SUPPLEMENTARY MATERIAL

The noncoincidence phenomenon of Acetonylacetone C=O Stretching in binary mixtures and the aggregation induced split theory

Huigang Wang*, Hang Xu, Qiuna Liu, Xuming Zheng

Department of Chemistry, and Key Laboratory of Advanced Textiles Materials and Manufacture Technology of the Ministry of Education, and Engineering Research Center for Eco-Dyeing and Finishing of Textiles of the Ministry of Education, Zhejiang Sci-Tech University, Hangzhou 310018, P. R. China.
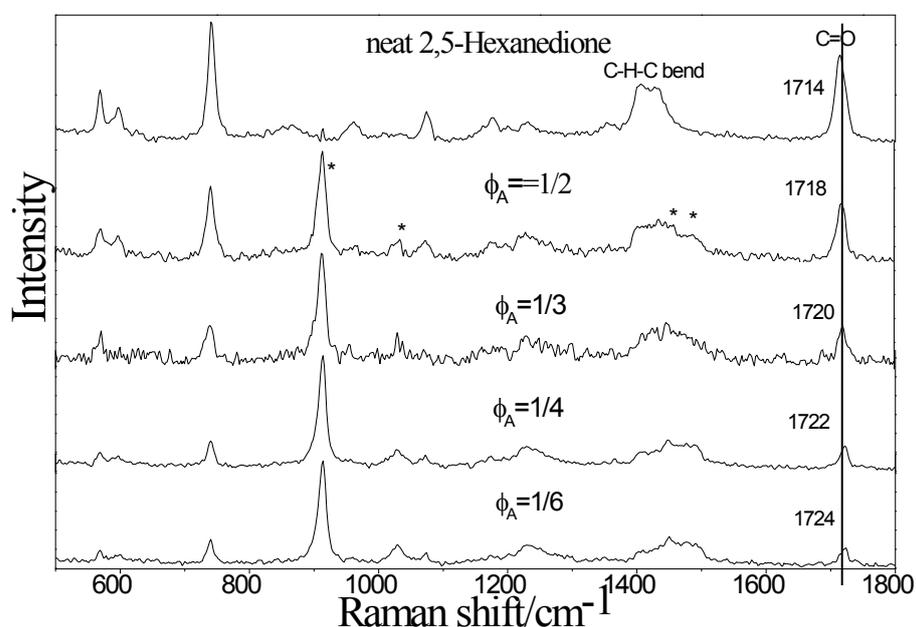
Figure S1 FT-Raman spectra in the region 400–1800 cm^{-1} for neat Acetonylacetone and at four other volume fractions of Acetonylacetone, 0.5, 0.33, 0.25and 0.16, in the binary mixture (Acetonylacetone +THF)

Cis and Trans form of acetonylacetone have C=O Raman activity vibrational freq. at 1770cm-1 and 1781 cm-1 respectively, we have also carried out IRC/path scan for Cis to Trans form, it is shown in figure S1. This is a barrierless process from cis to trans, in solution we normally believe the acetonylacetone bears anti form predominantly, but this is not the case the Raman spectra shows, because we learn from figure3 that it splited as isotropic and anisotropic parts in most of the concentrated solution. The concentration effect demonstrates that the aggregation structure is formed by intermolecular, instead of intramolecular.
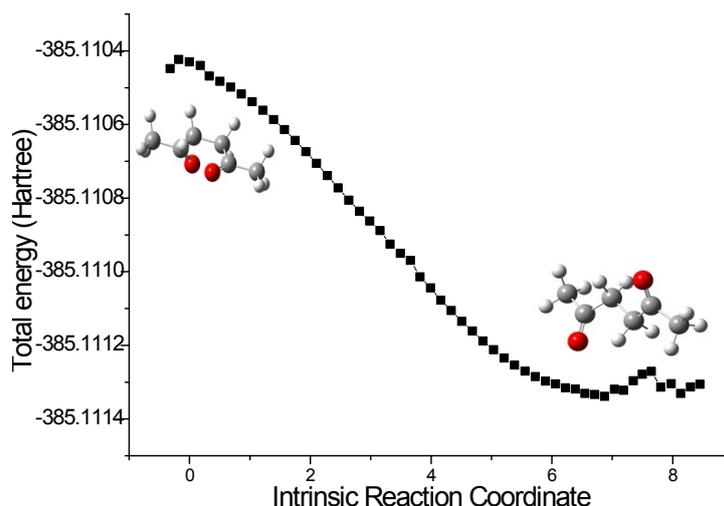
figure S2. Total energy along IRC

With the DFT calculated Gaussian Output File of the acetonylacetone, we can also get the isotropic and anisotropic spectrum theoretically from the dimer model DFT calculations. Gaussview or Multiwfn can transform the dimer frequencies into Raman spectra. the original output file could be regarded as $I\text{VV}(v_{VV})$, we interested in C=O vibration, so we focus our attention on the C=O frequency and their depolarization ratio, with the depolarization ratio ρand corresponding Raman activity of C=O vibration, we can get the depolarized Raman activity of C=O vibration, with caussview we can transform to spectra, that is, the depolarized Raman spectra, I_{VH} of C=O vibration. Similarly, according to

$$I\text{iso}(v_{VV}) = I\text{VV}(v_{VV}) - \frac{4}{3}I\text{VH}\,(v_{VH})$$

we can get the isotropic Raman activity, to finally get I_{iso} *spectra.*

Isotropic and anisotropic Raman spectra of C=O vibration
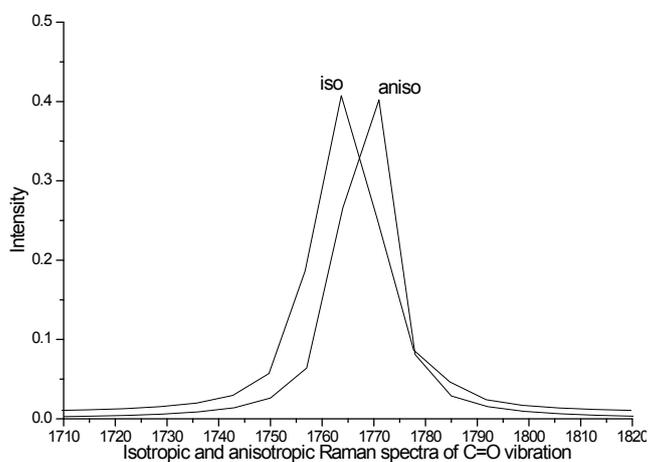
Figure S3. the isotropic and anisotropic spectrum theoretically from the dimer model DFT calculations

Table S1. The DFT/PCM calculated C=O vibrational frequencies, depolarization ratios, Dielectric constant (ε) , Dipole moments (μ)/D, and Δv_{NCE} in a variety of solvents.

Solvents	Freq	D.ratio	Dielectric constant (ε)	Dipolemoments (μ)/D	Δv_{NCE}(cm^{-1})
Acetonylacetone	1768/1760	0.41/0.32			7.6
THF	1772/1770	0.75/0.45	7.58	1.70	1.9
DMSO	1768/1766	0.75/0.45	46.70	4.30	1.4
H$_2$O	1767/1767	0.75/0.45	78.36	5.70	1