Assignment of the B3LYP/6-31G(d,p) and BLYP/PW normal mode vectors

Normal mode analysis for porphycene (Pc) was carried out using two approximations to DFT, B3LYP/6-31G(d,p), as implemented in Gaussian 03 package, and BLYP/PW, as implemented in CPMD package. As a result, two sets of normal mode eigenvectors were obtained ($\boldsymbol{w}_i$ and $\boldsymbol{e}_j$, for B3LYP/6-31G(d,p) and BLYP/PW, respectively). The correspondence between the two sets was established by introducing two metrics in the $3N$-dimensional space: scalar product ($s_{ij} = \boldsymbol{w}_i \cdot \boldsymbol{e}_j$) and the root mean square deviation ($r_{ij} = \surd(\boldsymbol{w}_i - \boldsymbol{e}_j)^2/3N$). The two distance measures were calculated for all possible combinations ij of the normal mode eigenvectors, and pairs ($\boldsymbol{w}_i$, $\boldsymbol{e}_j$) of the corresponding vectors were found by locating the corresponding pairs of indices (i, j) for which $s_{ij} \approx 1$ (s was not strictly equal to 1, as it would have been in the case of parallel vectors, because normal mode vectors depend on the electronic potentials, which were different in the two cases). The RMSD criterion ($r_{ij} \approx 0$) was applied as an additional check. The assignment was, in most cases, unambiguous. In a few cases when it was doubtful (i. e. yielding $s_{ij} \approx 0.5$ for two different values of j) the graphical visualization of molecular vibrations served as the ultimate guide. Since the experimental spectra were assigned using the B3LYP/6-31G(d,p) calculations, the mapping between B3LYP/6-31G(d,p) and BLYP/PW normal modes resulted in the mapping between BLYP/PW frequencies and the experimental ones. Subsequent comparison of the computed frequencies with the experimental IR peak positions required applying a correction due to errors introduced by the approximate form of the exchange-correlation functional used in the DFT calculations. The correction factor c for each Pc isotopologue was obtained in a standard way by minimizing the sum of squared deviations from the experimental frequencies. The values of the correction factors obtained for the frequencies discussed in this paper are given in the main text. Error estimate for the BLYP/PW frequencies f_i was provided by optimizing the geometry of Pc molecule in two symmetrical *trans* configurations (see lower panel in Scheme 2) and calculating the corresponding normal mode frequencies. Had there been no finite basis set and grid-related errors, the difference between corresponding frequencies in the two sets should have been zero. In our case the RMSD of the two sets of values is approximately 5 cm^{-1} and it can serve as a numerical error estimate of the PW method.

Assessment of the inter-mode coupling strength

The assessment of the perturbation in the harmonic frequency of one normal mode due to the interaction with the other modes can be estimated according to the following procedure. The $3N$-dimensional electronic potential energy function is projected on a one-dimensional subspace spanned by the i-th normal mode vector by displacing the molecule from the equilibrium configuration $\boldsymbol{r}_0$ along the normal mode vector $\boldsymbol{e}_i$, and by calculating the total energy $E(\boldsymbol{r}_{i,k})$ at configurations $\boldsymbol{r}_{i,k} = \boldsymbol{r}_0 + k\,\Delta\,\boldsymbol{e}_i$, where $k = (-K_{min}, \ldots, 0, \ldots, K_{max})$ with $K = K_{max} + K_{min} + 1$ points separated by intervals Δ. The negative and positive displacements, $d_i^- = -K_{min}\Delta$ and $d_i^+ = +K_{max}\Delta$, i. e., displacements in the positive and negative directions along the axis determined by $\boldsymbol{e}_i$, are chosen in such a way that the amplitude $a_i = d_i^+ - d_i^-$ is equal to the average amplitude of the i-th mode as extracted from the AIMD trajectories used for the IR spectra computations. This ensures that the projection covers the relevant region of the phase space, sampled by the system at measurement conditions. The unperturbed harmonic frequency f_i, i. e., the eigenfrequency the i-th normal mode would have had if the other modes had been kept frozen, is found by fitting $E(\mathbf{r}_{i,k})$ with a quadratic function and using standard expression for the force constant of the harmonic oscillator. A similar procedure is routinely used in many vibrational analysis algorithms with $K=3$. An extension proposed here follows the same procedure which is used to calculate the harmonic frequency of a given mode i while keeping the system displaced along the second normal mode j by a constant displacement d_j. As there are two displacements d_j^+ and d_j^- for each mode j, two perturbed frequencies f_{ij}^+ and f_{ij}^- are obtained for the pair of modes i,j that encompass the frequency range in which the fundamental frequency f_i is perturbed by molecular motions along the normal mode j. The same procedure, repeated for all $3N-1$ normal modes $j \neq i$ yields the inter-mode coupling pattern for the mode i.