# Phonon dynamics and electron-phonon coupling in pristine picene

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## Supplementary Data

Table 1 reports the vibrational frequencies of picene isolated molecule, as obtained from DFT calculations (B3LYP, 6-31G(d)), performed with the Gaussian03 package. The mode label follows the usual Mulliken convention [1]. Both the computed and scaled frequencies are reported. The scaled factor is 0.9613 for all the frequencies [2]. The slight differences between the scaled frequencies and those reported in the main paper is due to the fact that here we report the frequencies of the isolated (gas phase) molecule, whereas in the paper we give the frequencies of the molecule embedded in the crystal.

Table 2 reports the full set of observed frequencies between 500 and 1700 $cm^{-1}$ (in IR, we start from 600 $cm^{-1}$ due to the limits of the IR microscope detector). The observed frequencies are compared with those reported in Table 1 for the corresponding assignments, proposed in the rightmost column of Table 2. We also report the values of the experimental and calculated IR and Raman intensities. To ease the comparison, we report in any case the percentage value relative to a value of 100 assumed for the most intense band.

Finally, Fig. 1 offers a visual comparison between experimental and calculated Raman and IR spectra. Again, no absolute scale is used for the intensities, as only the relative values are measured. The Figure shows a satisfactory agreement between experiment and calculation, particularly for what concerns the IR intensities.

## References

[1] R. S. Mulliken, J. Chem. Phys. **23**, 1997 (1955).

[2] A. P. Scott and L. Radom, J. Phys. Chem. **100**, 16502 (1996).

Table 1: Calculated vibrational frequencies of picene isolated molecule. Frequencies ($\omega$) in $cm^{-1}$.

| Label | $\omega_{calc}$ | $\omega_{scaled}$ | Label | $\omega_{calc}$ | $\omega_{scaled}$ |
|---|---|---|---|---|---|
| $a_1\nu_1$ | 3244.1 | 3118.6 | $b_2\nu_{69}$ | 3228.6 | 3103.6 |
| $\nu_2$ | 3237.3 | 3112.0 | $\nu_{70}$ | 3223.5 | 3098.8 |
| $\nu_3$ | 3218.6 | 3094.0 | $\nu_{71}$ | 3210.4 | 3086.1 |
| $\nu_4$ | 3206.3 | 3081.2 | $\nu_{72}$ | 3204.8 | 3080.8 |
| $\nu_5$ | 3190.3 | 3066.8 | $\nu_{73}$ | 3190.1 | 3066.6 |
| $\nu_6$ | 3183.8 | 3060.6 | $\nu_{74}$ | 3182.7 | 3059.6 |
| $\nu_7$ | 3178.5 | 3055.5 | $\nu_{75}$ | 3178.3 | 3055.3 |
| $\nu_8$ | 1673.0 | 1608.3 | $\nu_{76}$ | 1678.6 | 1613.6 |
| $\nu_9$ | 1668.8 | 1604.2 | $\nu_{77}$ | 1662.2 | 1597.9 |
| $\nu_{10}$ | 1643.1 | 1579.5 | $\nu_{78}$ | 1622.2 | 1559.4 |
| $\nu_{11}$ | 1572.4 | 1511.6 | $\nu_{79}$ | 1584.7 | 1523.3 |
| $\nu_{12}$ | 1561.5 | 1501.1 | $\nu_{80}$ | 1529.2 | 1470.0 |
| $\nu_{13}$ | 1485.9 | 1428.4 | $\nu_{81}$ | 1498.0 | 1440.1 |
| $\nu_{14}$ | 1479.0 | 1421.7 | $\nu_{82}$ | 1472.1 | 1415.2 |
| $\nu_{15}$ | 1413.1 | 1358.4 | $\nu_{83}$ | 1438.7 | 1383.0 |
| $\nu_{16}$ | 1395.9 | 1341.9 | $\nu_{84}$ | 1398.1 | 1344.0 |
| $\nu_{17}$ | 1377.1 | 1323.8 | $\nu_{85}$ | 1358.9 | 1306.4 |
| $\nu_{18}$ | 1306.5 | 1255.9 | $\nu_{86}$ | 1293.7 | 1243.7 |
| $\nu_{19}$ | 1304.8 | 1254.3 | $\nu_{87}$ | 1267.4 | 1218.3 |
| $\nu_{20}$ | 1278.5 | 1229.0 | $\nu_{88}$ | 1252.2 | 1203.7 |
| $\nu_{21}$ | 1230.6 | 1183.0 | $\nu_{89}$ | 1202.6 | 1156.1 |
| $\nu_{22}$ | 1223.6 | 1176.3 | $\nu_{90}$ | 1192.0 | 1145.9 |
| $\nu_{23}$ | 1190.7 | 1144.6 | $\nu_{91}$ | 1163.1 | 1118.1 |
| $\nu_{24}$ | 1177.5 | 1131.9 | $\nu_{92}$ | 1074.2 | 1032.6 |
| $\nu_{25}$ | 1102.8 | 1060.2 | $\nu_{93}$ | 1059.7 | 1018.7 |
| $\nu_{26}$ | 1066.7 | 1025.5 | $\nu_{94}$ | 894.4 | 859.8 |
| $\nu_{27}$ | 928.8 | 892.9 | $\nu_{95}$ | 870.5 | 836.8 |
| $\nu_{28}$ | 877.4 | 843.5 | $\nu_{96}$ | 800.5 | 769.5 |
| $\nu_{29}$ | 744.6 | 715.8 | $\nu_{97}$ | 687.8 | 661.4 |
| $\nu_{30}$ | 655.9 | 630.5 | $\nu_{98}$ | 561.7 | 540.0 |
| $\nu_{31}$ | 596.3 | 573.3 | $\nu_{99}$ | 528.7 | 508.3 |
| $\nu_{32}$ | 528.0 | 507.5 | $\nu_{100}$ | 487.8 | 468.9 |
| $\nu_{33}$ | 427.0 | 410.5 | $\nu_{101}$ | 477.6 | 459.1 |
| $\nu_{34}$ | 261.8 | 251.7 | $\nu_{102}$ | 284.0 | 273.0 |

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Table 1 – Continued

| | | | | | |
|---|---|---|---|---|---|
| $\nu_{35}$ | 142.8 | 137.3 | | | |
| $a_2\nu_{36}$ | 985.4 | 947.3 | $b_1\nu_{53}$ | 985.1 | 947.0 |
| $\nu_{37}$ | 957.5 | 920.4 | $\nu_{54}$ | 966.3 | 928.9 |
| $\nu_{38}$ | 941.5 | 905.0 | $\nu_{55}$ | 943.8 | 907.3 |
| $\nu_{39}$ | 925.1 | 889.4 | $\nu_{56}$ | 879.6 | 845.5 |
| $\nu_{40}$ | 876.3 | 842.4 | $\nu_{57}$ | 832.2 | 800.0 |
| $\nu_{41}$ | 842.6 | 810.0 | $\nu_{58}$ | 821.5 | 789.7 |
| $\nu_{42}$ | 799.8 | 768.8 | $\nu_{59}$ | 767.9 | 738.2 |
| $\nu_{43}$ | 766.8 | 737.1 | $\nu_{60}$ | 751.0 | 721.9 |
| $\nu_{44}$ | 717.1 | 689.4 | $\nu_{61}$ | 660.4 | 634.8 |
| $\nu_{45}$ | 599.0 | 575.8 | $\nu_{62}$ | 539.3 | 518.4 |
| $\nu_{46}$ | 561.0 | 539.3 | $\nu_{63}$ | 510.8 | 491.1 |
| $\nu_{47}$ | 477.4 | 459.0 | $\nu_{64}$ | 424.1 | 407.7 |
| $\nu_{48}$ | 393.0 | 377.8 | $\nu_{65}$ | 260.2 | 250.2 |
| $\nu_{49}$ | 316.3 | 304.1 | $\nu_{66}$ | 213.5 | 205.2 |
| $\nu_{50}$ | 186.7 | 179.4 | $\nu_{67}$ | 105.0 | 101.0 |
| $\nu_{51}$ | 111.4 | 110.0 | $\nu_{68}$ | 40.7 | 39.1 |
| $\nu_{52}$ | 47.7 | 45.9 | | | |

Table 2: Vibrational spectra and assignment of neutral picene. Frequencies ($\omega$) in $cm^{-1}$. The IR and R intensities, both experimental and calculated, are given as percentage of the mode with strongest intensity.

| Experimental | | | | Calculation | | | Assignment |
|---|---|---|---|---|---|---|---|
| $\omega$ | $I_{IR}(b)$ | $I_{IR}(a)$ | $I_R$ | $\omega$ | $I_{IR}$ | $I_R$ | |
| 518 | | | 13 | 507.5 | 0 | 0 | $a_1\nu_{32}$ |
| 588 | | | 53 | 573.3 | 0 | 0 | $a_1\nu_{31}$ |
| 644 | | | 60 | 630.5 | 0 | 1 | $a_1\nu_{30}$ |
| 729 | 9 | | | | | | |
| | | | | 715.8 | 0 | 2 | $a_1\nu_{29}$ |
| 731 | | 13 | 92 | | | | |
| 737 | 73 | 40 | | | | | |
| | | | | 721.9 | 9 | 0 | $b_1\nu_{60}$ |
| 743 | 100 | | | | | | |

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Table 2 – Continued

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 754 | 59 | 42 | | } | 738.2 | 90 | 0 | $b_1\nu_{59}$ |
| 759 | 44 | | | | | | |
| 791 | 8 | | | | | | |
| 807 | 91 | 44 | | | 789.7 | 100 | 0 | $b_1\nu_{58}$ |
| 821 | 18 | | | } | 800.0 | 31 | 0 | $b_1\nu_{57}$ |
| 823 | | 12 | | | | | | |
| 829 | 20 | | | | 836.8 | 19 | 0 | $b_2\nu_{95}$ |
| 864 | 9 | 13 | 18 | | 843.5 | 1 | 0 | $a_1\nu_{28}$ |
| 867 | | 10 | | } | 845.5 | 12 | 0 | $b_1\nu_{56}$ |
| 869 | 21 | | | | | | |
| 944 | 5 | 4 | | | 907.3 | 4 | 0 | $b_1\nu_{55}$ |
| 947 | 15 | 9 | | | 928.9 | 1 | 0 | $b_1\nu_{54}$ |
| 967 | 5 | | | | 947.0 | 0 | 0 | $b_1\nu_{53}$ |
| 1025 | | 5 | | | | | | |
| 1032 | | 6 | 46 | | 1025.5 | 1 | 3 | $a_1\nu_{26}$ |
| 1139 | | 12 | | | 1131.9 | 2 | 0 | $a_1\nu_{24}$ |
| 1147 | | | 15 | | 1144.6 | 0 | 1 | $a_1\nu_{23}$ |
| 1198 | | | 25 | | 1183.0 | 0 | 6 | $a_1\nu_{21}$ |
| 1265 | 31 | 35 | | | 1254.3 | 13 | 4 | $a_1\nu_{19}$ |
| 1275 | 24 | 29 | | | 1255.9 | 19 | 0 | $a_1\nu_{18}$ |
| 1345 | | | 19 | | 1323.8 | 2 | 22 | $a_1\nu_{17}$ |
| 1374 | | | 50 | | 1341.9 | 0 | 49 | $a_1\nu_{16}$ |
| 1379 | | | 100 | | 1358.4 | 1 | 100 | $a_1\nu_{15}$ |
| 1431 | 16 | | | } | 1421.7 | 8 | 19 | $a_1\nu_{14}$ |
| 1432 | | 32 | 28 | | | | | |
| 1437 | | 11 | | } | 1428.4 | 3 | 11 | $a_1\nu_{13}$ |
| 1439 | 13 | | 36 | | | | | |
| 1507 | | 6 | | | 1501.1 | 1 | 0 | $a_1\nu_{12}$ |
| 1516 | 4 | 8 | | | 1511.6 | 0 | 7 | $a_1\nu_{11}$ |
| 1576 | | | 21 | | 1559.4 | 0 | 7 | $b_2\nu_{78}$ |
| 1584 | 6 | | | } | 1579.5 | 6 | 0 | $a_1\nu_{10}$ |
| 1585 | | 9 | | | | | | |

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Table 2 – Continued

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1600 | | | 19 | 1597.9 | 2 | 2 | $b_2\nu_{77}$ |
| 1606 | 6 | 7 | 20 | 1604.2 | 5 | 4 | $a_1\nu_9$ |
| 1620 | 4 | | 50 | 1608.3 | 0 | 5 | $a_1\nu_8$ |

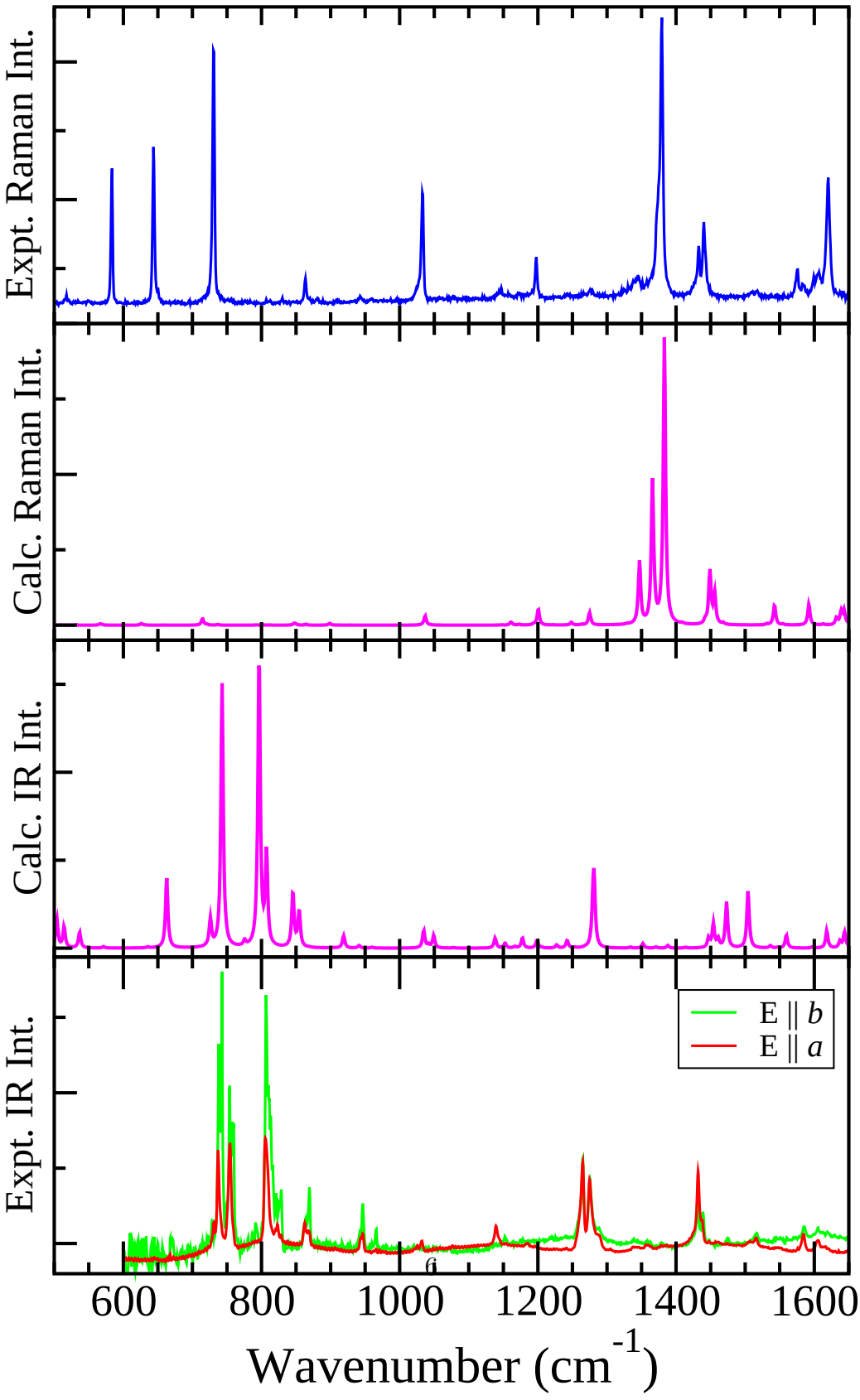


Figure 1: Experimental vs. calculated Raman and IR spectra of picene. The intensity scale is in arbitrary units.