

# Dimers of Cyclic Carbonates: Chirality Recognition in Battery Solvents and Energy Storage

Franz Kollipost, Susanne Hesse, Juhyon J. Lee, and Martin A. Suhm

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Supplementary Information

Table S1: Spectroscopic data: Observed supersonic jet peak positions for EC and PC in  $\text{cm}^{-1}$

EC (C-O)	$\tilde{\nu}$	EC (C=O)	$\tilde{\nu}$	PC (C-O)	$\tilde{\nu}$	PC (C=O)	$\tilde{\nu}$
D <sub>A</sub>	1086	T <sub>C</sub>	1852	D <sub>A</sub> /T <sub>A</sub>	1045	T <sub>G</sub>	1839
A	1088	T <sub>C</sub>	1832	D <sub>A</sub> <sup>het</sup>	1051	D <sub>G</sub> <sup>het</sup>	1840
B	1127	T <sub>C</sub>	1838	D <sub>A</sub>	1067	D <sub>G</sub> <sup>hom</sup>	1844
D <sub>B</sub>	1156	D <sub>C</sub>	1850	D <sub>A</sub> <sup>het</sup>	1075	F	1846
		D <sub>C</sub>	1859	A	1076	D <sub>G</sub> <sup>het</sup>	1846
		C	1869	D <sub>B</sub> <sup>hom</sup>	1099	G	1863
		B		B	1101	H	1870
		C		C	1112		
		D <sub>C</sub>		D <sub>C</sub>	1125		
		D <sub>C</sub> /T <sub>C</sub>		D <sub>C</sub> /T <sub>C</sub>	1152		
		D <sub>E</sub> <sup>het</sup>		D <sub>E</sub> <sup>het</sup>	1169		
		E		E	1172		
		D <sub>E</sub> <sup>hom</sup>		D <sub>E</sub> <sup>hom</sup>	1188		
		D <sub>E</sub> <sup>het</sup>		D <sub>E</sub> <sup>het</sup>	1190		
		D <sub>E</sub> <sup>hom</sup>		D <sub>E</sub> <sup>hom</sup>	1195		
		D <sub>E</sub> <sup>het</sup>		D <sub>E</sub> <sup>het</sup>	1196		
		T <sub>E</sub>		T <sub>E</sub>	1229		

Table S2: Examination of possible combination states  $\tilde{\nu}_P$  available for Fermi resonance with the carbonyl stretching vibration in the EC dimer (1850/1859  $\text{cm}^{-1}$ ) and hypothetically for the monomer (1869  $\text{cm}^{-1}$ ). Monomer fundamentals  $\tilde{\nu}_M$  are listed together with predicted or experimental symmetric ( $\Delta\tilde{\nu}_D(A_g)$ ) and antisymmetric ( $\Delta\tilde{\nu}_D(A_u)$ ) dimer shifts.

pair of vibrations	$\tilde{\nu}_M$	est. $\tilde{\nu}_P$ for		est. $\tilde{\nu}_P$ for	
		monomer	$\Delta\tilde{\nu}_D(A_g)$	$\Delta\tilde{\nu}_D(A_u)$	dimer
asymm. $\text{CH}_2$ rocking	690 <sup>c</sup>	1817	+9 <sup>c</sup>	+29 <sup>a</sup>	1855 <sup>d</sup>
asymm. C–O stretch	1127 <sup>a</sup>				
centr. C out of plane	768 <sup>b</sup>	1856	+9 <sup>c</sup>	+3 <sup>c</sup>	1863/1851
symm. $\text{CH}_2$ –O stretch	1088 <sup>a</sup>		–8 <sup>c</sup>	–2 <sup>a</sup>	
C–C stretch	960 <sup>b</sup>	1841	+7 <sup>c</sup>	+8 <sup>c</sup>	1850/1851
ring breathing	881 <sup>b</sup>		+2 <sup>c</sup>	+2 <sup>c</sup>	
asymm. C–O stretch	1127 <sup>a</sup>	1842	+23 <sup>c</sup>		1867
O–C–O bend	715 <sup>b</sup>		+2 <sup>c</sup>		

<sup>a</sup> measured in this work

<sup>b</sup> from the literature [Fortunato *et al.*, *Spectrochimica Acta*, 1971, **27A**, 1917]

<sup>c</sup> B3LYP/6-311++G(d,p) harmonic predictions

<sup>d</sup> favored assignment

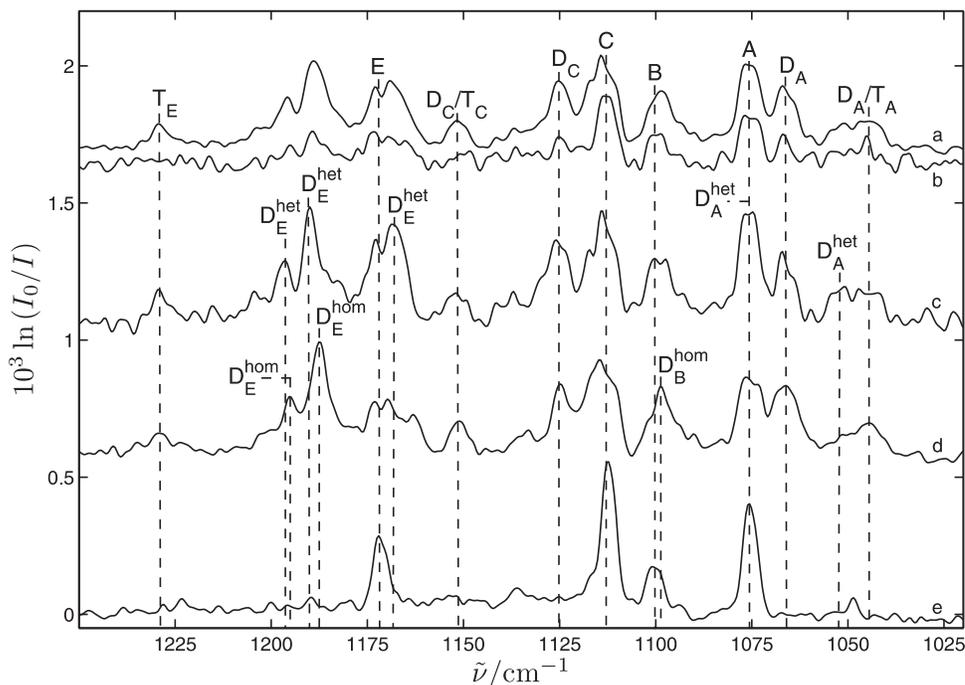


Figure S1: Heated jet spectra of PC in the C–O range: Racemic PC at a) 80 °C and b) 50 °C; c) synthetic heterochiral spectrum (2a-d); d) enantiopure PC. e) Monomer-dominated jet spectrum, 600 mm nozzle,  $\approx 1$  bar stagnation pressure. The dimer bands were related to monomer vibrations according to their proximity to the monomer bands. For E there are two blue-shifted dimer bands in the homochiral ( $D_E^{\text{hom}}$ ) and heterochiral ( $D_E^{\text{het}}$ ) spectrum, respectively, that show a small effect of chirality recognition, considering the slight frequency differences between the two spectra. Besides a trimer band ( $T_E$ ) with stronger blue shift, which is found in all spectra at high concentration, a single red-shifted dimer band ( $D_E^{\text{het}}$ ) dominates the heterochiral spectrum. For C two blue-shifted cluster bands ( $D_C/T_C$  &  $D_C$ ) are assigned, of which the more strongly shifted one may originate from a trimer. Only one slightly red-shifted homochiral dimer signal ( $D_B^{\text{hom}}$ ) is attributed to B. A heterochiral dimer signal ( $D_A^{\text{het}}$ ) coincides with A. There is another heterochiral dimer band ( $D_A^{\text{het}}$ ) red shifted to A and two red shifted cluster peaks ( $D_A$  and  $D_A/T_A$ ) which appear in all three spectra types. Again, the most shifted band may originate from a trimer vibration.

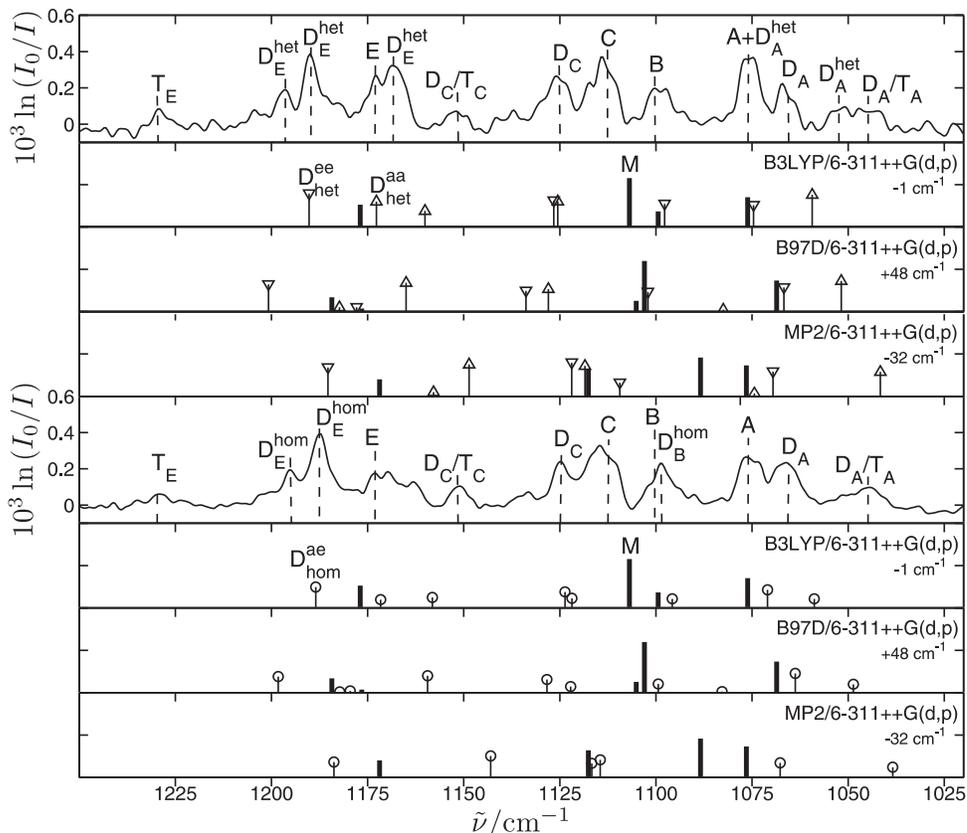


Figure S2: Comparison between hetero- (upper half) and homochiral (lower half) dimer peaks and corresponding calculations of PC in the C-O range. Calculated wavenumbers have all been shifted uniformly to optimize the match between experimental and calculated monomer peaks for each method. The applied shifts for the fingerprint region deviate clearly between EC (Fig. 2) and PC for all levels of theory, as expected for non-local vibrations. The dimer peaks of the homochiral spectrum are mostly explained by the calculated shifts of  $D_{\text{hom}}^{\text{ae}}$ . B3LYP shows the best agreement for the monomer wavenumbers and the calculated dimer peaks are in fair agreement with the spectra. MP2 fails to predict the vicinity of B and C correctly. All calculations predict only one blue-shifted band for E, which is the major inconsistency between experiment and calculations. Fermi resonance is a more likely explanation than additional dimer structures. When comparing the vibrational predictions for  $D_{\text{het}}^{\text{ee}}$  to the heterochiral spectrum, not all features can be explained. In fact, the blue-shifted dimer peak  $D_{\text{E}}^{\text{het}}$ ,  $D/T_{\text{C}}$  and the more strongly shifted dimer peak  $D_{\text{A}}^{\text{het}}$  are best assigned to the less stable dimer  $D_{\text{het}}^{\text{aa}}$ . Again MP2 shows rather poor performance in the C-O range, whereas B3LYP and B97D are in fair agreement.