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Supporting Information for Molecular Dynamics Simulations Predict an Accelerated Dissociation of H_2CO_3 at the Air-Water Interface

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Metadynamics

We employed metadynamics and CPMD to calculate the dissociation energy barrier of H_2CO_3 for configuration B2. The metadynamics calculations were carried out using the PLUMED package[1] (version 1.3.0) and the CPMD package[2] (version 3.15.1). We used the direct Lagrangian version of metadynamics,[3] in which the Lagrangian, L_{MTD}, has the following form:

$$L_{MTD} = L_{CP} - V(t,s), \tag{1}$$

where L_{CP} is the CPMD Lagrangian and $V(t,s)$ is the history-dependent biasing potential acting on the collective variables (CVs), which is given by

$$V(t,s) = W \sum_i \exp\{-\frac{(s-s^i)^2}{2(\Delta s')^2}\}. \tag{2}$$

In the above equation, W is the Gaussian height, $s = \{s_1, s_2, \ldots\}$ is the vector of CVs, s^i is a vector of the values of the CVs at metadynamics step i, and $\Delta s'$ is the Gaussian width. When all of the potential wells have been filled with these Gaussians, the total biasing potential added gives an estimate of the free energy as a function of the fictitious particle coordinates, i.e.,

$$F(s) = -\lim_{t\to\infty} V(t,s). \tag{3}$$

Parameters

The parameters associated with the various CVs used in our metadynamics simulations are summarized in the following table:

	CV_1	CV_2
Gaussian height, W (hartee)	0.0002	0.0002
Gaussian width, $\Delta s'$	0.02	0.05
Metadynamics time step, Δt (a.u.)	200	200
p	6	8
q	24	24
d_0 (Å)	1.60	1.20
λ	-	20

Table 1: Metadynamics parameters for the dissociation of H_2CO_3.

Error estimation

We estimated an error bar of 1.5 kcal/mol in our metadynamics simulations using the procedure given in Refs.[4] and.[5] It should be noted that the size of the error bars may be reduced by decreasing the height of the Gaussian hills and the frequency at which they are added, at the cost of increasing the simulation time. Some possible sources of error in these types of simulations have already been discussed in Ref.[6]

References

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