# Electronic Supplementary Information for:

## Stark Tuning Rates of Organic Carbonates Used in Electrochemical Energy Storage Devices

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Table S1. Average peak position of C=O modes for all carbonate solvents.

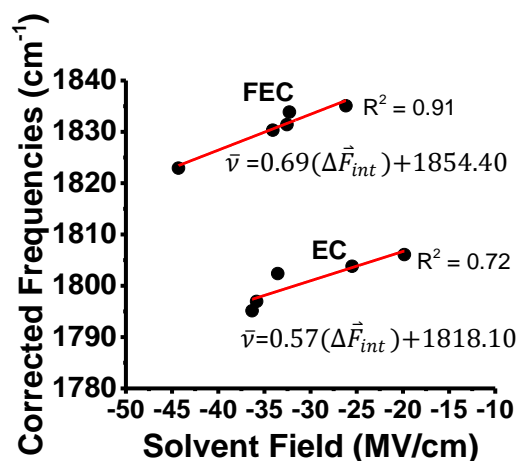| Carbonate Solute (Solvent) | Average Peak Position ($cm^{-1}$) |
|---|---|
| DEC (THF) | 1746.36 |
| DEC (dibutyl ether) | 1749.05 |
| DEC (acetonitrile) | 1744.64 |
| DEC (chloroform) | 1741.16 |
| DEC (dichloromethane) | 1743.01 |
| DEC (dimethylsulfoxide) | 1741.28 |
| DEC (hexane) | 1748.78 |
| EC (THF) | 1811.31 |
| EC (chloroform) | 1807.40 |
| EC (dichloromethane) | 1807.81 |
| EC (toluene) | 1812.78 |
| EC (1,3-dioxolane) | 1808.95 |
| FEC (THF) | 1838.61 |
| FEC (chloroform) | 1836.02 |
| FEC (dichloromethane) | 1834.64 |
| FEC (dimethylsulfoxide) | 1828.52 |
| FEC (1,3-dioxolane) | 1836.35 |

Table S2. Average solvent electric field values used for field frequency calibration

| Solvent | DEC | | EC | | FEC | |
|---|---|---|---|---|---|---|
| | Average | Std. Dev. | Average | Std. Dev. | Average | Std. Dev. |
| 1,3-dioxolane | | | -33.54 | 10.56 | -32.28 | 10.51 |
| acetonitrile | -10.64 | 10.99 | | | | |
| chloroform | -18.95 | 15.57 | -36.32 | 13.02 | -32.55 | 13.18 |
| dibutyl ether | -1.67 | 5.24 | | | | |
| dichloromethane | -15.59 | 13.19 | -35.84 | 16.17 | -34.08 | 11.90 |
| dimethylsulfoxide | -10.01 | 9.72 | | | -44.30 | 12.19 |
| hexane | -0.08 | 0.74 | | | | |
| tetrahydrofuran | -5.50 | 7.30 | -25.48 | 8.00 | -26.16 | 8.01 |
| toluene | | | -19.83 | 7.14 | | |

As shown in Table 1, the Stark tuning rate of FEC is nearly twice as large as that of EC based on the slope of the field-frequency calibration (Figure 5b), though they differ by only a single atom distant from the carbonyl probe. Comparison of identical solvent calculations as shown in Table S2 indicates that the average electric field for EC and FEC are nearly identical, consistent with the similarity in overall structure, but the experimental frequency shifts are nearly twice as large across the solvent span for FEC per (MV/cm) in Figure 5b. Whether this is due to discrepancies between the parameterization of the carbonate solvents in MD simulations (i.e. requiring higher level calculations to determine the atomic charges), or a suggestion that the overall bond displacement is more sensitive in the case of FEC, remains to be determined. As may be expected for a local high frequency mode such as a carbonyl, the C and O atom of EC and FEC exhibit nearly identical atomic charges consistent with their overall structures. The simple 1-dimensional model for describing the linear Stark effect and the Stark tuning rate as presented in reference 37 is $|\Delta\vec{\mu}|=q*\Delta d$, where q is the bond's charge and $\Delta d$ is the change in bond length between the vibration's first-excited state and ground state. In this model, either the overall charge of the bond or bond displacement will lead to a significant change in $|\Delta\vec{\mu}|$. As previously mentioned, the overall charge at the O and C atoms of the C=O are nearly identical for EC and FEC at the level of theory used herein, suggesting that this difference then arises from the bond displacement. This could in principle be modeled using the anharmonic shift as determined from 2D-IR, though this is beyond the scope of this manuscript.
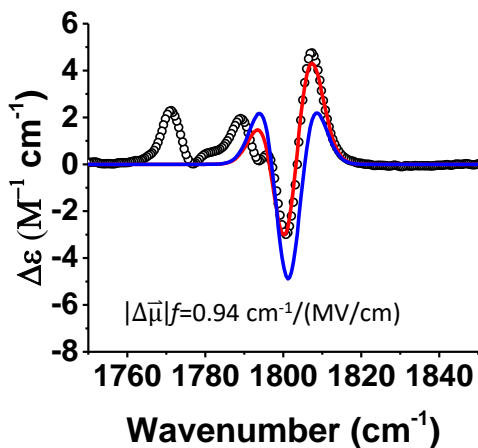


**Figure S1**. Stark spectrum of EC in 2-MeTHF scaled to 1 MV/cm. Raw data is shown as black dots, The line of best fit (red trace) is qualitatively similar to the 2nd-derivative of the absorbance spectrum. The Stark tuning rate is listed in the bottom right in units of cm-1/(MV/cm).

**Figure S2**. Corrected C=O frequencies with use of a perturbation model.

**Table S3**. frequencies corresponding to corrected C=O modes, using a perturbation model referenced in sources[1-3]

| Carbonate Solute (Solvent) | Average C=O peak position corrected for fermi resonance $(cm^{-1})$ |
|---|---|
| EC (toluene) | 1806.06 |
| EC (chloroform) | 1797.31 |
| EC (dichloromethane) | 1798.83 |
| EC (dioxolane) | 1802.37 |
| EC (THF) | 1803.35 |
| FEC (dioxolane) | 1833.85 |
| FEC (chloroform) | 1831.38 |
| FEC (dichloromethane) | 1830.33 |
| FEC (dimethylsulfoxide) | 1822.93 |
| FEC (THF) | 1835.06 |

An example of the effect different solvents have on changes to both the position and amplitudes of the C=O stretch and $F_R$ mode is plotted below. For clarity, only two spectra are plotted in Figure 2 for EC (1M EC dissolved in THF and ACN) ; spectral data for all solvents is recorded in table S3. Briefly described, the perturbation model has been used to extract an unperturbed C=O frequency ($\delta_0$) through the coupling constant (W), calculated by the difference ($\delta$) between the observed vibrational frequencies of the $F_R$ ($v_+$) and C=O ($v_-$) modes and their intensity ratio (R). As an example of this concept, consider the following plot with intensity and absorption (I and $v_{+/-}$) variables labeled:
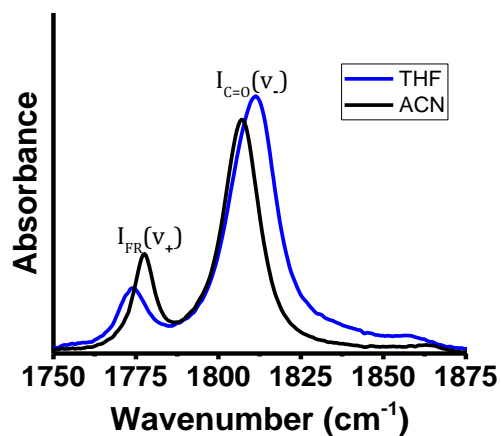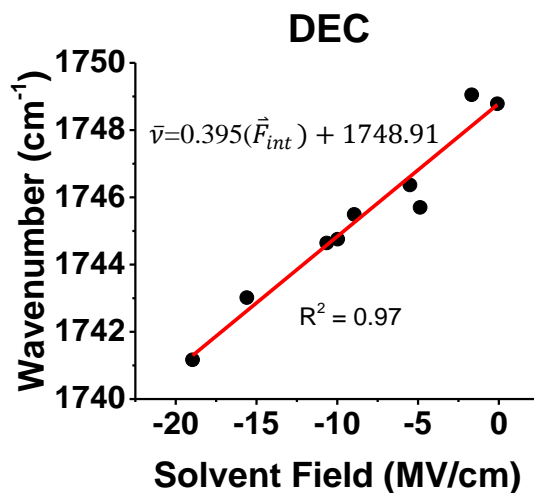
**Figure S3**. The intensities of the carbonyl ($I_{C=O}$) and Fermi resonant ($I_{FR}$) modes, for EC change when solvated by acetonitrile and tetrahydrofuran (ACN and THF, respectively). The absorption values also shift.
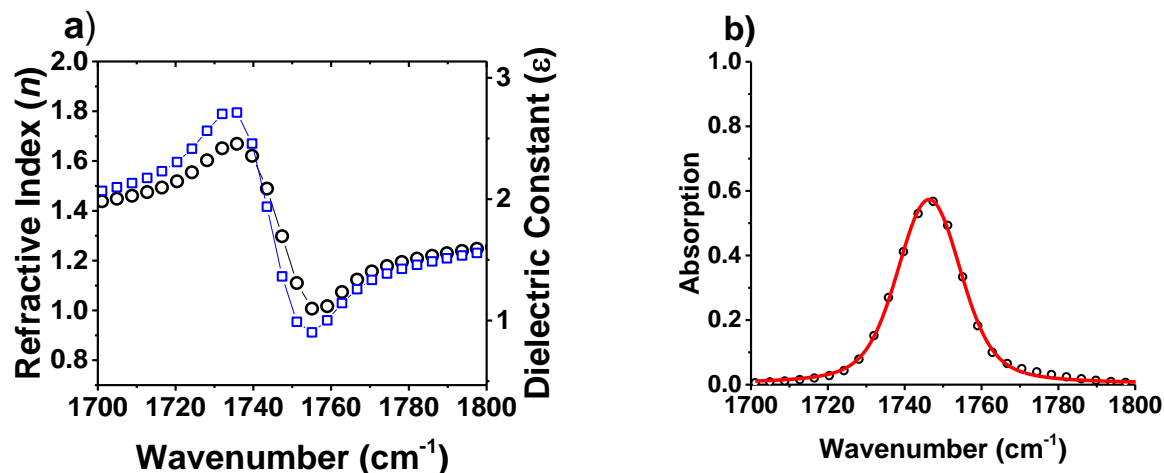
$R = \dfrac{I_{C=O}}{I_{FR}}$

$\delta = v_{+} - v_{-}$

$W = \dfrac{\delta}{R+1}\sqrt{R}$

$\delta_0 = [\delta^2 - 4W^2]^{1/2}$



**Figure S4**. Expanding the range of solvent fields for DEC, used as an example because it exhibits no $F_R$ interference, changes its tuning rate by ~5% and exhibits a lower coefficient of determination ($R^2$).

**Figure S5**. (a) Infrared ellipsometry of DEC, exhibiting the refractive index (n, open circles) and dielectric constant (ε, open squares) as a function of wavenumber. (b) Absorption spectrum of DEC, from which optical constants were obtained.
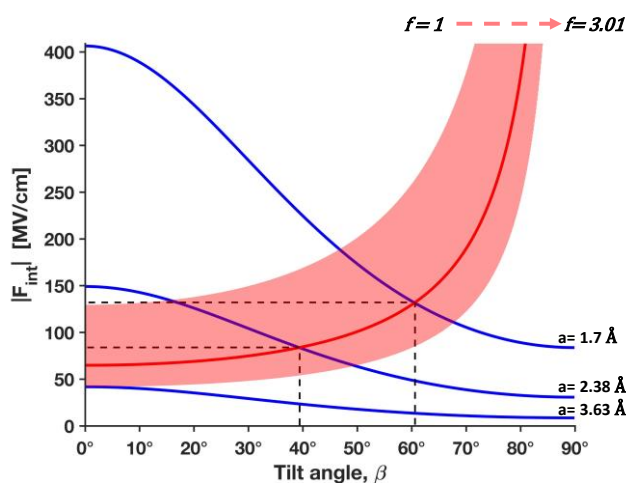


**Figure S6**. The C=O mode of EC red shifts by 40 cm$^{-1}$ (from 1868 cm$^{-1}$ in the gas phase[4] to 1820 cm$^{-1}$ on the surface of graphite[5]). Using optical constants of the electrolyte solvent ε = 89.6,[6] refractive index n = 1.419,[7] dipole moment μ = 4.81D[8] and C=O bond length of 1.15 Å,[9] the application of Eq. 1-3 resolves fields between 83.9-132.1 MV/cm between angles of 39.4-60.6°, respectively. The value representing the red line is when *f*=2.

**References**

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