Molecular Simulations of Analyte Partitioning and Diffusion in Liquid Crystal Sensors: Supporting Information

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Calculation of LC order parameter and director vector

The P_2 order parameter is related to the average angle between a mesogen and the LC director vector, θ , by Equation S1:

$$P_2 = \frac{3}{2}\cos^2\theta - \frac{1}{2}$$
 (S1)

 θ can be calculated as the angle between the molecular axis of a mesogen, which we define as the principal axis corresponding to the largest moment of inertia, and the LC director vector. This calculation requires the definition of a director vector. In the bulk LC systems studied in the main text, the nematic phase is obtained by decreasing the temperature of an initially isotropic LC until a phase transition occurs. This procedure does not enforce any specific director vector for the resulting nematic phase (*i.e.*, it need not align with a Cartesian axis of the simulation box). This behavior is unlike the interfacial system, for which the director vector aligns with the *z*-direction during system relaxation due to the lateral interactions between mesogen molecules. We thus determine the director vector for the bulk phase systems using Q-tensor theory.¹ The Q tensor is defined in Equation S2:

$$Q_{\alpha\beta} = \langle \frac{3}{2} \cos \theta_{\alpha} \cos \theta_{\beta} - \frac{1}{2} \rangle \tag{S2}$$

 α and β indicate two Cartesian directions and θ_{α} and θ_{β} are the angles between the molecular axis and the α and β directions. The ensemble average indicates an average over all mesogens and configurations. The diagonal elements of the Q tensor are the P_2 order parameters with respect to each Cartesian direction. The director vector is defined as the direction along which the P_2 order parameter is maximized, which likely does not correspond to one of the Cartesian directions. Therefore, we identified the director vector by performing an eigenvalue decomposition on the Q tensor. The eigenvector with the largest eigenvalue is the director vector and the corresponding eigenvalue is the largest P_2 order parameter. The eigenvectors also serve as an internal coordinate system for the LC that was used in the diffusivity calculations described below.

We calculated the Q tensor and performed the corresponding eigenvalue decomposition in Python using the *mdtraj* module. P_2 order parameters reported in the main text are the largest eigenvalues obtained from the decomposition, time-averaged over all molecular configurations.

Parameterization of mesogens

We followed a previously recommended approach to develop an all-atom (AA) model for 4-Cyano-4'-pentylbiphenyl (5CB).² Most force field parameters were obtained from the Generalized AMBER force field (GAFF), including Lennard-Jones parameters for all atoms, bond lengths, bond angles, and dihedral potentials. GAFF is a suitable AA force field because it preserves the same Lennard-Jones interactions used in the 5CB united atom model developed by Tiberio *et al*, which accurately reproduces key structural parameters of bulk 5CB.³⁻⁵ To improve the accuracy of the standard GAFF parameterization, we performed density functional theory (DFT) calculations to refit the partial charges of all 5CB atoms and reparameterize dihedral potentials in the 5CB biphenyl ring.

DFT calculations were performed in *Gaussian16* using the B3LYP functional with the 6-31g* basis set. Partial charges for all atoms were fit using the CHELPG method, which minimizes the error between the electrostatic potential generated by a set of point charges and the electrostatic

potential obtained from DFT at points on the molecular surface. We also introduced a constraint to require that the net dipole of the molecule reproduces the DFT result. Partial charges obtained from this method are shown in Figure S1a.

We fit 5CB intramolecular dihedral parameters to DFT calculations using Gaussian scan calculations. In this approach, atomic positions were adjusted such that the dihedral samples a range of angles; for each angle, all molecular coordinates were relaxed to the "tight" convergence criterion. Parameters for the GAFF dihedral potentials were then fit to reproduce the DFT calculations. The specific dihedrals that were refit are highlighted in Figure S1b. The dihedral potential obtained from the DFT calculation, from the original GAFF parameter set, and from the refit dihedral potentials are compared in Figure S1c for the dihedral indicated in the inset schematic.

TL205 does not contain the biphenyl ring that required parameterization in 5CB. Therefore, these dihedrals were not reparametrized.



Figure S1. a) 5CB molecule labeled with partial charges fit to DFT calculations. **b)** 5CB atoms highlighted in cyan to indicate the dihedrals that were reparametrized. **c)** Dihedral energies calculated using DFT, MD using the standard GAFF parameterization, and MD using the GAFF parameterization with refit dihedral potentials. The energy is shown as a function of the dihedral angle for the specific dihedral highlighted in the inset diagram.

Parameterization of analytes

Analyte AA models were developed by using Lennard-Jones and bond parameters from GAFF and fitting partial charges to DFT calculations. DFT calculations and charge fitting were performed using the same methodology described above for the 5CB parameters to ensure a consistent force field parameterization strategy. This parameterization approach was used for glutaraldehyde (GLU), dimethyl methylphosphonate (DMMP), methane (CH₄), carbon dioxide (CO₂), nitrogen dioxide (NO₂), ozone (O₃), and sulfur dioxide (SO₂). Alternative models were used for chlorine (Cl₂) and water (H₂O) as described below. Structures of all analytes and their assigned partial charges are shown in Figure S2a (for analytes used for experimental validation) and Figure S2b (for atmospheric analytes).

For H₂O, we used the Simple Point Charge/Extended (SPC/E) model, which is a widely used water model that reproduces bulk water properties. To confirm that the specific choice of water model does not affect the results in the main text, we also calculated solvation free energies in 5CB using two alternative models: the TIP3P water model (another common model) and a water model in which partial charges were obtained using the same approach used to parameterize analytes (CHELPG with a constrained dipole) and LJ interactions were obtained from GAFF (*i.e.*, following the same approach used for the other analytes). Figure S2c shows that solvation free energies are within 1 k_BT for all three models, and thus we assume that the results with SPC/E are reasonable.

For Cl_2 , fitting the partial charges following the approach used for other analytes would yield no partial charges. In a previous study, virtual sites bearing partial charges were added to help reproduce the electrostatic potential of Cl_2 .⁶ We followed this approach and generated two virtual sites that were placed colinear with the two Cl atoms as shown in Figure S2b. The partial charges on these virtual sites and the chlorine atoms were assigned in the same manner as the other analytes. The distance of the virtual sites was determined to be 0.1 nm by minimizing the RMSE between all the electrostatic potential fits. This distance is equal to the same virtual site distance obtained in a prior study⁶.

To verify the analyte partial charge assignments, Figure S2d compares analyte dipole moments computed by DFT, dipole moments computed using the fitted partial charges, dipole moments computed using the original GAFF partial charges (which are based on the nearest neighbors of each atom), and dipole moments obtained experimentally and listed in the NIST database. Dipole moments were computed using Equation S3 which relates the dipole moment, D, to the assigned partial charges, q_i , and corresponding atomic positions, r_i :

$$\mathcal{D} = \sum q_i r_i \tag{S3}$$

The dipole moments obtained from the assigned partial charges are in good agreement with both the DFT and experimental values, suggesting that the partial charge assignments are reasonable. The GAFF-assigned partial charges significantly overestimate the dipole moments for O_3 and SO_2 , suggesting that GAFF charge assignments are less accurate than the refit partial charges.

Finally, we checked the robustness of the solvation free energies in 5CB by comparing values for SO_2 , NO_2 , and CO_2 obtained from calculations using the refit partial charges to values obtained from calculations using the original GAFF partial charges. Figure S2e shows that the solvation free energies for NO_2 and CO_2 are similar for both charge assignments, which is consistent with the relatively small contribution of electrostatic interactions to these analytes' solvation free

energies (Figure 4a of the main text) and the analytes' small dipole moments (Figure S2d). However, the solvation free energy for SO_2 significantly varies depending on the charge assignment. Notably, the free energy is much more negative for the GAFF-assigned charges. We regard this solvation free energy as spurious because the GAFF-assigned charges produce a dipole moment that is much larger than the experimental value, leading to the more favorable partitioning in 5CB. These results thus emphasize the importance of re-fitting analyte partial charges.



Figure S2. Structures of **a**) analytes used for experimental validation and **b**) atmospheric analytes. Analyte structures are labeled with partial charges fit to DFT calculations. Virtual sites are drawn for Cl₂. **c**) Solvation free energies in 5CB for three water models: SPC/E, TIP3P, and GAFF parameters with refit partial charges. **d**) Analyte dipole moments computed using DFT, computed using atomic partial charges fit to DFT calculations, computed using GAFF-assigned partial charges, and obtained from the NIST database. **e**) Comparison of solvation free energies in 5CB computed using the GAFF-assigned charges, and the fitted charges.

Analyte diffusivity in the bulk LC and near the vapor-LC interface

We computed the diffusivity of each analyte in the bulk LC system by separately calculating the mean-squared displacement, *MSD*, in each vector direction corresponding to the eigenvectors of the Q-tensor (described in the above section entitled *Calculation of LC order parameter and director vector*) using Equation S4:

$$MSD_{\alpha}(\Delta t) = \langle \left(x_{\alpha}(t + \Delta t) - x_{\alpha}(t) \right)^{2} \rangle_{n,t}$$
(S4)

 α indicates a vector direction with respect to the internal coordinate system defined by the eigenvectors of the Q tensor, x_{α} is the position of the analyte projected onto the α vector, Δt is the time delay, and the average is computed over all trials and all possible increments of Δt . The diffusivity, D_{α} , is then defined by Equation S5:

$$D_{\alpha} = \frac{1}{2} \frac{d \, MSD_{\alpha}}{d \, (\Delta t)} \tag{S5}$$

Diffusivities were calculated in 3 independent 100-ns simulations and the standard error between these simulations was used to compute error bars. We separately calculated the diffusivity in the direction parallel to the director vector and the diffusivity in the direction perpendicular to the director vector, which was defined as the average of the diffusivity computed along the other two axes of the internal coordinate system. Figure S3 shows the diffusivity of each analyte in each of the LC bulk systems.



Figure S3. Diffusivities parallel/perpendicular to the director vector for a) 5CB and b) TL205.

We also calculated the diffusivity as a function of the *z*-component of the distance between the analyte and the vapor-LC interface (d_z) . $D(d_z)$ was determined from the umbrella sampling trajectories by measuring the standard deviation in the reaction coordinate, σ_z , and the analyte position autocorrelation function, $C_{zz}(t)$, using Equation S6⁷:

$$D(d_{\rm z}) = \frac{\sigma_{d_{\rm z}}^4}{\int_0^\infty C_{zz}(t)dt}$$
(S6)

Figure S4 shows the diffusivity of H_2O , Cl_2 , and SO_2 as a function of d_z . For comparison, the dashed lines indicate the values of the diffusion coefficient computed in the bulk LC system in the direction parallel to the director vector (the director vector in the interfacial system is aligned with the *z*-axis). The diffusivity profiles indicate that analyte diffusivities are similar to their bulk values throughout most of the interfacial region until increasing in the vapor region. These diffusivity profiles were used to compute the interfacial permeability in Figure 4 of the main text.



Figure S4. *z*-component of the analyte diffusivity as a function of the distance from the vapor-LC interface. Dashed lines indicate bulk diffusivities parallel to the director vector.

Convergence of solvation free energies and PMF measurements

To determine that simulations were performed for a sufficient amount of time, we analyzed the convergence of the solvation free energy and PMF calculations. For these tests, we calculated the corresponding free energy as a function of the sampling time used for the calculation. Figure S5a shows the solvation free energy for SO₂ in bulk 5CB as a function of sampling time for three independent measurements. All calculations converged after 4 ns. Figure S5b shows the convergence of the PMF for translocating SO₂ across the vapor-LC interface. Convergence was assessed by measuring the value of the PMF at $d_z = -6$ nm, which is a value of the reaction coordinate that should correspond to bulk LC. The value of the PMF for this value of the reaction free energy computed in Figure S5a. Figure S5b shows that the PMF converged after approximately 40 ns of sampling time.



Figure S5. a) Convergence of solvation free energy for SO₂ in bulk 5CB as a function of sampling time. Colors indicate different trials. b) Convergence of the PMF for SO₂ partitioning across the vapor-LC interface. The value of the PMF at d_z = -6 nm is shown as a function of sampling time. Dashed horizontal lines in both plots indicate the bulk solvation free energy reported in the main text.

Mass-transport model for sensor activation

We base our modeling framework on the mass-transport model derived by Hunter and Abbott⁸ that was used to describe the response of chemoresponsive LC sensors to vapor-phase DMMP. In this prior work, the sensor activation time, t_{act} , was related to the time required for DMMP to accumulate within the LC film to reach a threshold activation concentration, C_{act} . The model assumed that the analyte concentration within the LC film was constant (*i.e.*, there was no gradient in concentration) and that the analyte concentration at the substrate was in equilibrium with the analyte concentration in the film. The activation time was then estimated using values for the DMMP diffusivity and Henry's law constant that were estimated based on literature sources. In this work, we obtain these latter two quantities for a range of analytes using MD simulations. We thus seek to adjust the Hunter and Abbott mass-transport model to utilize MD-derived measurements of analyte permeability to predict changes in sensor activation times.



Figure S6. Schematic of mass-transport model.

In the derivation below, we relax assumptions made in the model by Hunter and Abbott. We first assume that analyte transport across the LC film is in a pseudo steady-state regime in which the time required to develop a steady-state concentration profile is small compared to the sensor activation time $(t \gg \frac{\delta^2}{2D})$ such that there is a constant concentration gradient throughout the film (illustrated in Figure S6). We further assume that analyte is consumed irreversibly by "reacting" (e.g., adsorbing to) with the substrate, allowing a concentration gradient to be maintained. If the reaction time is slow, then the analyte will accumulate at the substrate, leading to a non-zero concentration C_{sub} . If analyte transport across the LC film is fast then this model reduces to the Hunter and Abbott model; however, the results in the main text show that all analytes partition less favorably than DMMP into the LC film, suggesting that transport may be slower for these analytes and justifying an alternative mass-transport model. It is also possible that the reaction time at the substrate is fast, in which case no analyte accumulation will occur. This regime is also explored in the sections below. We begin by considering the case where analyte accumulates at the substrate as illustrated in Figure S6.

The flux of analyte, J, to the vapor side of the vapor-LC interface is defined in Equation S7:

$$J = k_c (C_{vap} - C_{int}) \tag{S7}$$

 k_c is the mass transfer coefficient due to convection, C_{vap} is the concentration of analyte in the vapor stream (far from the interface), and C_{int} is the concentration of analyte on the vapor side of the vapor-LC interface (Figure S6). We assume analyte on the vapor side of the interface is in

equilibrium with analyte on the LC side of the interface. These two concentrations are then related by the partition coefficient, K_p , defined in Equation S8:

$$K_p = \frac{C_{int}}{C_{LC}} \tag{S8}$$

 C_{LC} is the concentration of analyte on the LC side of the vapor-LC interface. K_p can be related to the MD-derived solvation free energy using Equation 7 in the main text. In 5CB, all solvation free energies are negative and accordingly $K_p \ll 1$ for all analytes, leading to higher analyte concentrations on the LC side of the vapor-LC interface as indicated in Figure S6.

Analyte molecules that partition into the LC at the vapor-LC interface must diffuse to the substrate to activate the sensor (*e.g.*, by adsorbing to the substrate and inducing a corresponding change in mesogen orientation). If we assume the LC is in a pseudo steady-state regime, without any boundary layers present in the film, the flux through the film is given by Equation S9:

$$J = \frac{D}{\delta} (C_{LC} - C_{sub})$$
(S9)

 C_{sub} is the concentration at the substrate at any given time, *D* is the analyte diffusion coefficient in the direction parallel to the flux, and δ is the film thickness. By combining Equations S7-S9 and eliminating C_{int} , we obtain Equation S10:

$$J = \frac{1}{\frac{1}{k_c} + \frac{\delta K_p}{D}} (C_{vap} - C_{sub})$$
(S10)

Equation S10 relates the flux to the difference between the analyte concentration in the vapor stream and the analyte concentration at the substrate interface. Equation S11 combines the prefactors of the concentration difference to define the overall mass transfer coefficient, K_{ov} , which accounts for mass transport across the vapor-LC interface and across the LC film:

$$K_{ov} = \frac{1}{\frac{1}{k_c} + \frac{\delta K_p}{D}}$$
(S11)

 K_{ov} includes two quantities that can be derived from simulations (K_p and D), the LC film thickness (δ) which can be modified experimentally, and the mass-transfer coefficient due to convection (k_c). The latter two terms are expected to be independent of the analyte properties, while the simulation-derived quantities explicitly account for LC-analyte interactions. We simplify Equation S11 by combining the two simulation-derived quantities into the permeance, \mathcal{P} , defined as:

$$\mathcal{P} = \frac{D}{K_p} \tag{S12}$$

$$K_{ov} = \frac{1}{\frac{1}{k_c} + \frac{\delta}{\mathcal{P}}}$$
(S13)

We next seek to relate the sensor activation time to analyte permeance. Following the model of Hunter and Abbott,⁸ we assume that the sensor activation time, t_{act} , corresponds to the time at which the average analyte concentration in the LC film, \bar{C} , reaches a threshold value, C_{act} .

Because analyte accumulation increases C_{sub} as a function of time, a mass balance on the bulk LC yields Equation S14:

$$J = K_{ov} (C_{vap} - C_{sub}) = \frac{\partial \bar{C} V}{\partial t A} = \frac{\partial \bar{C}}{\partial t} \delta$$
(S14)

In the pseudo steady-state regime we can write \bar{C} in terms of C_{sub} using Equation S15:

$$\bar{C} = \frac{1}{2}(C_{sub} + C_{int}) \tag{S15}$$

If we assume that C_{int} is constant in time because the concentration of analyte at the vapor-LC interface is determined by equilibrium partitioning of analyte from the vapor phase, then \bar{C} is proportional to C_{sub} . Substituting Equation S15 into Equation S14 and integrating yields:

$$\int_{0}^{t_{act}} \frac{K_{ov}}{\delta} dt = \frac{1}{2} \int_{0}^{C_{act}} \frac{dC_{sub}}{C_{vap} - C_{sub}}$$
(S16)

$$t_{act} = \frac{\delta}{2K_{ov}} \ln\left(\frac{C_{vap}}{C_{vap} - C_{act}}\right)$$
(S17)

Equation S17 indicates that t_{act} decreases with increasing K_{ov} and therefore with increasing \mathcal{P} as expected. For sufficiently high \mathcal{P} , t_{act} only depends on mass transport at the vapor-LC interface expressed through k_c . This regime occurs for DMMP as shown in Figure 6a of the main text, agreeing with the results of Hunter and Abbott.⁸ Sensor activation times for different analytes can be compared using Equation S17 if we assume that C_{act} is similar for all analytes interacting with a given substrate. In this case, we can calculate the simulation-derived permeance to obtain K_{ov} via Equation S13 and normalize t_{act} by the activation time for a known analyte (e.g., DMMP) to eliminate the unknown quantity C_{act} . If we further assume that C_{act} does not depend on film thickness, we can determine the apparent power dependence of the activation time on the film thickness:

$$\frac{d\ln(t_{act})}{d\ln(\delta)} = \frac{\left(\frac{1}{k_c} + \frac{2\delta}{\mathcal{P}}\right)}{\left(\frac{1}{k_c} + \frac{\delta}{\mathcal{P}}\right)}$$
(S28)

Equation S18 indicates that the sensor activation time should scale linearly with thickness if the analyte permeance is large and mass transport across the vapor-LC interface is rate-limiting, whereas the sensor activation time should scale quadratically with film thickness if the analyte permeance is small and mass transport across the LC film is rate-limiting. These relationships thus provide the means for experimentally verifying the mass-transport model predictions for a single analyte.

As an alternative mass transport model, we can instead assume that analyte interactions with the substrate lead to a fast reaction that results in zero analyte concentration at the substrate ($C_{sub} = 0$). The sensor activation time can then be interpreted as the time necessary for sufficient analyte molecules to react with the substrate, thereby displacing mesogens and inducing an optical transition. To identify this activation time, we assume that there is a limited number of substrate sites available to react with analyte molecules and define the number of sites per unit area as S_A and the fraction of sites that have interacted with the analyte as θ . The flux of analyte molecules to the substrate can then be related to the change in θ by Equation S19:

$$J = S_A \frac{d\theta}{dt} \tag{S39}$$

Setting C_{sub} to zero in Equation S10 for cases with a large thermodynamic driving force and equating the flux to Equation S19 yields Equation S20:

$$K_{ov}C_{vap} = S_A \frac{d\theta}{dt}$$
(S20)

We define the fraction of sites that must interact with the analyte to trigger sensor activation as θ_{act} . Integrating Equation S20 with respect to time then yields the sensor activation time:

$$K_{ov}C_{vap} \int_{0}^{t_{act}} dt = S_A \int_{0}^{\theta_{act}} d\theta$$
 (S21)

$$t_{act} = \frac{S_A \theta_{act}}{K_{ov} C_{vap}} \tag{S22}$$

By substituting the definition of K_{ov} defined in Equation S13 into Equation S22, we can eliminate the surface site density (S_A), fraction of sites necessary for a response (θ_{act}), and vapor phase concentration (C_{vap}) by normalizing t_{act} by the time necessary for DMMP activation in 5CB, t_{DMMP} , since this quantity is known experimentally⁸, leading to Equation S23:

$$\frac{t_{act}}{t_{DMMP}} = \frac{K_{ov,DMMP}}{K_{ov}} = \frac{\left(\frac{1}{k_c} + \frac{\delta}{\mathcal{P}}\right)}{\left(\frac{1}{k_c} + \frac{\delta}{\mathcal{P}_{DMMP}}\right)}$$
(S23)

Equation S23 is equivalent to Equation 9 in the main text but does not assume that C_{act} is similar for different analytes. The assumptions used to derive Equation S23 include that surface chemistry is barrierless with a large thermodynamic driving force, which may be the case for certain detection schemes. In addition, it is assumed that the surface site density between different detection schemes are similar, which is generally of order 1 site per 10^{15} cm². The last assumption is that θ_{act} does not change by orders-of-magnitude between systems. For systems that have somewhat similar surface chemistries, this may be the case.

Comparing Equations S17 and S22 shows that both models yield an identical dependence on K_{ov} , and thus on the simulation-derived \mathcal{P} . Both models depend on system-specific quantities that dictate activation: C_{act} in Equation S17 and $S_A \theta_{act}$ in Equation S22. The primary differences between these equations lie in the dependence on the film thickness, δ , and the vapor stream concentration, C_{vap} . Varying these parameters experimentally could reveal which transport model is more accurate for a given experimental system. Figure 6b in the main text shows the predicted dependence of sensor activation times on film thickness using Equation S18 because this model is consistent with the prior model of Hunter and Abbott, which was used to predict DMMP activation times in 5CB.⁸ The thickness dependence would only differ by a constant factor if Equation S22 were used instead. Since both Equations S17 and S22 predict the same dependence on \mathcal{P} , the results in Figure 6a of the main text are consistent with both equations. More experimental evidence is required to determine which equation best represents a given LC system; as a result, we only compare values of \mathcal{P} for different analytes in TL205 in Figure 7.

TL205 solvation free energy breakdown

Figure 4a of the main text decomposes the solvation free energy of each analyte in 5CB into contributions due to electrostatic interactions and Lennard-Jones interactions. SI Figure S7a shows the same decomposition for solvation free energies in TL205. In comparison with the interactions with 5CB, analytes experience comparable LJ interactions. However, the favorable electrostatic interactions are decreased in TL205 compared to 5CB. This result can be rationalized by the bulk dielectric constant of each species. Typically, the dielectric constant within a liquid crystal varies with the angle with respect to the director vector, which yields the property of birefringence. Experimentally, the dielectric constant of 5CB is 19.7 along the director vector and 6.6 in the orthogonal direction.⁹ For TL205, the dielectric constant is 8.68 along the director vector suggests that polar analytes will partition less favorably into the bulk, explaining the trend in the electrostatic contribution to the solvation free energy.



Figure S7. a) Representation of well-mixed TL205 LC system. **b)** Comparison of the solvation free energy (ΔG_{solv}) and contributions due to Lennard-Jones and electrostatic interactions in TL205.

Polarizable Continuum Model Calculations

We compared the solvation free energies calculated using the all-atom (AA) model to solvation energies calculated with DFT using a Polarizable Continuum (PC) Model in Gaussian09 version D.01.¹¹ PC model calculations were calculated using Equation S24:

$$\Delta G_{\rm solv} = G_{\rm solv} - G_{\rm no\ solv} \tag{S24}$$

We employed M06-2X-D3(SMD=benzonitrile)/def2-TZVP level of theory for the G_{solv} calculations. The $G_{no\ solv}$ calculations were performed using the same level of theory, but without including the Self-Consistent Reaction Field (SCRF): M06-2X-D3/def2-TZVP.¹²⁻¹⁵ Figure S8 compares the solvation free energies computed using the AA model and the PC model. In general, the two models are in good agreement. The largest error (0.11 eV) between these models is for the case of H₂O. However, this error is within the mean squared error of DFT for adsorption on metal surfaces (0.2 eV).¹⁶ Therefore, the PC model using benzonitrile is generally sufficient for comparisons with DFT calculations involving small molecules in 5CB. For other applications, these errors may be considered too large because a 0.06 eV difference is equivalent to one order of magnitude difference in reaction rates. The AA model predictions are closer to experimental results (Figure 3b in the main text), and thus we recommend the AA model for applications where errors of 1-2 k_BT are important.



Figure S8. Comparison between solvation free energies in 5CB computed using molecular dynamics with the AA model in explicit 5CB and using DFT calculations with the Polarizable Continuum (PC) model with benzonitrile as the solvent. The red entry for NO₂ is close to zero and therefore not visible.

System visualization

Figure S9 shows snapshots of all six atmospheric analytes of interest in the vacuum phase and in bulk 5CB and TL205 to illustrate typical system configurations.



Figure S9. Visualization of analytes in vacuum phase, 5CB, and TL205. The snapshots within the LCs have been equilibrated for 100ns.

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