Electronic Supplementary Material (ESI) for Chemical Science.
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Supporting Information

One-step electric-field driven methane and formaldehyde synthesis from liquid methanol

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(Dated: September 23, 2016)

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I. *Ab initio* molecular dynamics calculations

We used the plane-wave/pseudopotentials software package Quantum ESPRESSO [1], based on the Car-Parrinello (CP) approach [2], to perform *ab initio* molecular dynamics (AIMD) of a sample of methanol molecules under the action of intense electric fields applied along a given direction (corresponding to the z axis). The implementation of an external field in numerical codes based on density functional theory (DFT) can be achieved by exploiting the modern theory of polarization and Berry's phases [3–5] (see, *e.g.*, Ref. [6]). Our sample contained 32 CH_3OH molecules (*i.e.*, 192 atoms) arranged in a cubic cell with side parameter $a = 12.93$ Å, so as to reproduce the experimental density of 0.79 g/cm^3 at about 300 K. As usual, the structure was replicated in space by using periodic boundary conditions.

We carried out *ab initio* simulations at the nominal temperature of 300 K. We gradually increased the intensity of the electric field with a step increment of about 0.05 V/Å from zero up to a maximum of 0.60 V/Å. In the zero-field case we executed a dynamics of almost 6 ps whereas, for each other value of the field intensity, we ran the dynamics for at least 2 ps, thus cumulating a total simulation time of about 35 ps. Moreover, once the chemical reaction leading to the production of formaldehyde, methane, and water occurred, a rough stability analysis of the formed species was carried out. Indeed, in a parallel CP molecular dynamics simulation, the electric field has been switched off and the dynamics of the system has been followed for a time longer than 20 ps as pointed out in the main text.

The fictitious electronic mass was set to a value of 300 a.u., with a cutoff energy of 35 Rydberg (Ry) and a cutoff energy for the charge density of 280 Ry, which allowed us to adopt a timestep of 0.12 fs. With such cutoff values the sample is described in a realistic way since the core electronic interaction is being depicted through ultrasoft pseudopotentials (USPP). As for exchange and correlation effects, we adopted the Perdew-Burke-Ernzerhof (PBE) functional [7], which belongs to the generalized gradient approximation (GGA). The dynamics of ions was simulated classically within a constant number, volume, and temperature (NVT) ensemble, using the Verlet algorithm and a Nosé-Hoover thermostat set at a frequency of 13.5 THz.

II. Density Functional Theory calculations

The Wannier centers calculation is based on the evaluation of the Maximally Localised Wannier Functions (MLWF) [8, 9] as implemented in Quantum ESPRESSO by means of the Wannier90 [10] code. In particular, after a standard self-consistent field (SCF) calculation conducted at the field strength that render barrierless the reaction (*i.e.*, 0.55 V/Å), a band calculation at the Γ point has been carried out in order to obtain the Bloch states. Because of the usage of USPP in order mimic the core electronic interaction, our system is characterized by 224 bands. This value corresponds also to the number of the MLWFs and thus to the number of the Wannier centers. The used formalism [10] works by minimising the total spread of the MLWF in the real space and this is done in the space of unitary matrices that describe rotations of the Bloch states. As a consequence, the kind of calculation implemented in Wannier90 is independent of the basis set used in the underlying band calculation [10].

In order to better visualize and quantify the solvent effects in screening the bare action of the applied electric field on the reactant atoms of the reaction, a Löwdin population analysis has been also performed. Four cases have been taken into account: two of them refer to the counterions in absence of the field, in the gas phase and with the explicit solvent (Fig. S1-a/c), whereas the same two systems have been also considered in the presence of the field that realizes the reaction in our AIMD simulation (Fig. S1-b/d). The coloration of the molecules shown in Fig. S1 reveals that the field-induced polarization is strongly screened by the solvent. The valence electron populations present on each atomic species in the reactant ions are also listed in Table S1. In the zero-field case the methoxide oxygen is more electrically charged in the liquid phase than in the gas, and the methyloxonium carbon is more positive in presence of the explicit solvent than it is in the respective gas phase. In addition to these evidences, the most interesting clues concern the field-induced polarization effects. In fact, in presence of the external field the two reactants counterions show a huge polarization when compared to the gas. Mainly because of the orientation of the field, the electronegative head (*i.e.*, the oxygen) of the methoxide ion has in gas phase a considerable lower electron population than that of the unperturbed case, *i.e.*, 5.75 vs. 6.51, respectively. For the same reason, on the other hand, the carbon atom of the $CH_3OH_2^+$ species in gas phase shows a sensibly larger electron population with respect to that in the zero-field case, *i.e.*, 4.51 vs. 4.24, respectively. By explicitly taking into account the solvent effects, the

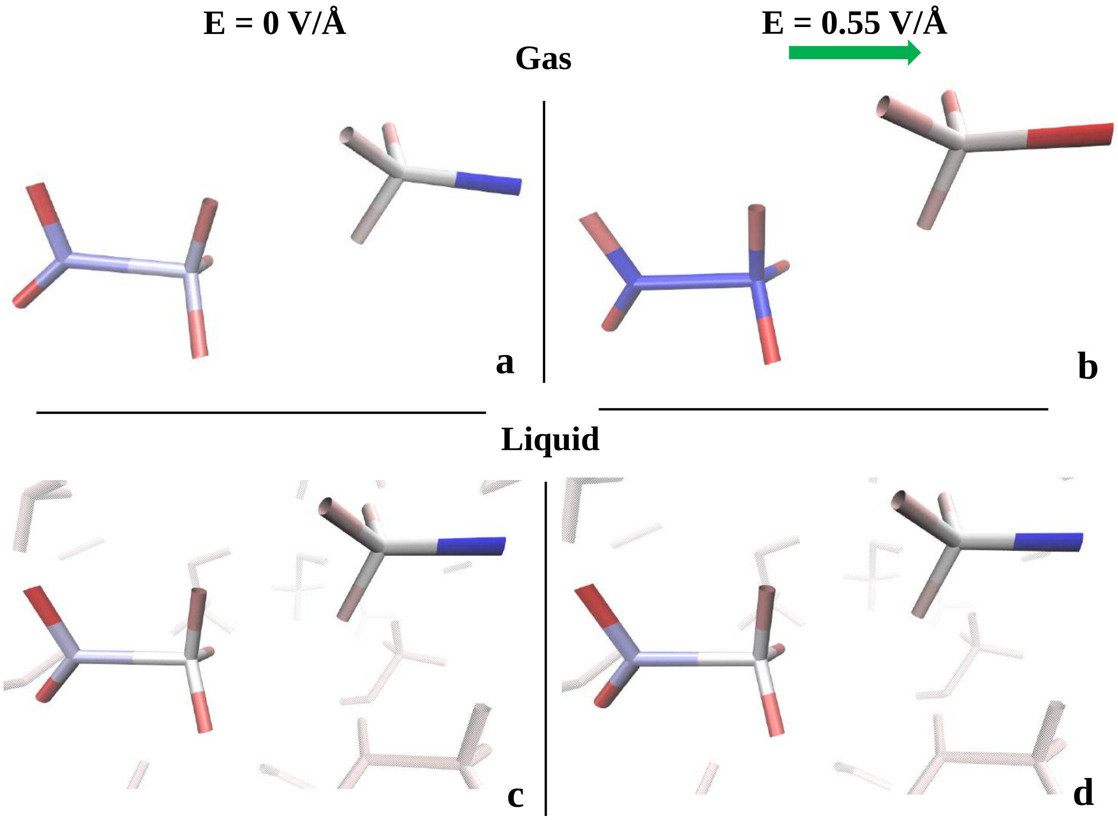

FIG. 1. Löwdin population analysis of $CH_3OH_2{}^+$ and CH_3O^- in the gas phase (a,b) and in the liquid phase (c,d) without (a,c) and with an external electric field at a strength of 0.55 V/Å (b,d). The green arrow shows the field orientation. The coloring method follows the atomic electron populations shown in Table S1. In particular, here are plotted the atomic population values relative to the expected ideal atomic valence population (*i.e.*, 6 for the oxygen, 4 for the carbon, and 1 for the hydrogen atoms). Deep blue coloration indicates a strong positive value with respect to the expected ideal valence population whereas a deep red coloration illustrates a strong negative value with respect to the expected valence population.

situation dramatically changes. The results described in Tab. S1 and better visualized in Fig. S1 show indeed that the field-induced polarization effects manifest in the gas phase are no longer detectable in the liquid case. All the atomic electron populations of methyloxonium and methoxide ions are almost independent of the application of the field, suggesting that local solvent effects are extremely significant in assisting the investigated reaction. The Löwdin population analysis has been performed by projecting the wavefunctions onto their standard atomic basis sets. By using a simple gaussian broadening, the projected density of states and the Löwdin populations have been thus evaluated.

By considering an ideal isolated gas phase system composed by $CH_3OH_2{}^+$ and CH_3O^- without any electrical perturbation and at the same temperature of 300 K, another kind of analysis, which has not been reported in the main text, has been performed. Exploiting the

	E=0 V/Å				E=0.55 V/Å			
Atom	$\mathbf{CH_3OH_2{}^+}$		$\mathbf{CH_3O^-}$		$\mathbf{CH_3OH_2{}^+}$		$\mathbf{CH_3O^-}$	
	Gas	**Liq**	**Gas**	**Liq**	**Gas**	**Liq**	**Gas**	**Liq**
H_1	0.61	0.61			0.74	0.62		
H_2	0.63	0.65			0.83	0.65		
O	6.33	6.32	6.51	6.63	6.52	6.34	5.75	6.57
C	4.24	4.18	4.11	4.14	4.51	4.19	4.10	4.13
H_3	0.79	0.80	0.96	0.97	0.78	0.80	1.00	1.00
H_4	0.78	0.79	0.90	0.93	0.78	0.78	0.82	0.92
H_5	0.80	0.81	0.89	0.93	0.81	0.81	0.81	0.92

TABLE I. Löwdin atomic valence electron populations of the two reactants counterions (*i.e.*, methyloxonium and methoxide), in the gas (Gas) and in the liquid (Liq) phases both in presence and in absence of an external electric field. The rows corresponding to oxygen and carbon atoms have been highlighted since, in principle, the eventual field-induced polarization effects are more evident on these atomic sites. $H_{1,2}$ sites refer to the "alcoholic" hydrogen atoms of $CH_3OH_2{}^+$ whereas $H_{3,4,5}$ represent the methyl hydrogen atoms of the latter and of CH_3O^-.

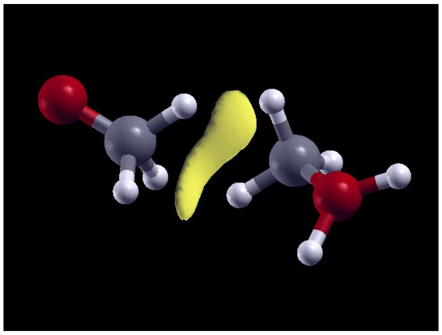

FIG. 2. NCI present between the two local reactants in the gas phase just before the formation of formaldehyde, methane, and water in a collateral numerical experiment. The isovalue chosen in order to visualize the NCI surface is 0.4 but any value between 0.3 and 0.6 allow for a correct visualization of them.

same molecular geometry shown in the upper panel of Fig. S1, the intermolecular interactions between the local reactants have been evaluated through the non covalent interactions (NCI) scheme [11], as shown in Fig. S2. Strong NCI arise when the two counterions are close to each other as can be argued also by the strong polarized state in which they lie (see the Löwdin population analysis). This means that a not negligible force acts just in the portion of space which lies in the middle of the two species. Indeed, by performing both CP [2] and Born-Oppenheimer molecular dynamics of the two ions in the gas phase starting from this configuration, it has been shown that the reaction spontaneously proceeds without any external electric field.

III. Metadynamics calculations

To the aim of investigating reaction (1) of the main text, a series of Car-Parrinello simulations have been carried out in the liquid phase in conjunction with a very recently presented path-Collective Variables (path-CV) metadynamics (MetD) approach [12], as recently implemented in the PLUMED-1.3 software [13]. This formalism employs the matrices of coordination numbers in order to define a given molecular state and, as usual for the path-CV [14], exploits two collective variables – namely, S and Z – on which the free energy uniquely relies upon. The former variable represents the progress along the chemical transformation and the latter the distance from an ideal pathway. Although this method represents an extremely powerful tool in sampling the CV space and thus in accurately reproducing the free energy landscape of very simple chemical reactions, when a relatively complex system (such as methanol) is tackled, MetD simulations based on the path-CV show difficulties in achieving by itself the required statistical convergence. This means that if one is interested only in the location of the relevant free energy basins of the reaction, the exclusive employment of MetD is sufficient whereas, when an accurate estimation of the free energy is desired, other techniques such as Umbrella Sampling (US) [15] can be suitably exploited in a complementary fashion.

During the preliminary MetD calculations by employing the method proposed in Ref. [12], the following parameters have been adopted for the coordination function (see Eq. 3 in Ref. [12]): $N = 6$, $M = 12$, $R^0_{SS'} = 1.8$ Å for $S, S' =$ C,O, 1.5 Å for $S =$ C,O, $S' =$ H, and 1.4 Å for $S = S' =$ H. We chose the parameter λ such that $\lambda D(R_k, R_{k,k'}) \sim 2.3$. The MetD potential was composed of Gaussians with widths $\sigma_S = 0.02$ and $\sigma_Z = 0.1$ and initial height 6 kcal·mol^{-1} deposed every 35 fs. We performed this calculation within the well-tempered scheme [16] with a bias factor equal to 53 kcal·mol^{-1}. Finally, in all simulations we restricted the maximum Z values explored by employing a semi-parabolic wall potential. Once the locations of the relevant minima on the free energy landscapes have been obtained within this approach, the final sampling on the CV space has been conducted via the US [15] technique. In particular, in the zero-field regime case, 74 parabolic potentials have been employed in order to fill and probe the CV space and, in some critical cases, also in conjunction with proper linear corrections to the functional form of the bias potential. These 74 independent biased simulations were recollected by means of the Weighted Histogram Analysis Method (WHAM) [17–20], which is capable to reconstruct the underlying free energy. The same protocol has been applied to the liquid phase reaction under the effect of a field strength of 0.30 V/Å. Here, perhaps, 87 independent US simulations have been necessary in order to fill the relevant CV space since the sampling in some tricky portions of it (*i.e.*, close to the transition state) required more rigid parabolic bias potentials.

Finally, in order to characterize the transition states both in presence of a field strength of 0.30 V/Å and in the metadynamics-driven reaction in the zero-field regime, a committor analysis [21] has been performed. By choosing dozens of structures that were considered as plausible candidates for being the transition state of each simulation, 40 unbiased trajectories of 200 fs each have been performed. We have identified a configuration as belonging to the transition state ensemble when it is committed to the reactants or products basin with a probability of $50 \pm 10\%$.

A. Metadynamics in the gas phase

A gas phase variant of reaction (1) has been also investigated by exploiting Born-Oppenheimer molecular dynamics joined with the previously described MetD protocol. Firstly, a well-tempered path-CV MetD approach [12] has been carried out. The chosen parameters are the same listed in the previous Section with the following exceptions. The bias factor has been set to 110 kcal·mol^{-1} whereas a deposition rate of the Gaussians equal to 50 fs has been imposed. The subsequent US calculations have been conducted by employing 50 parabolic potentials in the fieldless case and 23 in the presence of a field strength of 0.25 V/Å.

The solvent plays a central role in assisting the treated reaction. Generally speaking the interactions that characterize a bimolecular reaction in condensed phase are ultimately different with respect to the gas phase counterpart [22]. Indeed the molecules participating in a liquid phase reaction experience solute-solvent interactions which occur in the dozens femtosecond scale [23]. Moreover, as thoroughly highlighted in the main text, local intense fields carried by the ionic species in the solvent act as the catalyst of the reaction. Nevertheless, the mere study of the features characterizing the field-induced changes in the gas

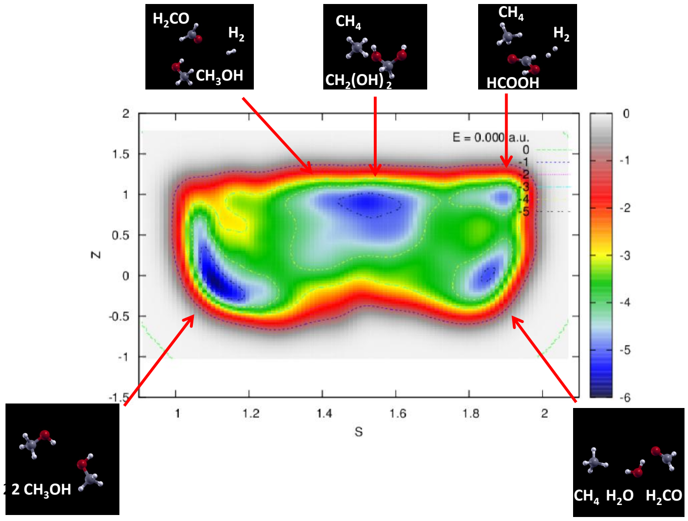

FIG. 3. "Exploratory" (not converged) FES projected onto the path-CV space of reaction 1 performed in the gas phase and in the zero-field regime. Three basins separate the reactants and the products. In ascending order of S (progress along the reaction path) we have: 1) reactants: two methanol molecules; 2) a methanol, a formaldehyde, and a hydrogen molecule; 3) a formaldehyde monohydrate and a methane molecule; 4) a methane, a hydrogen, and a formic acid molecule; 5) products: a formaldehdye, a methane, and a water molecule.

phase reactions is *per se* an interesting work station. A double series of calculations, which are not treated in the main text, are here presented: one performed at zero-field regime and one at 0.25 V/Å. This latter value has been chosen because the application of higher field intensities in the gas phase led to difficulties in the typical electronic minimization procedure. The first interesting evidence of the application of an external electric field in the gas is the induced manifest enhancement of the selectivity of the reaction. Indeed in absence of the field, an exploratory metadynamics simulation displays the presence of at least three different intermediate states between the reactants and the products basins. By following the reaction progress (*i.e.*, going in ascending order of the parameter S) the explored metastable basins that the sample explores are associated with formaldehyde, dihydrogen, and methanol at first, then with methane and formaldehyde monohydrate and, finally, with methane, dihydrogen, and formic acid (see Fig. S3).

When a field intensity of 0.25 V/Å is applied, only one of these three basins survives, as shown in Fig. S4. Hence the application of an external electric field to a gas phase methanol sample induces an enhancement of the selective character of the reaction under investigation.

The characterization of the overall shape of the FES can give information on the selectivity of the reaction but, in order to accurately evaluate the relative energetics and compare them also with the condensed phase results, a direct sampling of the relevant regions of the CV

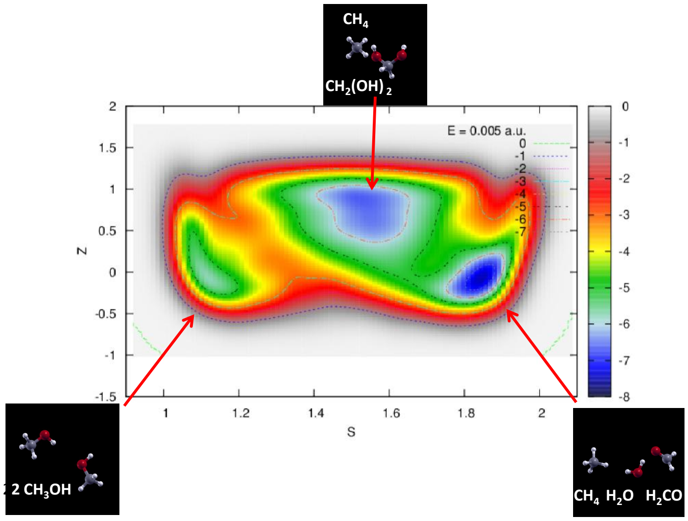

FIG. 4. “Exploratory” (not converged) FES of reaction 1 performed in the gas phase under the effect of a field strength of 0.25 V/Å. Two of the three basins previously observed in the absence of the electrical perturbation are not accessible under these circumstances. In ascending order of S we have: 1) reactants: two methanol molecules; 2) a formaldehyde monohydrate and a methane molecule; 3) products: a formaldehdye, a methane, and a water molecule.

space is mandatory. To this aim a series of Umbrella Sampling [15] simulations partially covering the reaction pathways have been carried out. By recollecting the independent data by means of the WHAM [17–20], estimates of the free energies have been obtained. The results are shown in Fig. S5. Again, the application of a moderate field accounts for the stabilization of the reaction products since the basin associated with them shows similar free energies to those of the reactants basin. Finally, it is straightforward to note that in both cases the involved free energies are sensibly higher than those characterizing the liquid phase reaction (see Fig. 3 and 4 in the main text). As pointed out in the main text, the solvent plays an extremely active role in assisting the investigated chemical reaction. Indeed even in absence of ionic molecular species in the solvent (see Fig. 3 in the main text) the reaction is favored with respect to its gas phase counterpart (Fig. S5, left).

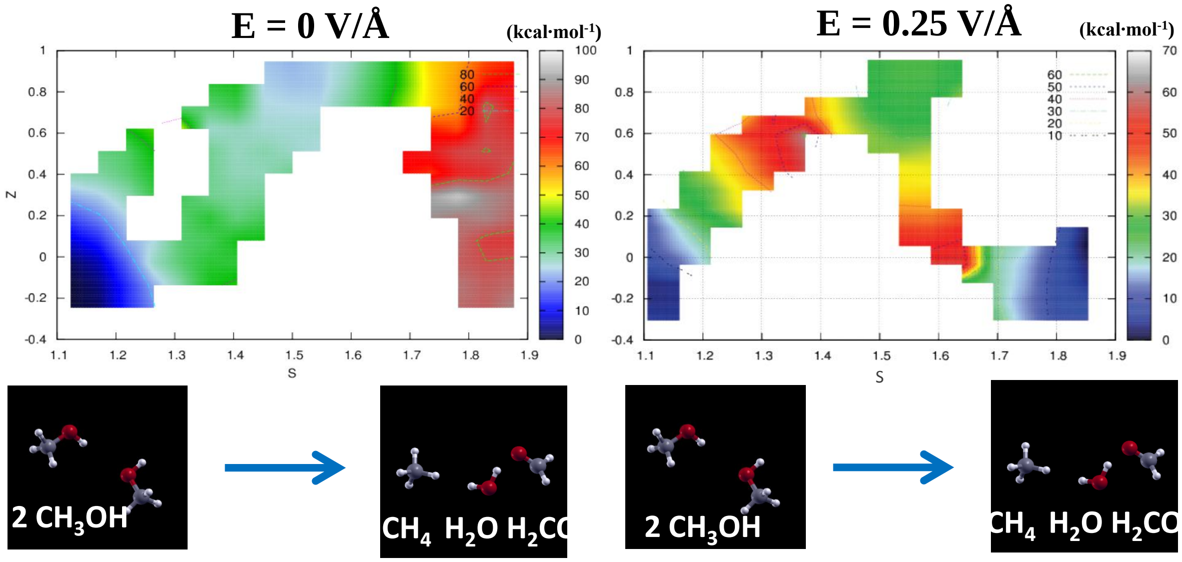

FIG. 5. FESs of the gas phase variant of reaction 1 in the zero-field regime (left) and in presence of a field strength 0.25 V/Å (right). The energy scale (depth) is in kcal·mol^{-1} whereas the S-axis and the Z-axis represent the progress along the reaction and a sort of distance from its ideal path, respectively. Low values of S characterize a system of two methanol molecules whereas high values of this parameter describe a sample composed by a formaldehyde, a methane, and a water molecule.

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