

Supporting information for:
A general time dependent approach to vibronic
spectroscopy including Franck-Condon,
Herzberg-Teller and Dushinsky effects.
Supporting information

Alberto Baiardi,[†] Julien Bloino,^{*,‡,†} and Vincenzo Barone[†]

*Scuola Normale Superiore, piazza dei Cavalieri 7, I-56126 Pisa, Italy, and Consiglio
Nazionale delle Ricerche, Istituto di Chimica dei Composti OrganoMetallici
(ICCOM-CNR), UOS di Pisa, Area della Ricerca CNR, Via G. Moruzzi 1, I-56124 Pisa,
Italy*

E-mail: julien.bloino@pi.iccom.cnr.it

1 OPA spectra of anthracene with temperature effects

Following previous studies,^{S1,S2} we report in Figure S1 a comparison between our time-dependent spectra and the experimental $S_1 \leftarrow S_0$ one-photon absorption (OPA) spectrum recorded by Ferguson and coworkers.^{S3} The theoretical spectrum was simulated at T=0K as often done with sum-over-states approaches and T=298K, which is similar to the temperature

*To whom correspondence should be addressed

[†]Scuola Normale Superiore, piazza dei Cavalieri 7, I-56126 Pisa, Italy

[‡]Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti OrganoMetallici (ICCOM-CNR), UOS di Pisa, Area della Ricerca CNR, Via G. Moruzzi 1, I-56124 Pisa, Italy

used in experiment (25–40°C). In order to facilitate band-shape comparison, the transition energy between the vibrational ground states of the initial and final electronic states was set to origin and the intensity of the associated band set to 1 (spectrum normalization). Band broadening was simulated by mean of Gaussian distribution functions with half-width at half-maximum of 150 cm^{-1} . The computed spectrum with no temperature effect is in good agreement with the experimental spectrum. As noted by Dierksen and Grimme,^{S1} the intensity difference at higher energy may be associated to a shift of the experimental baseline. Inclusion of temperature effects improves the agreement with experiment, in particular for the first band where the shoulder due to hot bands is clearly observable.

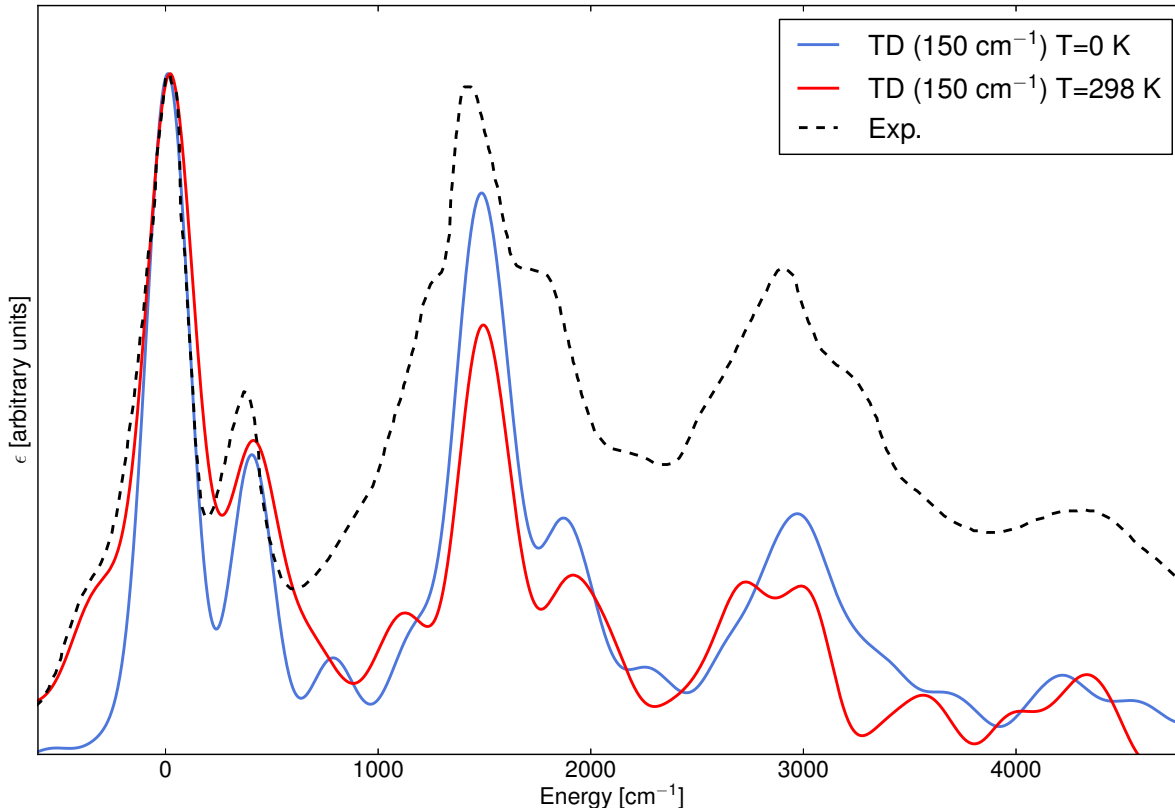


Figure S1: $S_1 \leftarrow S_0$ OPA spectrum of anthracene computed with the path integral (TD) approach compared to the experimental spectrum from Ref.^{S3} Broadening was simulated by mean Gaussian distribution functions with HWHM= 150 cm^{-1} . The theoretical spectra were simulated at the AH|FC level at T=0K (blue) and T=298K (red) in vacuum.

2 Photoionization spectrum of furan with temperature effects

As expected with such a small system, there is no visible temperature effects at 298K (Figure S2), so both band-shapes at T=0K and T=298K are very similar.

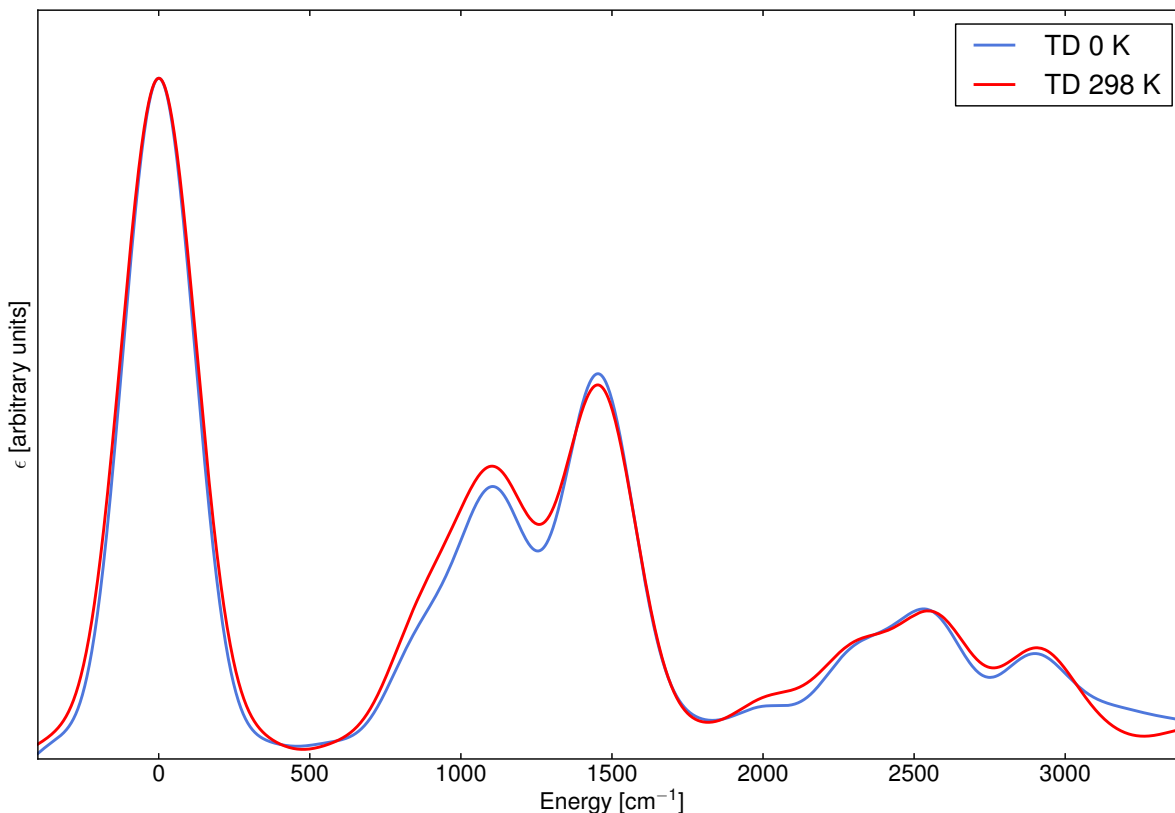


Figure S2: $\tilde{X}^2A_2 \leftarrow \tilde{X}^1A_1$ photoionization spectra of furan simulated with the path integral (TD) approach. Broadening was simulated by mean Gaussian distribution functions with HWHM=200 cm⁻¹. The theoretical spectra were simulated at the AH|FC level at T=0K (blue) and T=298K (red) in vacuum.

3 The SNSD basis set

The SNSD basis set used in this work, available online at http://dreamslab.sns.it/sites/default/files/download/gaussian/basis_sets/SNSD.gbs is listed below in the Gaussian Basis Set format.

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-H 0
6-31++G
P 1 1.00      0.000000000000
    0.7500000000D+00  0.10000000D+01
P 1 1.00      0.000000000000
    0.1450000000D+00  0.10000000D+01
****
-He 0
6-31G**
****
-Li 0
6-31+G**
****
-Be 0
6-31+G**
****
-B 0
6-31G
P 1 1.00      0.000000000000
    0.3500000000D-01  0.1000000000D+01
D 1 1.00      0.000000000000
    0.3430000000D+00  0.1000000000D+01
****
-C 0
6-31G
S 1 1.00      0.000000000000
    0.7500000000D+01  0.1000000000D+01
SP 1 1.00     0.000000000000
    0.5000000000D-01  0.1000000000D+01
D 1 1.00      0.000000000000
    0.8200000000D+00  0.1000000000D+01
D 1 1.00
    0.3180000000D+00  0.1000000000D+01
****
-N 0
6-31G
S 1 1.00      0.000000000000
    0.1260000000D+02  0.1000000000D+01
SP 1 1.00     0.000000000000
```

```

      0.5300000000D-01  0.1000000000D+01
D   1 1.00      0.0000000000
      0.1015000000D+01  0.1000000000D+01
D   1 1.00      0.0000000000
      0.1500000000D+00  0.10000000D+01
****
-O 0
6-31G
S   1 1.00
      0.1510000000D+02  0.1000000000D+01
SP  1 1.00      0.0000000000
      0.6500000000D-01  0.1000000000D+01
D   1 1.00      0.0000000000
      0.1190000000D+01  0.1000000000D+01
D   1 1.00      0.0000000000
      0.1800000000D+00  0.1000000000D+01
****
-F 0
6-31G
S   1 1.00
      0.1830000000D+02  0.1000000000D+01
SP  1 1.00      0.0000000000
      0.8300000000D-01  0.1000000000D+01
D   1 1.00      0.0000000000
      1.3700000000D+00  0.1000000000D+01
D   1 1.00      0.0000000000
      0.2300000000D+00  0.1000000000D+01
****
-Ne 0
6-31+G**
****
-Na 0
6-31+G**
****
-Mg 0
6-31+G**
****
-Al 0
6-31G
S   1 1.00      0.0000000000
      0.3100000000D+01  0.1000000000D+01
SP  1 1.00      0.0000000000
      0.1500000000D-01  0.1000000000D+01
D   1 1.00      0.0000000000
      0.1890000000D+00  0.1000000000D+01
D   1 1.00      0.0000000000
      0.0530000000D+00  0.1000000000D+01

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****
-Si 0
6-31G
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0.3600000000D+01 0.1000000000D+01
SP 1 1.00 0.0000000000
0.3300000000D-01 0.1000000000D+01
D 1 1.0 0.0000000000
0.2750000000D+00 0.1000000000D+01
D 1 1.0 0.0000000000
0.0823000000D+00 0.1000000000D+01

****
-P 0
6-31G
S 1 1.00 0.0000000000
0.5500000000D+01 0.1000000000D+01
SP 1 1.00 0.0000000000
0.3500000000D-01 0.1000000000D+01
D 1 1.00 0.0000000000
0.3730000000D+00 0.1000000000D+01
D 1 1.00 0.0000000000
0.1130000000D+00 0.1000000000D+01

****
-S 0
6-31G
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0.8000000000D+01 0.1000000000D+01
SP 1 1.00 0.0000000000
0.4100000000D-01 0.1000000000D+01
D 1 1.00 0.0000000000
0.4790000000D+00 0.1000000000D+01
D 1 1.00 0.0000000000
0.1520000000D+00 0.1000000000D+01

****
-Cl 0
6-31G
S 1 1.00 0.0000000000
0.8500000000D+01 0.1000000000D+01
SP 1 1.00 0.0000000000
0.4800000000D-01 0.1000000000D+01
D 1 1.00 0.0000000000
0.6000000000D+00 0.1000000000D+01
D 1 1.00 0.0000000000
0.1960000000D+00 0.1000000000D+01

****
-Br 0
S 3 1.00 0.0000000000

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```

0.4721881000D+01  0.1749732514D+00
0.2257555000D+01 -0.7074172290D+00
0.3896080000D+00  0.1258999543D+01
S  1 1.00          0.000000000000
0.1471340000D+00  0.1000000000D+01
P  3 1.00          0.000000000000
0.1896942000D+01 -0.2464576731D+00
0.9108990000D+00  0.3623179892D+00
0.3168550000D+00  0.8338469725D+00
P  1 1.00          0.000000000000
0.1095030000D+00  0.1000000000D+01
P  1 1.00          0.000000000000
0.3609700000D-01  0.1000000000D+01
D  1 1.00
0.4750000000D+00  0.1000000000D+01
D  1 1.00
0.1280000000D+00  0.1000000000D+01
****
-I  0
S  3 1.00          0.000000000000
0.2122765000D+01  0.2063429899D+01
0.1770481000D+01 -0.2869526473D+01
0.3130840000D+00  0.1404747074D+01
S  1 1.00          0.000000000000
0.1320000000D+00  0.1000000000D+01
P  3 1.00          0.000000000000
0.2432887000D+01  0.7732753148D+00
0.2137249000D+01 -0.1020833156D+01
0.3145460000D+00  0.1095666871D+01
P  1 1.00          0.000000000000
0.1049450000D+00  0.1000000000D+01
P  1 1.00          0.000000000000
0.3264100000D-01  0.1000000000D+01
D  1 1.00
0.3000000000          1.00000000
D  1 1.00
0.0900000000          1.00000000
****
-Zn 0
SP  6 1.00          0.000000000000
0.6936492000D+02 -0.4440098182D-02 -0.7689261805D-02
0.2362082000D+02  0.7505253308D-01 -0.2997981924D-01
0.1018471000D+02  0.2533111104D+00  0.7082410821D-01
0.4334082000D+01 -0.2881897118D+00  0.4046140897D+00
0.1810918000D+01 -0.7267052298D+00  0.4882324876D+00
0.7148410000D+00 -0.2133439088D+00  0.1751969956D+00
SP  3 1.00          0.000000000000

```

```

0.2823842000D+01  0.4898545031D-01 -0.1586762981D+00
0.1039543000D+01  0.2592794075D+00  0.8379326898D-01
0.1432640000D+00 -0.1115711463D+01  0.9840546881D+00
SP  1 1.00          0.0000000000000000
0.4929600000D-01  0.1000000000D+01  0.1000000000D+01
S   1 1.00          0.0000000000000000
0.1620000000D+00  0.1000000000D+01
D   3 1.00          0.0000000000000000
0.3370764000D+02  0.9262647815D-01
0.9061106000D+01  0.4002979920D+00
0.2738383000D+01  0.6896607863D+00
D   1 1.00
0.2440000000D+01  0.1000000000D+01
D   1 1.00          0.0000000000000000
0.7302940000D+00  0.1000000000D+01
D   1 1.00          0.0000000000000000
0.1620000000D+00  0.1000000000D+01

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References

- (S1) Dierksen, M.; Grimme, S. Density functional calculations of the vibronic structure of electronic absorption spectra. *The Journal of Chemical Physics* **2004**, *120*, 3544.
- (S2) Avila Ferrer, F. J.; Cerezo, J.; Stendardo, E.; Improta, R.; Santoro, F. Insights for an Accurate Comparison of Computational Data to Experimental Absorption and Emission Spectra: Beyond the Vertical Transition Approximation. *Journal of Chemical Theory and Computation* **2013**, *9*, 2072–2082.
- (S3) Ferguson, J.; Reeves, L. W.; Schneider, W. G. VAPOR ABSORPTION SPECTRA AND OSCILLATOR STRENGTHS OF NAPHTHALENE, ANTHRACENE, AND PYRENE. *Canadian Journal of Chemistry* **1957**, *35*, 1117–1136.