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Electronic Supporting Information for

Decoding the infrared signatures of pyramidal carbons in graphenic molecular nanostructures of interstellar origin

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Contents

Modeling of graphenic molecular nanostructures and IR spectra relevant to astronomical UIR emission bands

The employed B3LYP functional is a hybrid DFT Kohn-Sham approach that includes generalized exchange-correlation gradient corrections and some degree of exact Hartree-Fock exchange energy.[1] This functional has a proven efficacy predicting the electronic structures and IR absorption spectra of sp^2–hybridized polycyclic hydrocarbon species relevant to the unidentified infrared (UIR) bands.[2] The structures are optimized at the point group symmetry listed in Table 1, although in a few cases the next lower symmetry point-group was used to avoid saddle-point structures in the ionized state. Harmonic fundamental modes (ν=0→1) are computed at the same level of theory as for the electronic optimizations. The model spectra are simulated by convoluting fundamental modes with a Gaussian function profile of full-width height at maximum of 30 cm^{-1}. This value is consistent with astronomical observations[3] in the spectral range of 6--9 μm (1666--1111 cm^{-1}), which is the region where CC-stretch vibrational modes are found. Owing to the dynamics of the excitation-emission process, other band profiles can be more accurate when comparing with the UIR bands;[4] however, here we are mainly interested on demonstrating the structure-strain spectral relationship concept and Gaussian profiles serve for the purpose. Hot and combination bands can occur at the temperatures reached by the interstellar nanostructures,[5] but these are overshadowed by the stronger IR-active fundamentals[3, 4] and their contribution to the spectral profiles of the 6--14 μm astronomical UIR spectra is in most cases marginal.

To correct for effects of truncation of the basis function set and of the use of the harmonic approximation, we apply an unique frequency scaling factor of 0.965 and 0.971 to modes located in the 6--16 μm range for 6-31G and 6-31G(*d,p*), respectively. By exercising various factors, the scaled peak positions of IR bands were calibrated against the experimental peak positions of the buckybowl corannulene in neutral and cationic-protonated states recorded by FT-IR and IR-MPD spectroscopic techniques.[6] The spectrum of corannulene radical cation has also been reported but it cannot be used to calibrate with certainty harmonic frequencies since it is a Jahn-Teller dynamical system.[6] Tables S1—S4 list the peak positions in wavenumbers (cm^{-1}) of computed and measured bands, and corresponding percentage difference (*diff)* for a particular scaling factor. Bringing all harmonic peak positions to match the measured peak positions is evidently impossible since bands are carried by modes with different vibrational bond character. In general, high frequency modes, such as those characterized by aromatic C-H or C=C stretches, are subjected to larger dynamical anharmonic effects than lower frequency modes such as those characterized by aromatic C-H in-plane or C-H out-of-plane bending vibrations.[5, 7] Here, the criteria for selecting the two scaling factors are based on adjusting the peak positions of IR bands containing C=C stretching mode character. For neutral corannulene these bands occur at 1410 and 1433 cm^{-1}, whereas for protonated corannulene we focus on the C=C mode band at 1594 cm^{-1}. The condition consists of minimizing the relative error (|*diff*|) without incurring in a redshift of calculated harmonic C=C-mode bands relative to measured bands. This is a 'best-fitting' scheme learned after empirically scaling harmonic B3LYP spectra with respect to gas-phase IR spectra of numerous ionized polycyclic systems.[7, 8] It is based on the fact that C=C stretching modes display a larger anharmonic redshift than C-H in-plane and CH out-of-plane modes.[7] Since the two spectroscopic techniques inherently introduce different levels of anharmonic frequency shifts, a compromise is found between both. For the B3LYP/6-31G(*d,p*) level of theory, the two factors that do not redshift CC-mode IR bands relative to experimental values are 0.971 and 0.975 in the case of neutral corannulene. These two factors also have a similar relative difference. For the spectrum of protonated corannulene, the scaling factor 0.971 displays the lowest relative difference compared to 0.975, and hence 0.971 is selected. For the B3LYP/6-31G level of theory, the factor 0.965 provides a good compromise for the smallest |*diff*| without a redshift of CC-mode bands in both neutral and protonated spectra.

Table S1. Peaks positions (in cm^{-1}) of experimental IR bands of *neutral* corannulene compared to harmonic IR bands computed at B3LYP/6-31G(*d,p*) and scaled at various factors.

f_{exp}	f_{harm}	**0.962**		**0.966**		**0.971**		**0.975**	
837	857	824	*1.55*	827	*1.14*	832	*0.63*	835	*0.22*
1135	1167	1123	*1.06*	1128	*0.65*	1134	*0.13*	1138	*-0.3*
1314	1340	1289	*1.9*	1294	*1.49*	1301	*0.98*	1306	*0.58*
1410	1456	1401	*0.64*	1407	*0.23*	1414	*-0.3*	1420	*-0.7*
1433	1480	1424	*0.63*	1430	*0.21*	1437	*-0.3*	1443	*-0.7*
Average diff (%):			*1.16*		*0.74*		***0.23***		*-0.2*

Table S2. Peaks positions (in cm^{-1}) of experimental IR bands of *protonated* corannulene ion compared to harmonic IR bands computed at B3LYP/6-31G(*d,p*) and scaled at various factors.

f_{exp}	f_{harm}	**0.962**		**0.966**		**0.971**		**0.975**	
850	875	842	*0.94*	846	*0.53*	850	*0.01*	853	*-0.4*
1198	1222	1176	*1.84*	1181	*1.43*	1187	*0.92*	1192	*0.51*
1320	1369	1317	*0.23*	1322	*-0.19*	1329	*-0.71*	1335	*-1.1*
1394	1424	1370	*1.72*	1376	*1.31*	1383	*0.8*	1389	*0.39*
1594	1652	1589	*0.31*	1596	*-0.1*	1604	*-0.62*	1610	*-1*
average diff (%):			*1.01*		*0.6*		***0.08***		*-0.3*

Table S3. Peaks positions (in cm^{-1}) of experimental IR bands of *neutral* corannulene compared to harmonic IR bands computed at B3LYP/6-31G and scaled at various factors.

f_{expt}	f_{harm}	**0.955**		**0.960**		**0.965**		**0.970**	
837	880	840	*-0.4*	845	*-0.9*	849	*-1.4*	853	*-1.96*
1135	1190	1136	*-0.1*	1142	*-0.7*	1148	*-1.2*	1154	*-1.7*
1314	1360	1298	*1.19*	1305	*0.67*	1312	*0.15*	1319	*-0.37*
1410	1463	1397	*0.91*	1404	*0.39*	1412	*-0.1*	1419	*-0.65*
1433	1495	1427	*0.39*	1435	*-0.1*	1442	*-0.6*	1450	*-1.17*
Averaged diff (%):			*0.4*		*-0.1*		***-0.6***		*-1.17*

Table S4. Peaks positions (in cm^{-1}) of experimental IR bands of *protonated* corannulene ion compared to harmonic IR bands computed at B3LYP/6-31G and scaled at various factors.

f_{expt}	f_{harm}	**0.955**		**0.960**		**0.965**		**0.970**	
850	896	856	*-0.7*	860	*-1.2*	865	*-1.73*	869	*-2.26*
1198	1248	1192	*0.48*	1199	*-0.04*	1205	*-0.56*	1211	*-1.08*
1320	1385	1322	*-0.2*	1329	*-0.7*	1336	*-1.22*	1343	*-1.75*
1394	1438	1373	*1.51*	1380	*1*	1387	*0.48*	1395	*-0.04*
1594	1658	1583	*0.67*	1592	*0.15*	1600	*-0.37*	1608	*-0.89*
Averaged diff (%):			*0.36*		*-0.16*		***-0.68***		*-1.2*

Finally, please note that applying scaling factors to harmonic frequencies generated by quantum-chemical procedures is a necessary practice primarily due to the finite size of the basis set used. The success of a frequency calibration is strongly dependent on the theory, molecular system, and experimental technique used to record the relevant spectrum. Fortunately, in this investigation we don't rely on absolute frequency values of band positions, but rather on relative band positions. Thus, unscaled mode frequencies can also lead to the development of the structure-strain IR spectral concept central to reach the conclusions of this study.

Supplementary references

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