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Molecular dynamics simulations and anharmonic spectra of large PAHs

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Due to the difficulties in obtaining high-resolution infrared (IR) spectra of polycyclic aromatic hydrocarbon molecules (PAHs) from experiments, current study of PAHs have led to an ever-increasing reliance on computational quantum chemistry. Our recent results show that the second-order vibrational perturbations theory (VPT2) produce accurate anharmonic spectra, which are consistent well with the high-resolution low-temperature gas-phase experimental spectra of PAHs (Chen 2018). However, such method suffers from low efficiency of calculation, it only works for small molecules (less than 24 C-atoms). Moreover, high symmetric (D6h) molecules (e.g. coronene and circumcoronene) can not be calculated with such method (Mackie *et al.* 2016), but these species are actually expected to be highly abundant in space given their remarkable stability (Bauschlicher *et al.*2008).

Recently, we apply molecular dynamics (MD) simulations for producing anharmonic IR spectra of PAHs. In order to reduce the computational cost, the semi-empirical methods are utilized, which produce the potential energy surface (PES) efficiently at each step. The results are validated against the experimental spectra. A rather low value of the mean absolute error can be achieved with certain semi-empirical method and appropriate settings of the MD simulations, see our recent article for details (Chen *et al.* 2018).

As no assumptions about the shape of the PES is made, MD intrinsically accounts for anharmonicity, ro-vibrational couplings and temperature effects. In addition, MD is a time-dependent method, which has no restriction on the symmetry of the molecules. Therefore anharmonic IR spectra of molecules with D6h symmetry can also be produced by MD simulations. Using MD simulations, we manage to produce high-temperature anharmonic IR spectra of D6h PAHs, e.g. coronene and circumcoronene (Chen *et al.* 2018).

References

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