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The infrared spectra of polycyclic aromatic hydrocarbons containing a five-membered ring: symmetry breaking and the B3LYP functional

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Abstract. The infrared spectra of six molecules, each of which contains a five-membered ring, and their cations are determined using density functional theory; both the B3LYP and BP86 functionals are used. The computed results are compared with the experimental spectra. For the neutral molecules, both methods are in good agreement with experiment. Even the Hartree–Fock (HF) approach is qualitatively correct for the neutral species. For the cations, the HF approach fails, as found for other organic ring systems. The B3LYP and BP86 approaches are in good mutual agreement for five of the six cation spectra, and are in good agreement with experiment for four of the five cations where the experimental spectra are available. It is only for the fluoranthene cation where the BP86 and B3LYP functionals yield different results; the BP86 approach yields the expected C_{2v} symmetry, while the B3LYP approach breaks symmetry. The experimental spectra support the BP86 spectra over the B3LYP spectra, but the quality of the experimental spectra does not allow a critical evaluation of the accuracy of the BP86 approach for this difficult system.

Key words: Symmetry-breaking – Density functional theory – Vibrational frequencies

1 Introduction

There is now strong evidence that polycyclic aromatic hydrocarbons (PAHs) and/or their derivatives are responsible for the so-called unidentified IR bands, a family of discrete interstellar emission features observed in a wide variety of astronomical objects [1–3]. The combination of laboratory and computational studies [4, 5] has been very useful in improving the understanding of the nature of the PAH molecules in the interstellar emission regions. Specifically, it is now clear that this emission is dominated by cationic forms of PAHs. The majority of the available, relevant spectroscopic data on these species derives from studies of PAH cations generated by vacuum ultraviolet photoionization of the associated neutral molecules isolated in rare-gas matrices (matrix-isolation spectroscopy). Unfortunately, such measurements are difficult since the ionization efficiency of the in situ photolysis is typically no more than 5–10%. Consequently, the bands of the remaining neutral species may blend with or completely mask the cation peaks, rendering band intensities uncertain and leaving gaps in the spectral coverage. Ab initio calculations are thus invaluable both for interpretation of the experimental data as well as for filling in missing data.

We have previously computed the IR spectra of a variety of neutral PAH species and compared them with experimental spectra. We have found [6] that several relatively simple methods yield spectra that are in good agreement with experiment. Studies of the neutral molecules help us calibrate our methods, as well as confirm that the correct molecule, without significant impurities, is being examined in the experiment; however, the success of a method for the study of a neutral species does not confirm its use for a cation. For example, Hartree–Fock (HF), BP86 [7, 8], B3LYP [9, 10], and second-order Møller-Plesset perturbation theory (MP2) yield IR spectra of neutral naphthalene [6] that are in good agreement with experiment; however, when the same methods are applied to the naphthalene cation [6], only the BP86 and B3LYP approaches yield IR spectra that are in good agreement with experiment. The HF method fails because it completely neglects electron correlation; this results in a charge localization and a structure with C_{2v} symmetry rather than the correct D_{2h} symmetry. This distortion from the correct symmetry is commonly referred to as symmetry-breaking. The MP2 approach accounts for electron correlation and yields the correct D_{2h} symmetry; however, the level of the correlation

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treatment is too low to completely correct for the symmetry-broken HF reference, and the MP2 approach yields poor frequencies and intensities. This suggests that the density functional theory (DFT) approaches, which also add electron correlation at a low-level approximation, work because the orbitals are optimized with correlation included, rather than added in a second step as is done in the MP2 approach.

As the naphthalene cation work demonstrates, the best approach for the cost-effective calculation of IR spectra is one of the DFT approaches; however, the choice between the B3LYP and BP86 functional is not universal. Our experience has been that the geometries and frequencies are very similar at the B3LYP and BP86 levels of theory, but, in general, the B3LYP approach works somewhat better for organic molecules, while, in general, the BP86 works better for organometallic compounds. The energetic properties are almost always superior at the B3LYP level. On the basis of this experience, we have used the B3LYP approach for the study of the PAH molecules and their cations. While experience has shown that the DFT approaches can treat a very large number of systems accurately, even these approaches are susceptible to symmetry-breaking, as we have discussed previously [11] for metal-containing systems and show for an organic system in this report. The problem of symmetry-breaking has been discussed previously for small molecules [12–15], where it was shown that this problem can be solved using multiconfigurational approaches. Unfortunately, it would be difficult to apply these approaches to large PAH molecules, therefore it is of interest to investigate the application of DFT approaches to such a problem.

2 Computational methods

The geometries are optimized and harmonic frequencies computed using the HF, BP86, and B3LYP approaches. The basis sets are those developed by Frisch et al. [16]. Most of the calculations are performed using the 4-31G set. Previous studies have shown [6] this small set yields surprisingly good frequencies for the PAH molecules and cations. Its biggest failing is the overestimation of the C-H stretching intensity by a factor of about 2; however, the small size of the basis set allows the study of large molecules in a reasonable amount of computer time, which more than compensates for the overestimation of the C-H stretching intensity.

The default "finegrid" is used in all DFT calculations, except in one test where the grid is improved; the number of radial points is increased from 74 to 96 and the number of angular points from 302 to 974. The calculations are performed using the Gaussian 94 computer codes [17].

To illustrate the results, we present synthetic spectra and compare them with experimental spectra. To put the experimental and theoretical spectra on a more equivalent footing, the experimental spectra are analyzed and the band positions and relative intensities are used to generate synthetic spectra with a full width at half-maximum (FWHM) of 30 cm^{-1}, the natural linewidth of a molecule emitting under the conditions of the interstellar medium. Since the absolute intensity is unknown for the experimental results, the experimental spectra are scaled to look like the theoretical spectra that have been generated using the same FWHM. We reduce the FWHM to 20 cm^{-1} when we compare the different levels of theory to illustrate some of the smaller differences in the spectra. Finally we note that the B3LYP harmonic frequencies are scaled by 0.958, the BP86 by 0.986, and the HF by 0.91.

3 Results and discussion

3.1. Neutral molecules

The six molecules studied computationally in this work are shown in Fig. 1. The experimental spectra of five of the neutrals, fluoranthene, benzo[*a*]-, benzo[*b*]-, benzo [*j*]-, and benzo[*k*]fluoranthene, have been published previously [18]. In this work we report an experimental spectrum for acenaphthylene. The number of frequencies for these six molecules is very large and the frequencies are not tabulated here, but are available at http://ccf.arc.nasa.gov/~cbauschl/astro.data5r. In addition to the computed results for all six molecules and the experimental results for acenaphthylene, the Web page also includes the previously published experimental data for the benzofluoranthenes. This allows a clear comparison of the computed and experimental results.

The overall good agreement between theory and experiment for the IR spectra of the six neutral molecules is shown in Figs. 2–7. While the band positions are very good, there are differences between theory and experiment for the relative intensities of some bands, especially for closely spaced bands of the same symmetry. This is consistent with our previous experience [4, 6] where the relative intensity for two closely spaced bands is somewhat sensitive to the level of theory, while the sum of the two intensities is relatively insensitive to the level of theory used. For the C-H stretching region, which is not shown in the figures, theory and experiment agree relatively well for the positions, but the experimental intensities tend to be significantly smaller than those found in theory. This is consistent with previous work [6] that suggests the small 4-31G basis set tends to yield a C-H stretching intensity that is about a factor of 2 too large.

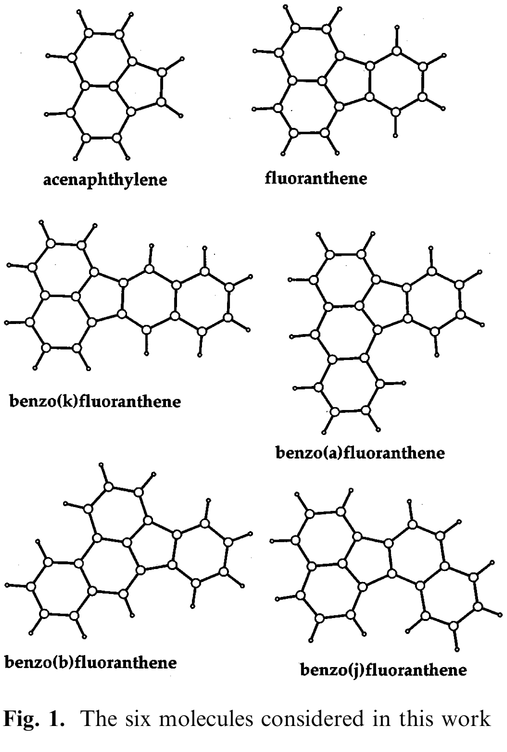

Fig. 1. The six molecules considered in this work

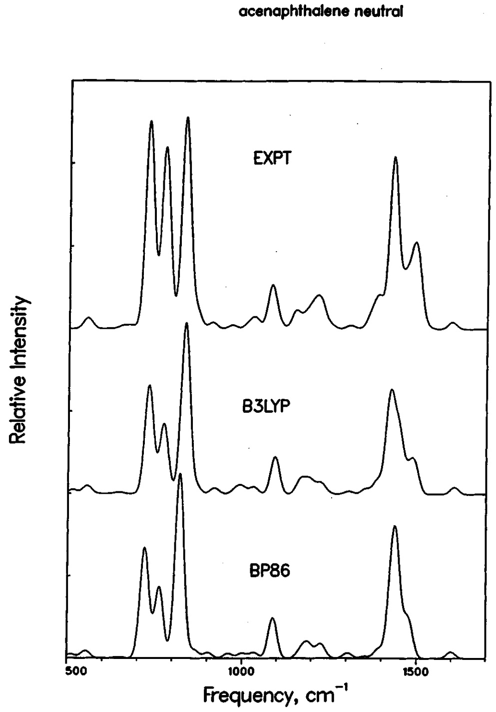

Fig. 2. The BP86, B3LYP, and experimental spectra of acenaphthylene. The full width at half-maximum (*FWHM*) is 30 cm^{-1}

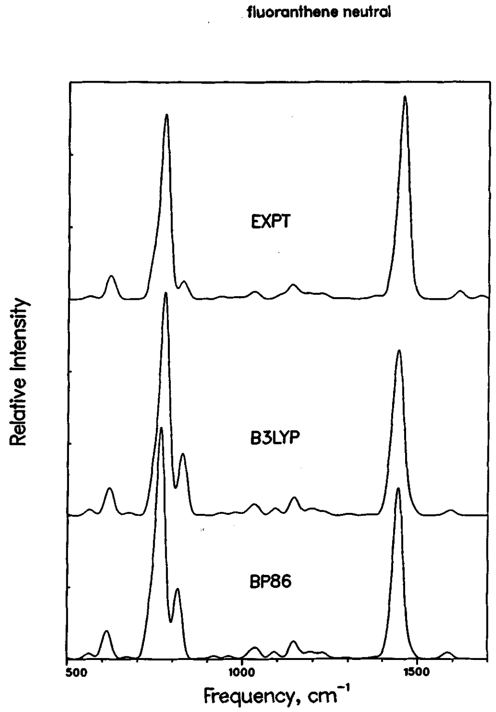

Fig. 3. The BP86, B3LYP, and experimental spectra of fluoranthene. The FWHM is 30 cm^{-1}

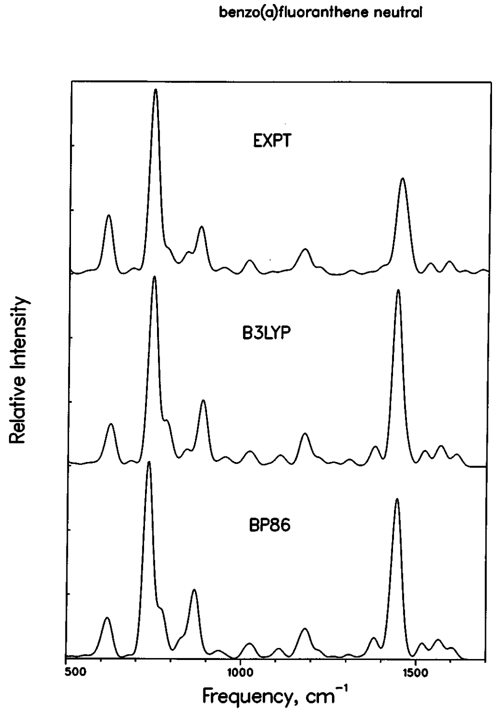

Fig. 4. The BP86, B3LYP, and experimental spectra of benzo[*a*] fluoranthene. The FWHM is 30 cm^{-1}

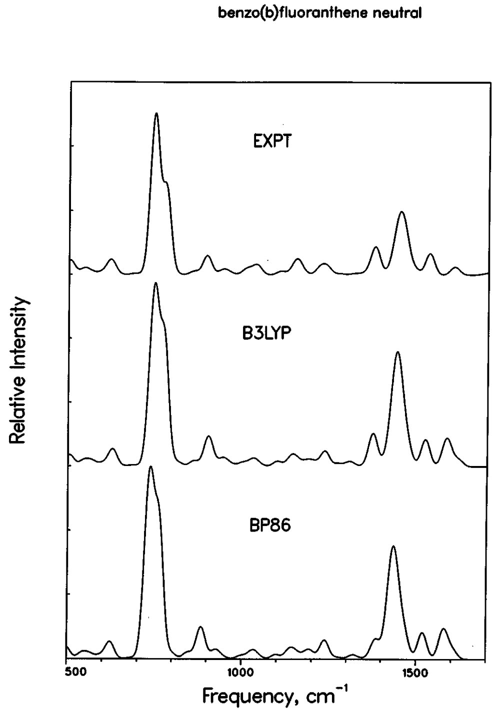

Fig. 5. The BP86, B3LYP, and experimental spectra of benzo[*b*] fluoranthene. The FWHM is 30 cm^{-1}

At the resolution shown in the figures, it is difficult to choose between the B3LYP and BP86 approaches. Assuming that all 214 assignments given in the Web file are correct, the average absolute errors for the BP86 and B3LYP approaches are 7.3 and 5.1 cm^{-1}, respectively. If only the strongest bands are considered, the B3LYP approach again works the best. See, for example, the strong bands near 825 cm^{-1}, where an inspection of the figures shows the B3LYP band positions are, in general, superior to those obtained using the BP86 approach;

however, it is clear that, overall, both methods perform well. Conversely, the agreement between theory and experiment for the six molecules strongly suggests that there are no significant contaminants present in the experimental studies.

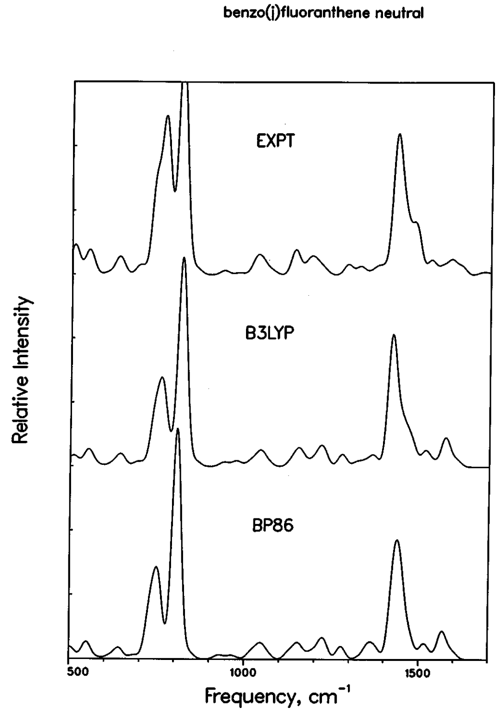

Fig. 6. The BP86, B3LYP, and experimental spectra of benzo[*j*] fluoranthene. The FWHM is 30 cm^{-1}

While the HF/4-31G spectra for the six neutral molecules are not shown, they are qualitatively correct, but less accurate than either of the DFT approaches. One obvious difference is that the HF band positions are not as accurate as those obtained at the DFT level, and this problem is not corrected by a single scale factor. For example in fluoranthene, a 0.91 scale factor brings the HF C-H stretch into good agreement with the B3LYP and BP86 approaches, while factors of 0.88 and 0.85 bring the HF bands at about 1450 and 800 cm^{-1}, respectively, into agreement with experiment.

3.2. Cations

Experiments were performed on the six molecules shown in Fig. 1. Excluding acenaphthylene, it was possible to obtain cation IR spectra. A detailed description of the experimental and DFT spectra for these five species will be presented elsewhere. Here we focus on the computational aspects of obtaining accurate harmonic frequencies for these species, and more specifically on the symmetry-breaking that occurs for the fluoranthene cation.

Before discussing the fluoranthene cation, we assess the accuracy of the methods for the remaining cations. The experimental and computed spectra of benzo[*a*]fluoranthene and benzo[*k*]fluoranthene are shown in Figs. 8 and 9. Overall, there is reasonable agreement between the experimental and DFT spectra, which is consistent with many other PAH systems [4–6] that do

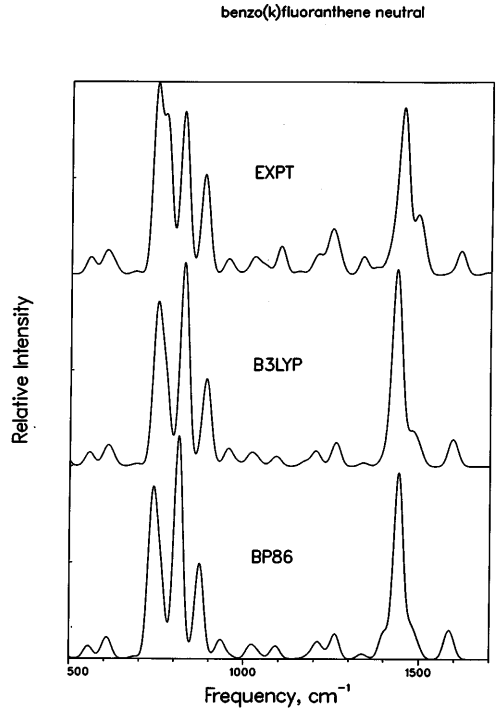

Fig. 7. The BP86, B3LYP, and experimental spectra of benzo[*k*] fluoranthene. The FWHM is 30 cm^{-1}

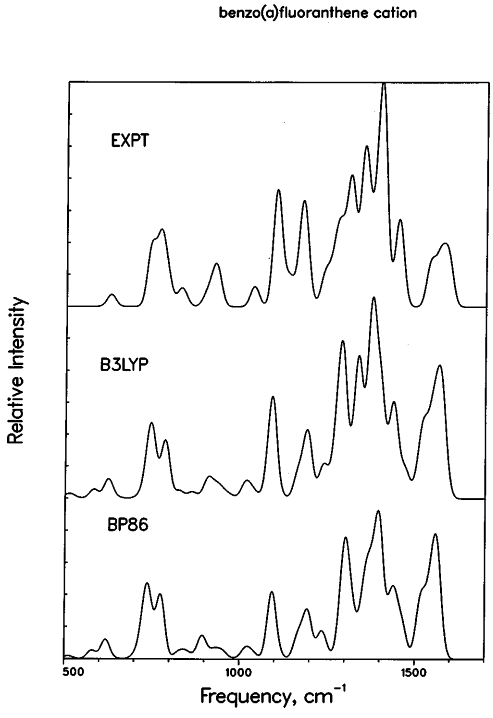

Fig. 8. The BP86, B3LYP, and experimental spectra of the benzo [*a*] fluoranthene cation. The FWHM is 30 cm^{-1}

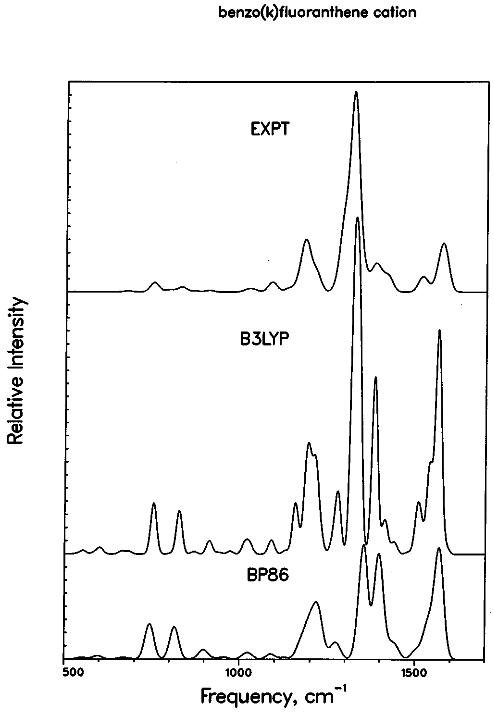

Fig. 9. The BP86, B3LYP, and experimental spectra of the benzo [*k*]fluoranthene cation. The FWHM is 30 cm^{-1}

not contain a five-membered ring. The DFT spectra contain bands missing in the experimental spectra, which we attribute to problems associated with the cation experiments. There are clearly some differences in relative intensities, which probably arise from problems with theory for the intensities of closely spaced bands and from the experimental cation problems. An inspection of the benzo[*k*]fluoranthene synthetic spectra, see Fig. 9, shows that the B3LYP band positions are superior to those obtained using the BP86 approach; the average absolute error for the five strongest band is 11.5 and 5.0 cm^{-1} for the BP86 and B3LYP levels of theory, respectively.

Due to its lower symmetry (C_s versus C_{2v}), the experimental spectrum of benzo[*a*]fluoranthene is more complicated than that for benzo[*k*]fluoranthene, having 26 bands with relative intensities of 0.1 or greater. The bands shown in Fig. 8 between 1236 and 1450 cm^{-1} are actually a superposition of 13 of the 26 strong bands. There is also some uncertainty in the correspondence between the bands found in theory and in experiment; for example, one pair of experimental bands appears to be associated with only one computed band. Assuming that this is due to a site splitting, we averaged this pair of bands and compared the resulting 25 experimental bands with theory. The average absolute errors of these 25 bands are 7.5 and 7.7 cm^{-1} for the BP86 and B3LYP levels of theory, respectively. While the average errors are consistent with those found for the neutral species, there are two bands that differ by more than 20 cm^{-1} with experiment at both the B3LYP and BP86 levels of theory. Thus the errors for the cations are somewhat larger than for the neutral species, but not dramatically so.

While we cannot use experiment to assess the accuracy of the computed results for the acenaphthylene cation, it is still important to compare the B3LYP and BP86 results, as acenaphthylene contains one less six-membered ring than fluoranthene while the benzofluoranthenes all contain one more six-membered ring. The B3LYP and BP86 spectra for acenaphthylene are shown in Fig. 10. The spectra are similar, with the biggest difference being near 1100 cm^{-1}. There are two b_2 bands in this region and the B3LYP has virtually all of the intensity in the lower frequency band, while the BP86 has 72% of the intensity in the higher of these two modes. This change in intensity coupled with a 20 cm^{-1} difference in the band positions results in the observed change in the spectra. Despite the differences, the two methods are in reasonable agreement. It is hoped that it will eventually be possible to obtain an experimental IR spectra of the acenaphthylene cation to allow us to critically evaluate the methods, but for now we take the agreement between the BP86 and B3LYP methods as indicating that we are able to describe the acenaphthylene cation, and therefore conclude that the size of the molecules is not a critical factor in determining the accuracy of the methods used.

The structure of the fluoranthene cation is optimized and the IR spectra are computed at the BP86 and B3LYP levels of theory. The BP86 approach yields a structure with C_{2v} symmetry, like the neutral species, while the B3LYP yields a planar C_s structure. Given the difference in the structural symmetry, it is not surprising that the IR spectra of the BP86 and B3LYP approaches differ; they are shown in Fig. 11 along with the experimental spectra. We first note that the experiment was

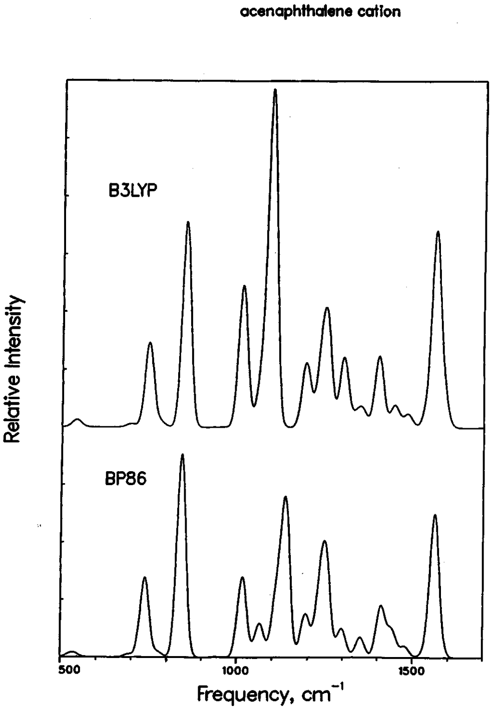

Fig. 10. The BP86 and B3LYP spectra of the acenaphthylene cation. The FWHM is 30 cm^{-1}

Table 1. The vibrational frequencies (in cm^{-1}) and relative intensities for the fluoranthene cation

BP86			Experiment		B3LYP		
Symmetry	Frequency	Relative intensity[a]	Frequency	Relative intensity	Symmetry	Frequency	Relative intensity[b]
b_1	753.2	0.654			a''	763.7	0.232
a_2	771.2	0.000			a''	783.2	0.009
a_1	801.4	0.002			a'	801.7	0.008
b_1	812.1	0.205	831.7	0.16	a''	824.1	0.076
a_2	877.8	0.000			a'	880.5	0.296
a_1	884.0	0.072			a''	893.5	0.000
a_2	909.4	0.000			a'	898.4	1.000
b_1	928.2	0.002			a''	923.9	0.000
b_1	944.1	0.003			a''	942.9	0.000
b_2	955.8	1.000			a''	959.0	0.001
b_2	976.7	0.597	1009.8/ 1015.5	0.71	a'	975.3	0.025
a_2	984.7	0.000			a''	1001.7	0.000
a_2	988.9	0.000			a'	1006.3	0.053
b_1	991.2	0.002			a''	1006.6	0.000
a_1	1012.9	0.043			a''	1008.1	0.001
b_2	1028.5	0.028			a'	1027.7	0.029
a_1	1050.1	0.034			a'	1048.3	0.024
a_1	1083.8	0.105			a'	1075.9	0.126
b_2	1090.0	0.500			a'	1084.5	0.122
b_2	1149.6	0.093			a'	1138.8	0.009
a_1	1188.1	0.011			a'	1187.6	0.036
a_1	1199.5	0.152	1183.4	0.57	a'	1193.2	0.083
b_2	1216.7	0.041			a'	1210.5	0.073
b_2	1229.1	0.283	1225.2	0.26	a'	1226.5	0.106
a_1	1269.0	0.185	1276.1	0.17	a'	1264.7	0.006
b_2	1275.9	0.069			a'	1272.9	0.193
b_2	1330.8	0.000			a'	1318.6	0.073
a_1	1343.1	0.347			a'	1337.4	0.198
a_1	1385.8	0.363			a'	1371.2	0.098
b_2	1395.5	0.018			a'	1402.5	0.010
a_1	1410.6	0.227			a'	1409.6	0.061
a_1	1434.8	0.478	1433.8	1.00	a'	1429.5	0.245
b_2	1437.0	0.180			a'	1444.0	0.075
a_1	1445.9	0.002			a'	1451.1	0.001
b_2	1472.2	0.049			a'	1475.0	0.024
b_2	1498.9	0.112			a'	1493.3	0.108
b_2	1511.5	0.038			a'	1520.9	0.119
a_1	1531.2	0.047			a'	1534.5	0.026
a_1	1572.0	0.543			a'	1570.3	0.255
a_1	1590.5	0.007			a'	1593.9	0.003

[a] The maximum band intensity is 196.28 km mol^{-1}

[b] The maximum band intensity is 489.73 km mol^{-1}

very difficult to perform, with only a weak ion signal. This, combined with neutral species still in the matrix means that weak bands might be missing. We have included the experimental spectra of the neutral species to help understand the obvious differences between the experimental and theoretical cation spectra. On the basis of the spectra of the cation and the neutral species, we assume that cation bands below 800 and above 1500 cm^{-1} are hidden by bands of the neutral species and therefore do not consider these differences further. To aid in the discussion, we have included the computed and experimental data in Table 1; note that we do not include the C-H stretching modes and have deleted the 22 lowest frequency theoretical frequencies. We first note that the strongest band in the B3LYP spectrum is at 898 cm^{-1}, which does not correspond to any of the bands in the experimental spectrum, and this is in a region where there are no bands from neutral species to obscure the cation band. If it corresponds to the strong bands at 1009.8 and 1015.5 cm^{-1}, this represents an error of more than 100 cm^{-1}. If it is assigned to the 831.7 cm^{-1} the error is smaller, but it is then difficult to assign the B3LYP band at 880.5 cm^{-1}. At the B3LYP level, the 898.4 cm^{-1} band is even more intense than the strongest band in the benzo[*k*]fluoranthene cation spectra, which seems inconsistent with the problems in obtaining an experimental spectrum. The BP86 approach results in two strong b_2 bands at 956 and 977 cm^{-1}, which suggests an error of up to 60 cm^{-1}. It is also possible that the BP86 approach has incorrectly assigned most of the intensity to the 956 cm^{-1} band instead of the 977 cm^{-1}, as we have observed previously for nearby bands of the same symmetry. In this case the BP86 approach is in error by about 30 cm^{-1}, which we have observed for other cations. An inspection of the table, shows that a plausible assignment can be made for the experimental bands to the BP86 spectrum, although there are missing bands, such as the strong BP86 band at

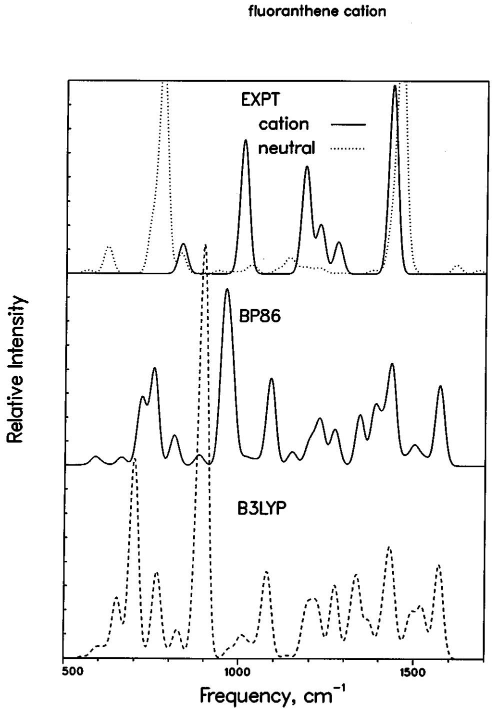

Fig. 11. The BP86, B3LYP, and experimental spectra of the fluoranthene cation. The experimental spectrum of the fluoranthene neutral species is also given. The FWHM is 30 cm^{-1}

1090 cm^{-1}. This is in contrast with the B3LYP approach, where it is difficult to assign the experimental spectrum. Thus the experimental spectrum appears to rule out the symmetry-broken B3LYP spectrum and supports the BP86 spectrum. Unfortunately, we cannot make a definitive assessment of the accuracy of the BP86 spectrum, but the results suggest that it may be only slightly less accurate than found for the previous systems.

Given the apparent failure of the B3LYP approach for fluoranthene, we studied acenaphthylene, fluoranthene, and benzo[*k*]fluoranthene in more detail, as they all have C_{2v} symmetry and differ in the number of six-membered rings (Fig. 1). We first note that there are two low-lying states of the cations. At the equilibrium geometry of the neutral molecules, we evaluate the BP86(B3LYP) $^2B_1 - {}^2A_2$ separation for acenaphthylene, fluoranthene, and benzo[*k*]fluoranthene; the values are −7.73(−8.30), 4.32(4.34), 15.00(14.58) kcal/mol, respectively, where the negative sign indicates that the ground state is $^2B_1$. The two states are closest for fluoranthene and the separation is very similar for the BP86 and B3LYP levels of theory, but only the B3LYP level breaks symmetry by mixing the $^2A_2$ and $^2B_1$ states. In Fig. 12 we plot the a_2 and b_1 orbitals of the neutral system and the highest doubly occupied and open-shell orbitals for the ion. The plot shows that for B3LYP the a_2 and b_1 π orbitals mix to localize the orbitals on one side of the molecule, which results in the cation undergoing a slight distortion away from C_{2v}. We should note that this symmetry-breaking is not related to the grid used in the numerical integration; tightening the grid increases the computation time by about a factor of 5, but leads to no significant differences; the maximum change in frequency is 1.8 cm^{-1} and 1 km mol^{-1} in intensity.

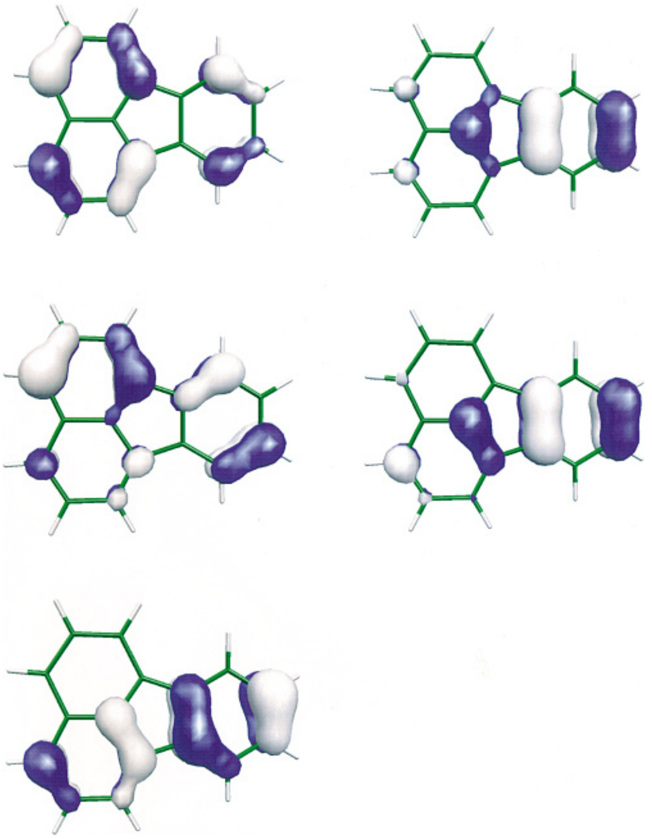

Fig. 12. The *top* two orbitals are the two highest orbitals of the neutral species. The *middle* two orbitals are the α and β associated with the doubly occupied orbital, while the *bottom* orbital is the open-shell orbital

The geometry was optimized and vibrational frequencies computed for the $^2B_1$ state of fluoranthene to investigate the possibility that both the BP86 and B3LYP approaches incorrectly order these two states. For both functionals, the $^2B_1$ state had one imaginary frequency. If the geometry was displaced in the direction indicated by the imaginary frequency, the solutions collapsed to those derived from the $^2A_2$ state. Thus all remaining tests were performed on the $^2A_2$ state, or the C_s solution derived from it.

In Fig. 13 we show the BP86 and HF spectra. While the HF spectrum has C_{2v} symmetry, like the BP86 one, the spectra are clearly very different. This failure of the HF method for the cation has been observed previously [6], and shows the importance of including electron correlation in the treatment of the cations. As already noted, the HF approach works much better for the neutral species.

In Fig. 14 we show BP86 spectra as a function of the basis set. There are only small changes with the addition of polarization functions on the carbon, with enhancing the size of the valence basis set, or with both basis set improvements. The same basis set tests are performed for the B3LYP level with the constraint of C_{2v} symmetry (see

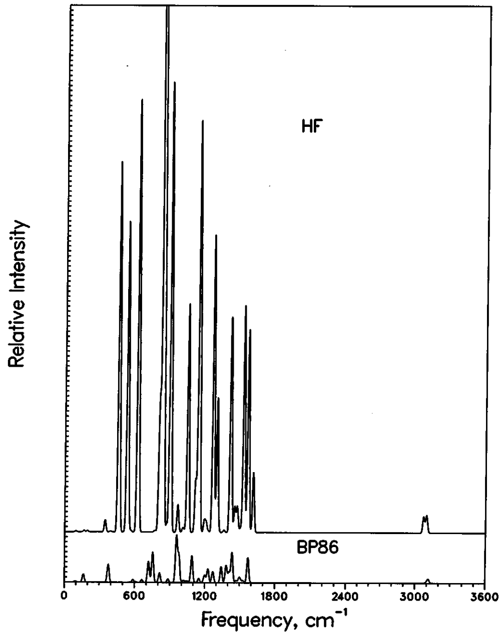

Fig. 13. The BP86 and Hartree–Fock spectra of the fluoranthene cation. The FWHM is 20 cm^{-1}

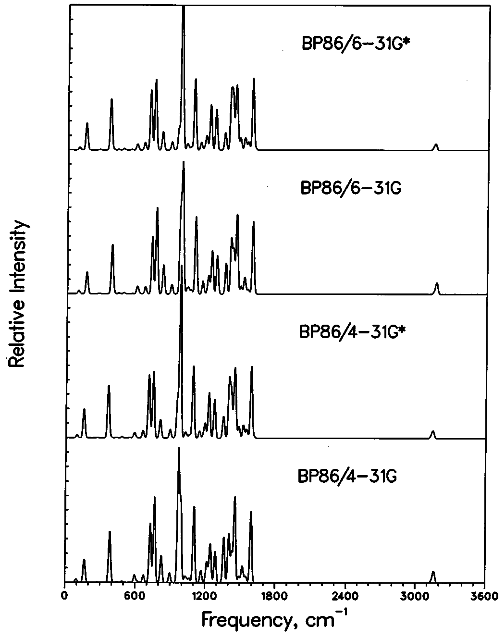

Fig. 14. The BP86 spectra of the fluoranthene cation for several different basis sets. The FWHM is 20 cm^{-1}

Fig. 15). Adding a polarization function to the 4-31G basis set makes a very small change in the spectra. Improving the valence basis set to 6-31G removes the imaginary frequency, but the largest change is the shift of the imaginary frequency to a small real frequency. Thus the spectra still look like the B3LYP/4-31G C_s spectra, not the BP86 spectra. Adding a polarization function to the 6-31G valence basis set results in an imaginary frequency; i.e., the B3LYP results are somewhat sensitive to

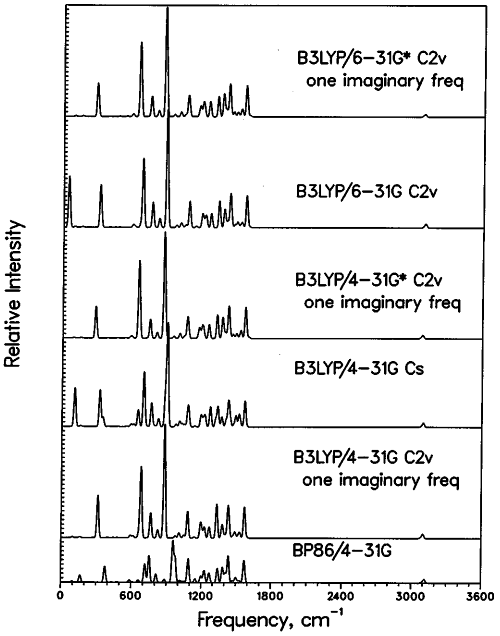

Fig. 15. The B3LYP spectra of the fluoranthene cation as a function of the basis set. The BP86 results in the 4-31G basis set are given for comparison. The FWHM is 20 cm^{-1}

the choice of basis set, and none of them look like the spectra obtained using the BP86 approach.

The B3LYP spectra are clearly inconsistent with the experimental spectra. The BP86 spectra are consistent with experiment, but there are some unexplained missing bands, and so a definitive comparison of the BP86 and experimental spectra is difficult. If one assumes that the missing experimental bands are due to problems associated with obtaining cation spectra, the BP86 approach has approximately the same accuracy for fluoranthene as for other cations; i.e., the BP86 approach has worked for the fluoranthene cation, while the usually more reliable B3LYP approach has failed.

4 Conclusions

In those cases where the B3LYP approach does not break symmetry, it appears to be slightly more accurate than the BP86 approach, but both methods appear to be in reasonable agreement with experiment and could be used to help interpret the experimental spectra. For the fluoranthene cation, where there are two states close in energy, the B3LYP approach appears to break symmetry resulting in a less-accurate spectrum. The BP86 approach appears to work as well for this cation as for many others; however, the experimental spectrum for the fluoranthene cation is not ideal, and therefore we are unable to definitively determine the accuracy of the BP86 approach. It appears that unexpected symmetry-breaking in the B3LYP approach can be detected by running the BP86 approach. In those cases where the two methods agree, the spectra can be expected to be accurate. In those cases where they disagree, additional tests will be required to determine the most accurate approach.

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