

Supporting Information

The Complex between Molecular Oxygen and an Organic Molecule: Modeling Optical Transitions to the Intermolecular Charge-Transfer State

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Preliminary Calculations for Energy Optimized Selected Structures

Preliminary calculations based on four optimized structures of the O₂-toluene complex (A, B, C and D in Figure 2 of the main text) using CAM-B3LYP/aug-cc-pVDZ in the TD-DFT formalism resulted in unique two-photon transitions over the range 260-310 nm (Figure S1). Both the absorption cross section and energy of these transitions depended appreciably on the structure of the molecular complex. Application of a Gaussian function ($\Gamma_{FWHM} = 0.35 \text{ eV}$) to the resultant “sticks” was used to simulate spectral broadening (Figure S1). Structure B, in which O₂ lies on top of the toluene π system, results in the largest absorption cross-section and the lowest transition energy ($\sim 310 \text{ nm}$).

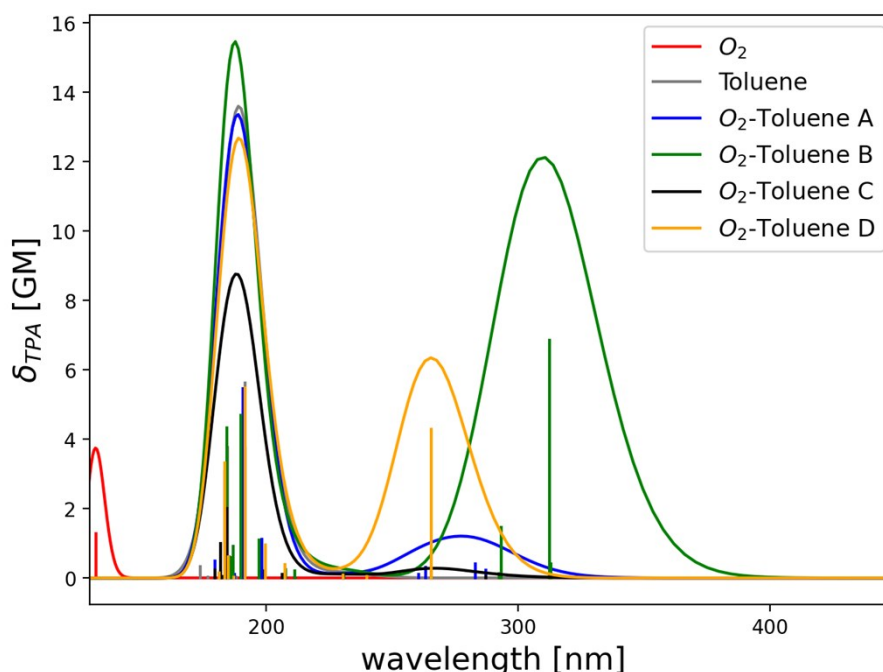


Figure S1. Two-photon spectra obtained from a TD-DFT calculation applied to the four toluene-O₂ structures shown in Figure 2 of the main text. A Gaussian broadening function ($\Gamma_{FWHM} = 0.35 \text{ eV}$) was applied to the “stick” transitions obtained from the calculation. Although transitions localized on oxygen and toluene were obtained at wavelengths shorter than $\sim 200 \text{ nm}$, discrete toluene-O₂ transitions were obtained over the range $\sim 260 - 310 \text{ nm}$.

While the CAM-B3LYP functional is fundamentally different from the ω B97X-D functional used for some of our other DFT calculations (*i.e.*, Figures S4 and S5), both are range-separated with a value of ω optimized to reproduce intramolecular charge transfer transitions, and both fail in their prediction of transition energies of intermolecular charge transfer transitions. As discussed in the main text, and as shown in Figures 6, S4, and S5, the ω B97X-D functional can only reproduce intermolecular transitions when the value of ω is changed.

Spectra as a Function of Intermolecular Distance

Using structure B (Figure 2), TD-DFT calculations show that as the intermolecular distance between toluene and oxygen increases, the energy of the CT transition correspondingly increases (*i.e.*, we see a systematic blue shift in the transition wavelengths) and the absorption cross sections for both one- and two-photon transitions decrease, albeit with a different dependence on intermolecular distance (Figure S2). These observations are consistent with expectation and the independent EOM-CCSD calculations (see main text), and can be ascribed to a decrease in the overlap between electron donor and acceptor wave functions as the intermolecular distance increases. At short intermolecular distances, interactions between more orbitals are involved, and the spatial profiles of these orbitals play a greater role in defining the calculated spectra (*i.e.*, the spectra appear more “structured”). The results in Figure S2 show that the same final state is populated in both one- and two-photon spectra, as expected given symmetry-based selection rules for a non-centrosymmetric system.¹

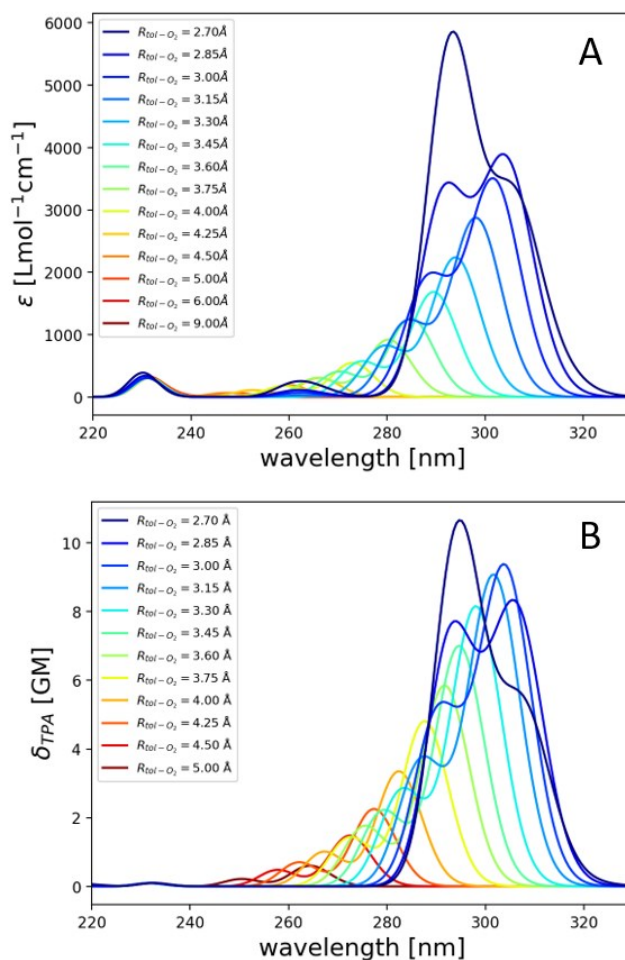


Figure S2. TD-DFT calculations (CAM-B3LYP/aug-cc-pVDZ) of (A) one- and (B) two-photon spectra for structure B of the toluene-O₂ complex as a function of the toluene-O₂ intermolecular distance R . In plotting the two-photon spectra, we show the total transition energy rather than the incident photon energy. As opposed to what is shown in Figure S1, the Gaussian broadening function applied to the “stick” transitions was reduced to $\Gamma_{FWHM} = 0.1$ eV.

Spectra as a Function of Intermolecular Rotation

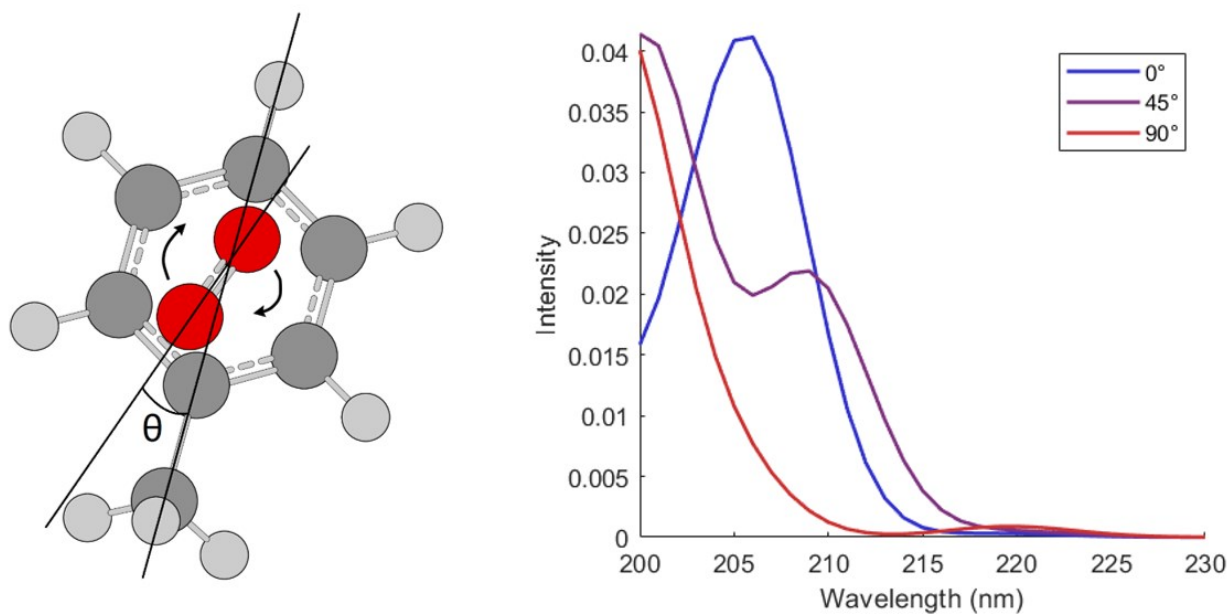


Figure S3. EOM-CCSD/aug-cc-pVDZ calculations of absorption spectra for structure B of the toluene-O₂ complex as a function of the rotation angle θ between oxygen and the pendant methyl group in toluene. The O-O internuclear axis is parallel to the plane of the aromatic ring and the intermolecular distance was maintained at 3.45 Å.

Parameters for the AMOEBA Polarizable Force Field

We take our starting point for the MD simulations in the AMOEBA force field (2009 version), where many small organic molecules, including toluene, are parametrized.² However, to our knowledge, molecular oxygen has not been appropriately parameterized to this end. To parametrize molecular oxygen for use with AMOEBA the equilibrium bond length (1.2156 \AA)³ and vibrational frequency (1580.19 cm^{-1})³ are readily available. A buffered 14-7 potential⁴ was employed to describe van der Waals interactions, using $r_0 = 1.705 \text{ \AA}$ and $\epsilon = 0.1245 \text{ kcal/mol}$ to parameterize oxygen. However, we need parameters that describe the polarizability and multipole moments of molecular oxygen.

The polarizability requires (a) the atomic polarizability (for which a standard value of 0.837 \AA^3 is taken for all instances of oxygen in the AMOEBA force field), and (b) a damping factor a , which “smears” the charge distribution. In AMOEBA, a universal factor $a = 0.39$ is used. However, we find that using $a = 0.72$ better reproduces the experimental polarizability tensor, and we use this value for atomic oxygen. Below, the calculated and experimental⁵ static polarizability tensors are shown:

$$\frac{\alpha'}{\text{\AA}^3} = \begin{pmatrix} 1.22 & 0 & 0 \\ 0 & 1.22 & 0 \\ 0 & 0 & 2.28 \end{pmatrix} [\textit{calculated}]$$

$$\frac{\alpha'}{\text{\AA}^3} = \begin{pmatrix} 1.21 & 0 & 0 \\ 0 & 1.21 & 0 \\ 0 & 0 & 2.28 \end{pmatrix} [\textit{experimental}]$$

For the multipole moments, we calculate the quadrupole moment, and, redundantly, the charge and dipole moment, based on an MP2/aug-cc-*p*VQZ⁶ computation of the electron density of $\text{O}_2(X^3\Sigma_g^-)$ in Gaussian 16.⁷ The results are very close to experimental results:⁸

$$\frac{Q}{D \text{\AA}} = \begin{pmatrix} 0.158 & 0 & 0 \\ 0 & 0.158 & 0 \\ 0 & 0 & -0.315 \end{pmatrix} [\textit{calculated}]$$

$$\frac{Q}{D \text{\AA}} = \begin{pmatrix} 0.155 & 0 & 0 \\ 0 & 0.155 & 0 \\ 0 & 0 & -0.310 \end{pmatrix} [\textit{experimental}]$$

Given this information, we calculated the appropriate AMOEBA parameters for O_2 using the Tinker 8 software package.⁹

The parametrization of oxygen is implemented in the AMOEBA force field by adding the following lines to the pertinent Tinker parameter file:

```
atom      351 102  O  "Dioxygen O2"          8 15.999  1
```

```

vdw      102      3.4100  0.1245
bond     102 102     846.98  1.2075
multipole 351 351  0      0.00000
          0.00000  0.00000  0.24984
          -0.22648
          0.00000 -0.22648
          0.00000  0.00000  0.45296
polarize 351      0.8370  0.7200  351

```

Details of the MD simulation

To get a starting structure for our MD simulation, we packed 100 toluene molecules with 1 oxygen molecule into a cubic box. This was done with the software Packmol.¹⁰ We minimized the resulting ensemble to an rms gradient of 0.01 kcal/(mol Å) per atom in the MD software package Tinker 8.⁹ We then ran a 100 ps NVT simulation (heating to room temperature) and a 1 ns NPT simulation (equilibrating to ambient pressure), and finally an NVT production run with a new volume as determined by the average volume of the last 0.5 ns in the NPT simulation. This final NVT simulation ran for 10 ns. We considered the first 100 ps of the production run to be equilibration. All simulations were performed in 1 fs time steps. Details of the simulations are summarized in Table S1.

Table S1. Simulation Details in the Tinker 8 Package.

	Total time / ns	Integrator	Thermostat	Barostat
NVT heating	0.1	r-RESPA	Bussi-Parrinello	-
NPT equilibration	1	Nosé-Hoover	Nosé-Hoover	Nosé-Hoover
NVT production	10	r-RESPA	Bussi-Parrinello	-

MD-Based Spectra Calculated Using Different Sampling Methods

Figures S4 and S5 show the TD-DFT calculated spectra obtained with different sampling methods using ω B97X-D/aug-pcseg-1, with an ω parameter of 0.5 Bohr⁻¹. This exercise shows that although the details of the spectra are different, the overall spectrum is largely independent of sampling method.

Center-of-Mass (com) Displacements

In this section, we discuss the details of the third sampling method based on com displacements. With this approach, we end up with 99 structures rather than 100 because we leave the first 100 ps for equilibration. Thus, in the discussion below, we only consider the part of the simulation from 101 to 10000 ps.

For every single picosecond, we first calculate the com-to-com distance between oxygen and every toluene molecule. We save the 1:1 complex with the shortest com-to-com distance. This gives us a distribution (a histogram) of com-to-com distances and we aim to reproduce that distribution in our selection of complexes.

We have 99 “windows” consisting of 100 potential structures separated by 1 ps (101-200 ps, 201-300 ps, ... 9901-10000 ps). Knowing the distribution of com-to-com distances, we take exactly 1 structure from each window such that the distribution is reproduced as well as possible. Figure S6 is a histogram of all 9900 structures and the 99 sampled structures. (An entirely perfect match is impossible due to rounding).

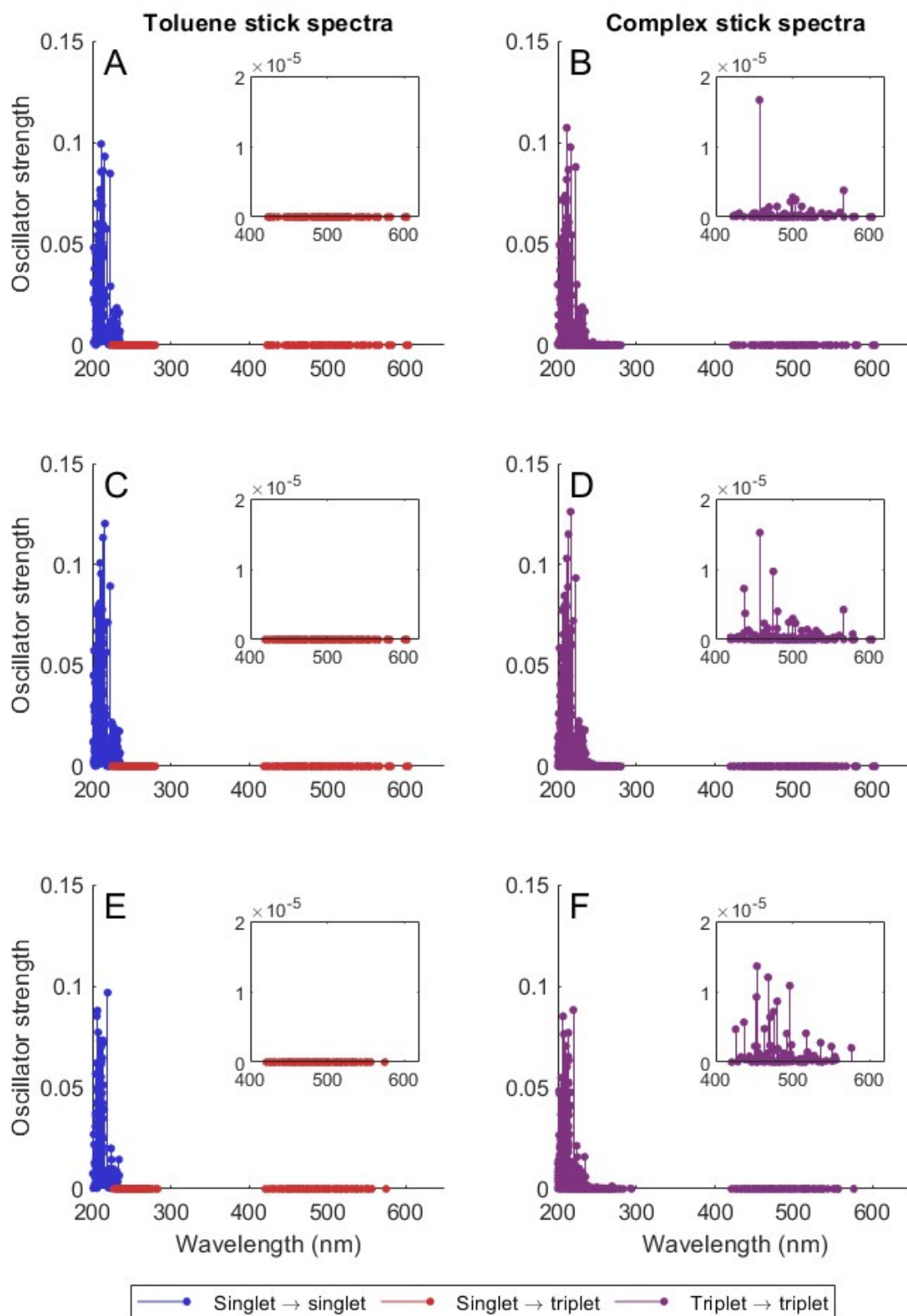


Figure S4. Spectra of discrete transitions (*i.e.*, “Stick” spectra) obtained using TD-DFT with three different sampling methods: (A and B) 1:1 complexes with the closest toluene defined as the one containing the atom closest to an oxygen atom. (C and D) 2:1 complexes with the closest and second-closest toluene defined as in panels A and B. (E and F) 1:1 complexes based on center-of-mass, com, displacements (see text).

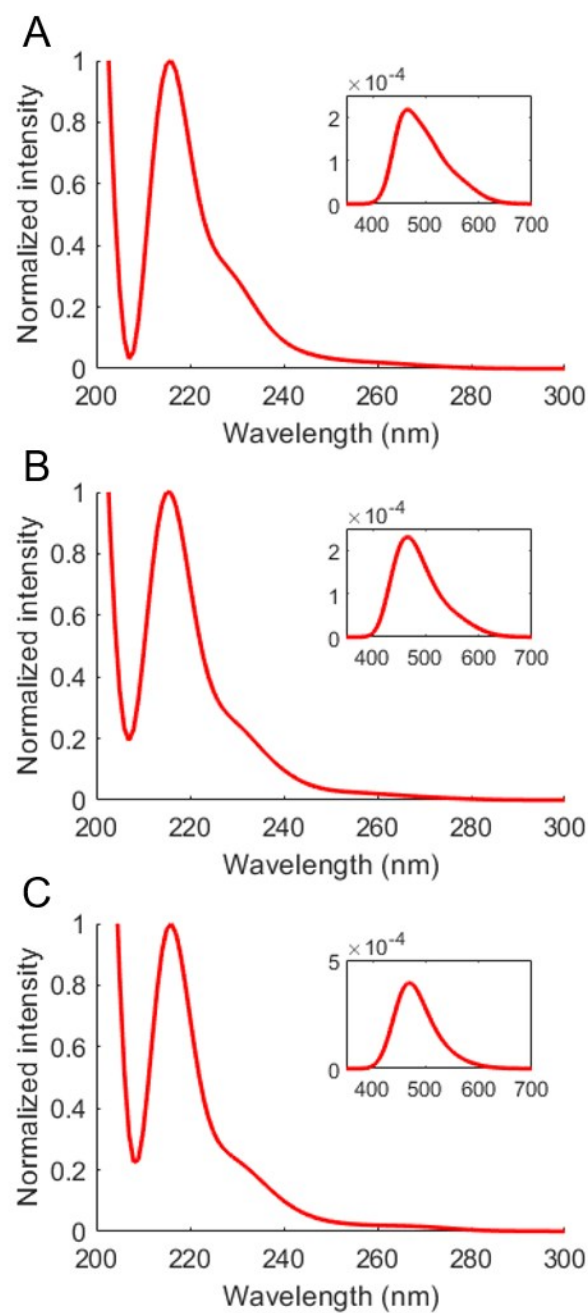


Figure S5. Broadened spectra obtained from the spectra shown in Figure S4 (see text for full discussion of the approach used). (A) 1:1 complexes, (B) 2:1 complexes, and (C) 1:1 complexes based on center-of-mass, com, displacements.

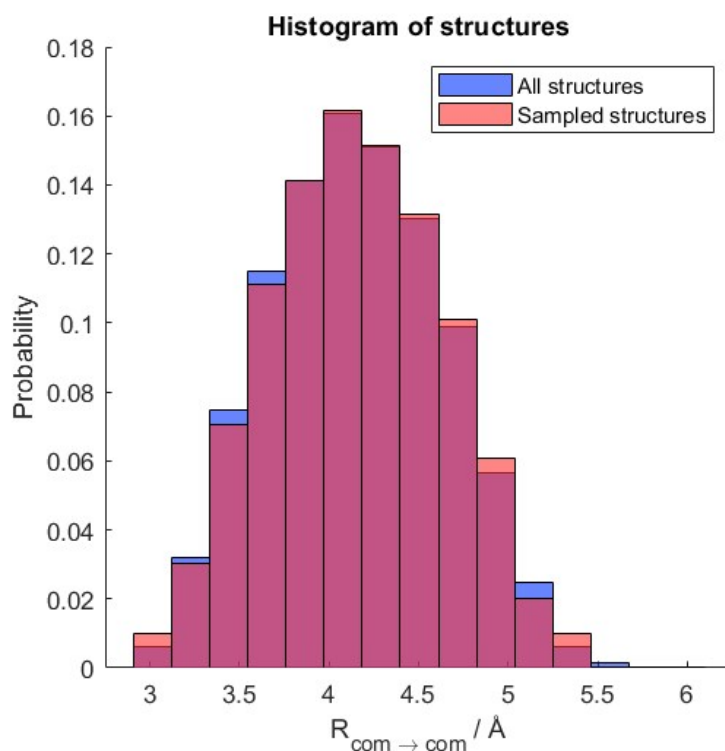


Figure S6. Histogram of com-to-com distances. Blue bars represent all 9900 structures; red bars the 99 sampled for the spectrum (the purple color shows the overlap between blue and red bars.)

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