

**Table 1** List of fundamentals in the singlet ground state of  $C_6H_5^+$  showing positive anharmonic corrections at one or both levels of theory, sorted by irreducible representation.  $A_2$  fundamentals are IR inactive, while  $B_1$  are IR active

$C_6H_5^+$						
mode	B2PLYP			B3LYP		
	harm. $\bar{\nu}$	anh. $\bar{\nu}$ ( $cm^{-1}$ )	anh-harm	harm $\bar{\nu}$	anh. $\bar{\nu}$ ( $cm^{-1}$ )	anh-harm
<b><math>A_2</math></b>						
1	371.0	448.4	77.4	379.4	417.8	38.4
2	452.5	561.9	109.4	462.7	483.9	21.2
3	933.6	963.4	29.8	932.8	915.5	-17.3
<b><math>B_1</math></b>						
1	407.8	436.6	28.8	415.8	396.8	-19.0
2	526.9	612.2	85.3	526.7	514.7	-12.0
4	842.0	960.1	118.1	847.4	830.6	-16.8

## Supplementary Material

### IR photofragmentation of the Phenyl Cation: Spectroscopy and Fragmentation Pathways

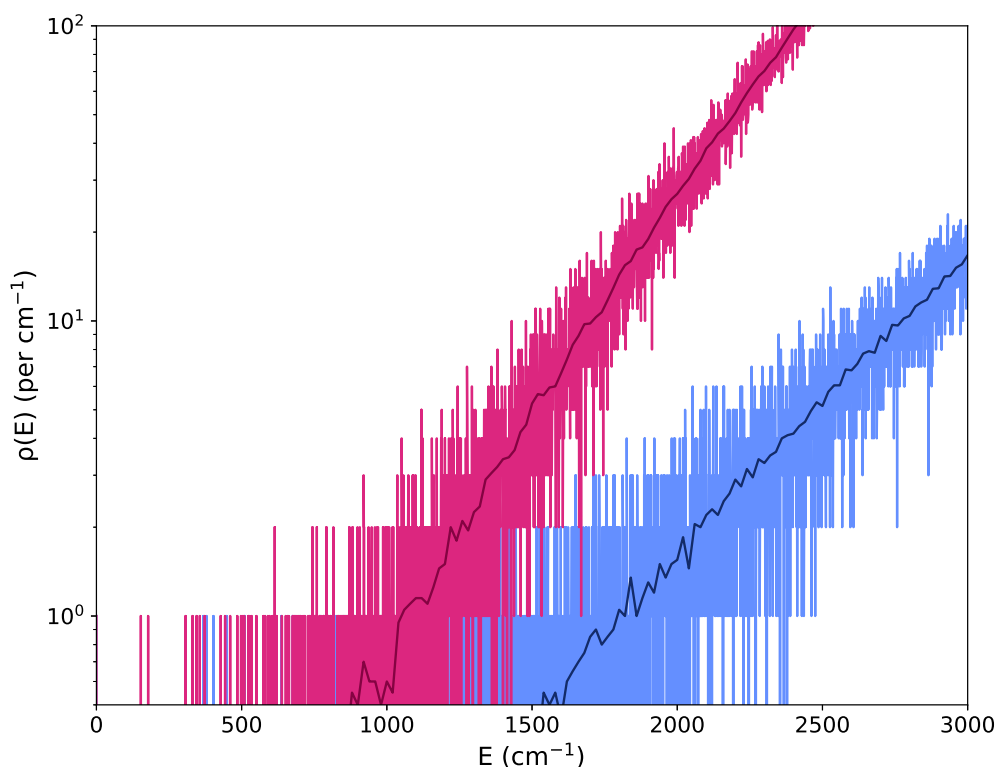
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#### Density of States

Previous attempts to record the IRMPD spectrum of gas-phase phenylium were unsuccessful. One potential cause for this is an insufficiently low IVR rate, necessary to mediate multiple-photon excitation. The IVR rate is linked to the vibrational density of states (VDOS). Fig. 1 shows the VDOS per  $cm^{-1}$  for the phenylium and the naphthylum cations (the smallest aryl studied so far with IRMPD), calculated using a direct count method on scaled harmonic frequencies.<sup>1</sup> The curves are accompanied by a smoothing (red), where the states are binned in 20  $cm^{-1}$  intervals. One here observes that the VDOS for naphthylum exceeds 1 per  $cm^{-1}$  only firmly above 1200  $cm^{-1}$ . Thus suggesting that already for naphthylum, sequential absorptions of photons, resulting in populating states higher than  $\nu = 1$ , are required before IVR becomes efficient. For phenylium, this regime is only reached around 2000  $cm^{-1}$ , suggesting that in this case even more photons need to be absorbed, and that the demand on IR intensity to drive these excitations should be similarly increased. The successful observation of IR-induced fragmentation illustrates the need for a high-fluence photon source like FELICE in the study of IRMPD-resistant molecules, as was also evidenced by the previous work at FELICE on three-<sup>2</sup> or four- atomic systems<sup>3-6</sup>, with dissociation energies higher than 1.8 eV. It is difficult to prove a direct link between the size of a system,<sup>7</sup> and hence with the vibrational density of states. However, it is perhaps telling that direct IR fragmentation of molecular systems with calculated binding energies exceeding 2 eV has been successful with a plethora of systems for the conventional FELIX beam lines (e.g. Oomens *et al.*<sup>8</sup>, Alvaro Galué and Oomens<sup>9</sup>); the only studies reporting IR-induced fragmentation of three- and four-atomic species were carried out using the FELICE beam lines<sup>2-6</sup>. As it is uncommon to report on failed experiments, only for the  $PtCH_2^+$  system was it explicitly reported that irradiation using the conventional FELIX beam line was fruitless<sup>10</sup>.

#### Anharmonic Calculations

Phenylium belongs to the  $C_{2v}$  point group and among its 27 fundamental vibrations, 24 are IR active (10  $A_1$  + 5  $B_1$  + 9  $B_2$ ). Initially, we performed VPT2 anharmonic calculations for  $C_6H_5^+$  and  $C_6D_5^+$  with the double hybrid functional B2PLYP<sup>11</sup> in conjunction with the triple zeta aug-cc-pVTZ basis set. The choice was motivated by the benchmark work on the anharmonicity of small to medium molecules<sup>12</sup>. However, the resulting spectrum did not compare well with the experimental spectrum: fundamentals were often blueshifted with respect to experimental peaks and strong modes appeared in regions of the spectra void of experimentally observed intensity. Inspection of the calculations revealed that some fundamentals, in particular modes of  $A_2$  and  $B_1$  symmetry, have exceptionally large positive anharmonic corrections, *i.e.*, these modes shift to higher frequency after anharmonic corrections (see Table 1). The  $A_2$  fundamentals can be described as symmetric out-of-plane (oop) modes involving different combinations of C-H groups. The  $B_1$  fundamentals are asymmetric oop



**Fig. 1** Harmonic vibrational density of states as function of energy for phenylium ( $C_6H_5^+$ , blue) and naphthylum ( $C_{10}H_7^+$ , magenta) with bins of  $1\text{ cm}^{-1}$  and smoothing with bins of  $20\text{ cm}^{-1}$ .

modes. Similar modes with large positive corrections are also present in  $C_6D_5^+$  and when triplet ground state multiplicity is considered.

Vibrational modes showing positive anharmonic corrections are very rare but some cases have been reported<sup>13,14</sup>. To test whether the vibrational modes with positive corrections reported here are indeed part of those special cases, we recalculated the anharmonic spectrum of  $C_6H_5^+$  and its perdeuterated counterpart at the B3LYP/N07D level, which is known to give quite accurate anharmonic vibrational spectra for Polycyclic Aromatic Hydrocarbons (PAHs)<sup>15,16</sup>. At B3LYP/N07D level, the previously unusual  $B_1$  modes now have negative anharmonic correction (they shifted to lower frequency after anharmonic corrections) and, of the  $A_2$  modes, only modes 1 and 4 in  $C_6H_5^+$  and only mode 1 in  $C_6D_5^+$  exhibit positive, albeit significantly smaller, anharmonic corrections (Table 1).

The test with a different level of theory together with lack of good match between the fully anharmonic spectrum provides strong evidence that the positive anharmonic corrections resulting from the calculations are spurious. We decided to choose the B3LYP/N07D level of theory to calculate the anharmonic spectra of both  $C_6H_5^+$  and  $C_6D_5^+$  and we treated the  $A_2$  modes harmonically, which showed positive anharmonic correction before. This was done in Gaussian 16 with the keyword *SkipPT2* that removes the derivatives with respect to any of the chosen normal modes. This implies that the anharmonic corrections of the remaining modes do not have contributions from the chosen modes. The new QFF anharmonic spectra showed an improved comparison to the experimental one in the case of  $C_6D_5^+$ . The harmonic treatment of its  $A_2$  mode at  $602\text{ cm}^{-1}$  cancelled its strong IR-active overtone appearing at  $671\text{ cm}^{-1}$  which does not have a counterpart in the experimental spectrum. For  $C_6D_5^+$ , differences between the two treatments are of 2-3  $\text{cm}^{-1}$ , both in maximum and average absolute deviations.

The QFF anharmonic spectrum of PAHs also exhibits modes with large negative corrections and harmonic treatment of the IR-inactive Raman-Active modes generally improves substantially the comparison of the theoretical spectrum to the experimental one<sup>17</sup>. The cause of this behaviour requires more investigation: only in few cases the results of QFF

anharmonic calculations of aromatic hydrocarbons have been compared to Raman spectra<sup>18</sup>. One reason could be that the predicted harmonic frequencies of these modes might show some dependence on the level of theory used, similar to what happens for the Kekulé modes in benzene and other hydrocarbons<sup>19,20</sup>. Alternatively, the harmonic term does not dominate the shape of the potential energy curve for these modes and thus the VPT2 treatment describes them poorly<sup>21</sup>.

## Notes and references

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