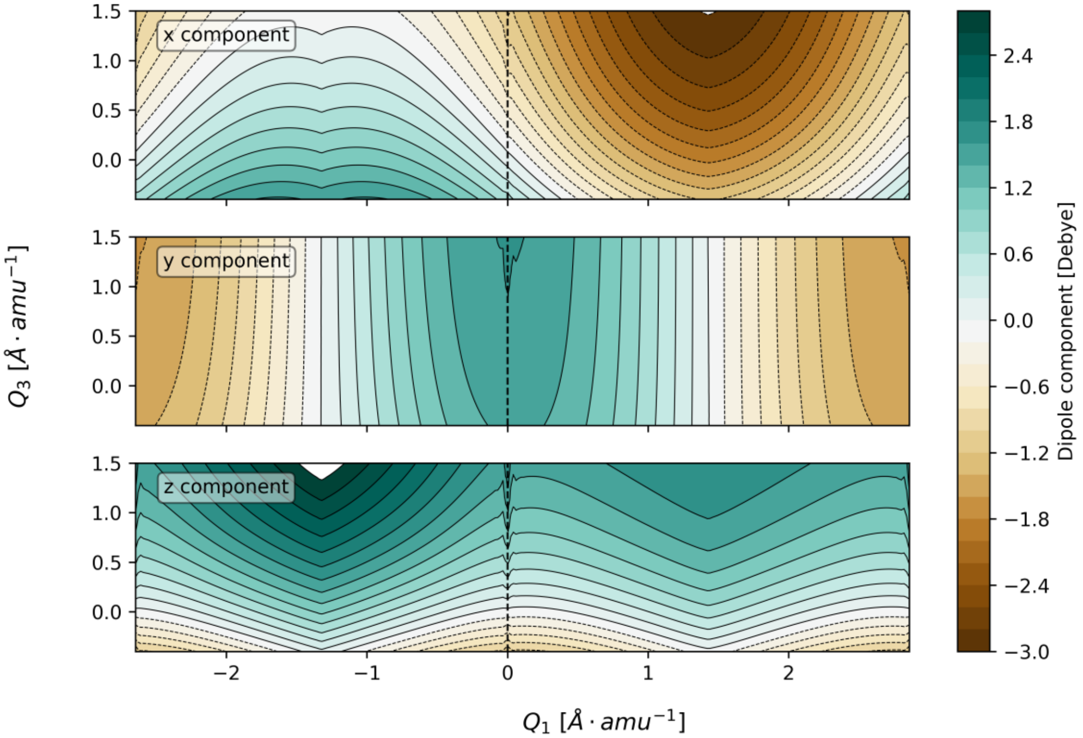

Figure S7: *Contour plots of the x, y and z components of the molecular electric dipole moment as a function of the normal coordinate Q_1 and Q_3. The dotted line divides the plots into cis (left) and \trans domains.*

5. The Relative Energy Gradient (REG) Analysis.

The REG method was developed by Thacker and Popelier [*J. C. R. Thacker and P. L. A. Popelier, "The ANANKE relative energy gradient (REG) method to automate IQA analysis over configurational change," Theor. Chem. Acc., vol. 136, no. 7, p. 86, Jul. 2017, doi: 10.1007/s00214-017-2113-z.*] and consists of measuring the ratio between the derivatives of each IQA contribution and the total energy variation over a reaction coordinate. This methodology has two objectives:

1. Determine the subset of energy contributions that preserves the chemical insights and best describes the overall profile of the total energy over any coordinate changes.
2. Extract chemical insight from the partitioned total energy.

The REG coefficient (m_{reg}) is given by:

$$m_{reg,i} = \frac{n\sum_{s=1}^{n}\left(E_{total}(s)E_i(s)\right) - \sum_{s=1}^{n}E_{total}(s)\sum_{s=1}^{n}E_i(s)}{n\sum_{s=1}^{n}E_{total}^2(s) - \left(\sum_{s=1}^{n}E_{total}(s)\right)^2}$$

where n is the number of points in the PES and s is the reaction coordinate. The greater the value of $m_{reg,i}$ the more important the contribution E_i to the overall behavior of the potential energy surface. Results for the REG analysis of *cis* and *trans* HONO are presented in Table S1. The PES was divided into two segments, going from the *cis* minimum to the transition state and from the transition state to the *trans* minimum. The atoms were numbered following the scheme: $H_{(1)}$-$O_{(2)}$-$N_{(3)}$=$O_{(4)}$.

Table S1: REG coefficients (m_{reg}) and correlation coefficient (R) for IQA contributions of the *cis* → *trans* isomerization.

IQA term	***cis* → TS**		**TS → *trans***	
	$m_{reg,i}$	**R**	$m_{reg,i}$	**R**
$V_{xc}^{N_{(3)},O_{(4)}}$	3.49	0.98	2.40	0.98
$E_{intra}^{O_{(4)}}$	1.47	1.00	1.14	0.99
$E_{intra}^{N_{(3)}}$	1.02	1.00	1.09	1.00
$V_{cl}^{H_{(1)},O_{(4)}}$	0.73	0.99	0.47	0.93
$V_{XC}^{O_{(2)},O_{(4)}}$	0.32	0.99	0.34	0.99
$V_{cl}^{H_{(1)},N_{(3)}}$	-0.57	-0.97	-0.41	-0.98
$V_{cl}^{N_{(3)},O_{(4)}}$	-0.96	-1.00	-0.61	-0.98
$V_{cl}^{H_{(1)},O_{(2)}}$	-1.04	-0.99	-1.00	-0.98
$V_{cl}^{O_{(2)},N_{(3)}}$	-1.31	-0.99	-1.12	-1.00
$V_{xc}^{N_{(3)},O_{(4)}}$	-1.80	-0.99	-1.29	-1.00

6. Dimensional analysis of WKB equation.

We know that the exponential factor of Eq. 8

$$\gamma = \frac{1}{\hbar}\int \sqrt{2V'(Q) - E'}\mathrm{d}Q$$

is a non-dimensional quantity, there which is easily verified since ħ has units of [g][m]^{2}[s]$^{-1}$ which are equal to the units resulting from the integral of momentum. Notice that both *V '(Q)* and *E'* are given in [J].

The conversion from [J] to [cm]$^{-1}$ is done by dividing *V '(Q)* and *E'* by the Plank constant times the speed of light, hc. That is: $V(Q) = V'(Q)/hc$ and $E = E'/hc$, with *V(Q)* and E given in [cm]$^{-1}$. Therefore, one can write:

$$\gamma = \frac{\sqrt{hc}}{\hbar}\int \sqrt{2\frac{V'(Q)}{hc} - \frac{E'}{hc}}\mathrm{d}Q$$

which results in

$$\gamma = \frac{2\pi c^{\frac{1}{2}}}{h^{\frac{1}{2}}}\int \sqrt{2V(Q) - E}\mathrm{d}Q$$