

## Supplementary Information

### **Nuclear quantum and H/D isotope effects on aromaticity: path integral molecular dynamics study**

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**Normal modes of benzene obtained by APFD/6-311G and CCSD(T)/aug-cc-pVQZ level of calculations.**

Table S1. Vibrational frequencies ( $\text{cm}^{-1}$ ) of benzene calculated using APFD/6-311G and CCSD(T)/aug-cc-pVQZ methods.

	APFD/6-311G	CCSD(T)/aug-cc-pVQZ
1	421.24	399.03
2	421.24	399.93
3	637.50	609.03
4	637.50	609.29
5	709.13	674.05
6	738.44	682.31
7	890.71	855.74
8	890.71	856.38
9	1014.28	972.17
10	1014.28	973.10
11	1019.28 ( <i>Breathing</i> )	973.63
12	1044.95	1004.04 ( <i>Breathing</i> )
13	1048.23	1017.04
14	1075.41	1054.16
15	1075.41	1055.31
16	1219.22	1157.72
17	1232.15	1189.19
18	1232.14	1190.42
19	1364.65 ( <i>Kekulé</i> )	1327.64 ( <i>Kekulé</i> )

20	1415.73	1372.21
21	1534.43	1507.50
22	1534.43	1508.45
23	1653.32	1635.38
24	1653.32	1635.74
25	3173.87	3168.16
26	3185.09	3178.41
27	3185.09	3178.87
28	3205.34	3194.76
29	3205.34	3195.11
30	3220.63 ( <i>C-H stretching</i> )	3204.93 ( <i>C-H stretching</i> )

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**The convergence of C-C and C-H bond distances with respect to the number of beads in the PIMD simulations of acetylene by the APFD/6-311G method.**

In order to confirm the convergence of C-C and C-H bond distances with respect to the number of beads, we performed PIMD simulations at the APFD/6-311G level with various numbers of beads using acetylene, which is the simplest molecule with C-C and C-H bonds, as the target molecule.

Figure S1 illustrated that the distribution of C-C bond distances converged at  $P = 8$  (green), while the C-H bond distances converged at  $P = 16$  (light blue). Therefore,  $P = 16$  is considered sufficient for the PIMD simulations of benzene.

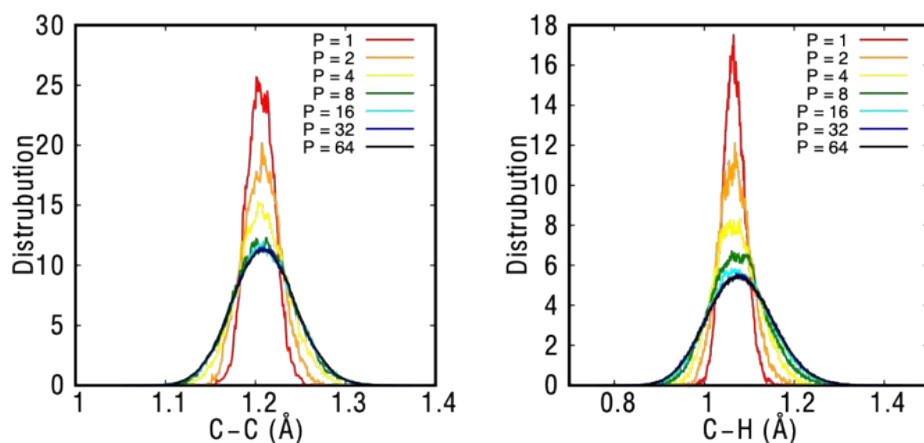


Figure S1. One-dimensional distributions of C-C and C-H bond distances obtained by PIMD simulations with various numbers of beads.

### The Classical Turning Points

For each vibrational mode, the extent of vibration resulting at the zero-point vibrational state was determined. As an example, the potential energy curve for the lowest energy normal mode,  $421.24\text{ cm}^{-1}$ , was shown in Figure S2 with the normal coordinate  $q$ . The zero-point vibration energy level was indicated by a dotted line in Figure S2.

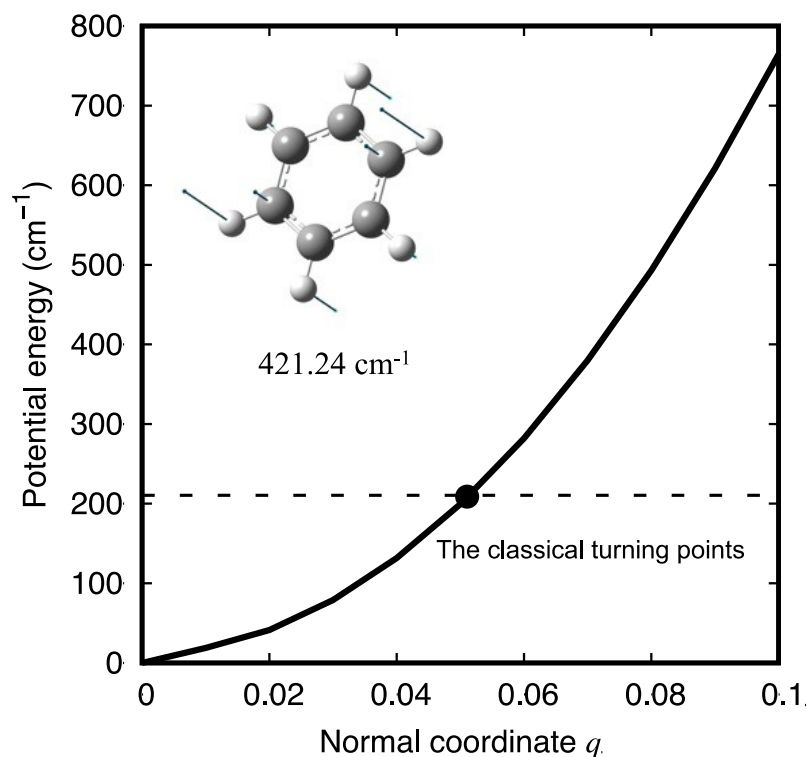


Figure S2. Potential energy curve for the 421.24 cm<sup>-1</sup> normal mode (solid line) in terms of the normal coordinate  $q$  and zero-point vibration energy (dotted line).

According to Figure S2, we could estimate that benzene in the vibration ground state vibrated up to the classical turning point. The classical turning point represents the intersection of zero-point vibration energy and normal mode motion, corresponding to the approximate maximum amplitude in the normal mode motion. To examine the effects of each normal mode on aromaticity, similar calculations were performed for all normal modes to obtain the classical turning point.