

Assignment of phantom bands in the solid-state infrared and Raman spectra of coronene: The importance of a minute out-of-plane distortion

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The molecular geometry and the normal modes properties of coronene are investigated by means of DFT(B3LYP) and restricted/Hartree–Fock calculations utilizing basis sets of triple zeta +polarization quality. The interpretation of the infrared and Raman spectra of coronene, especially in solid state, is critically revised. The phantom bands in the solid state, previously not understood, are readily assigned after considering a minute out-of-plane molecular distortion from D_{6h} to C_{2h} .
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I. INTRODUCTION

Coronene ([6]-circulene, $C_{24}H_{12}$) is the smallest member of the pericondensed benzenoid aromatic hydrocarbons (C_{6n} H_{6n}) with the highest possible D_{6h} symmetry. Its molecular structure and the closely related vibrational activity are of much current relevance to material science and astronomy. For instance, the molecule is often used as a model compound of graphene and graphitic materials. These studies on carbonaceous substances are well justified by their numerous and important technological applications (Mapelli *et al.*¹ and references cited). In the search of structure-property relationships, infrared and Raman spectroscopy have come forward as indispensable experimental and theoretical tool. It was argued^{1–5} that the appearance of the D band in the Raman spectra of all graphitelike materials with some degree of disorder and/or defects in the perfect crystalline structure is due to the formation of sp^2 islands (oligomers) of molecular size.

In parallel, a vast experimental and theoretical effort has been invested in the interpretation and assignment of the diffuse interstellar infrared emission bands (Mulas *et al.*⁶ and references cited). Polycyclic aromatic hydrocarbons, both in gas phase and in soot, have been alleged as the most possible carriers. As a model system coronene is constantly involved in the majority of these studies.

Clearly, a deep understanding of the molecular structure and vibrational motion of coronene is essential for the correct modeling of carbon-based materials on macroscale, as well as for the unambiguous molecular spectral identification in the observed interstellar radiation.

In the present study, we extend the current understanding of the properties of coronene. Based on our density functional quantum chemical calculations, we propose a novel interpretation of the solid-state infrared and Raman spectra of coronene. Experimental bands observed *only* in the solid-state infrared^{7,8} and solid-state Raman⁹ spectra but absent in the gas phase spectra,¹⁰ the so called phantom bands, are

readily assigned when a minute out-of-plane distortion (concomitant with a symmetry reduction from D_{6h} to C_{2h}) is considered. Such an out-of-plane distortion is consistent with single crystal x-ray structure measurements.¹¹

II. COMPUTATIONAL APPROACH

Molecular geometry and normal modes properties of neutral coronene are investigated with density functional theory (DFT) using the B3LYP functional as implemented in GAUSSIAN 98.¹² In addition, restricted/Hartree–Fock (RHF) calculations are carried out with GAMESS-UK.¹³ In this study, we utilized two basis sets constructed from a Dunning triple zeta (TZ) basis set¹⁴ augmented with p-polarization functions for the hydrogen atoms ($\alpha_p=0.75$) and d-polarization functions for the carbon atoms with either $\alpha_d=0.5$ or $\alpha_d=0.6$ referred here after as TZP($\alpha_d=0.5$) and TZP($\alpha_d=0.6$). The potential energy surface will prove to be very sensitive to such a small change in d exponent.

A. Density functional theory calculations

At B3LYP/TZP($\alpha_d=0.5$) level of theory, the optimized molecular geometry restricted to the D_{6h} point group represents a genuine minimum, i.e., the calculated Hessian matrix is positive definite. However at B3LYP/TZP($\alpha_d=0.6$) level, we located a first order transition state, i.e., one sizable negative eigenvalue of the Hessian matrix was found. The b_{2g} normal mode with the calculated imaginary frequency of $679i$ cm^{-1} caused an out-of-plane C_{2h} symmetry reduction. The latter result is unexpected since coronene is known to be flat and D_{6h} symmetrical. Notwithstanding, the majority of the corresponding harmonic frequencies calculated at both B3LYP/TZP($\alpha_d=0.5$) and B3LYP/TZP($\alpha_d=0.6$) levels of theory deviated from each other by only approximately 2 cm^{-1} . The few harmonic frequencies that showed an abnormal basis set dependence are summarized in Table I. Noticeable differences in the infrared and Raman intensities between all corresponding normal modes calculated with either TZP($\alpha_d=0.5$) or TZP($\alpha_d=0.6$) were not observed in D_{6h} symmetry constrained coronene.

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TABLE I. Harmonic frequencies (ω , cm^{-1}) calculated at B3LYP/TZP ($\alpha_d=0.5$) and B3LYP/TZP($\alpha_d=0.6$) level of theory that deviate more than 5 cm^{-1} upon change of basis set. Both calculations used the D_{6h} symmetry (constrained) molecular geometry optimized at the corresponding level of theory.

Irrep.	TZP($\alpha_d=0.5$)	TZP($\alpha_d=0.6$)
b_{2g}	561	679i
	773	709
e_{2u}	551	526
	771	739
	827	815
	676	668

Since internal instabilities in the Kohn–Sham determinant¹⁵ may cause the appearance of phantom imaginary frequencies, we carried out a stability analysis at the stationary points and found the Kohn–Sham determinants to be stable. When DFT is used additional care must be taken to insure sufficient numerical accuracy in the quadrature for the numerical integration. Thus we substituted the default “Fine-Grid” in GAUSSIAN 98 (Ref. 12) (75 radial shells and 302 angular points per shell) with the “UltraFine” grid (99 radial shells and 590 angular points per shell) and repeated the computational procedure. The normal modes properties, including the imaginary frequency, did not depend significantly on this parameter. A two-electron basis set incompleteness error, which is significantly different for planar versus non-planar geometries, was reported to be responsible¹⁶ for the artificial imaginary frequencies in benzene and arenes. However since Hartree–Fock and DFT are fundamentally *one-electron* theories, they are not likely to be sensitive to this *two-electron* basis set incompleteness error.¹⁶

Thus, we find a one-electron basis set incompleteness error to be the most probable cause for the abnormal computational basis set dependence of the potential energy surface of coronene. We still cannot argue against either the B3LYP/TZP($\alpha_d=0.5$) or B3LYP/TZP($\alpha_d=0.6$) calculations. Therefore, considering the possible symmetry reduction, we relaxed the geometrical D_{6h} symmetry constraints to

allow for out-of-plane C_{2h} symmetry distortion and reoptimized the molecular geometry using the B3LYP/TZP($\alpha_d=0.6$) method. The calculated positive definite Hessian matrix confirmed that the located stationary point, a slightly out-of-plane distorted coronene, is a minimum.

Most of the calculated normal modes properties (e.g., harmonic frequencies, infrared and Raman intensities) survived the small computational D_{6h} to C_{2h} symmetry reduction without being appreciably affected. Only a few b_{2g} and e_{2u} normal modes were profoundly altered (see Table II). The b_{2g} normal mode with calculated imaginary harmonic frequency of $679i \text{ cm}^{-1}$ (D_{6h} symmetry) corresponds to an a_g mode with calculated real harmonic frequency of 648 cm^{-1} at the C_{2h} symmetrical minimum. In addition, this peculiar normal mode is Raman active in the C_{2h} symmetry calculated Raman spectrum (see Table II). Other b_{2g} , as well as some of the e_{2u} normal modes (D_{6h} symmetry) not only changed in frequency but also gained Raman/infrared intensity upon D_{6h} to C_{2h} symmetry reduction (see Table II). Clearly, a comparison between the experimental and theoretical Raman and infrared spectra will shed light on whether symmetry reduction is supported or not.

For graphical illustration of the imaginary b_{2g} normal mode (the D_{6h} symmetry calculation) and the corresponding real a_g normal mode (the C_{2h} symmetry calculation) see Figs. 1 and 2 (Video 1 and Video 2), respectively.

B. Restricted Hartree–Fock calculations: Basis set or geometry

We have established that the usage of either the B3LYP/TZP($\alpha_d=0.5$) or the B3LYP/TZP($\alpha_d=0.6$) method leads to differences in the molecular geometry, potential energy surface and normal modes properties of coronene. Particularly, differences in the infrared and Raman intensities for some of the normal modes have been underlined. To avoid any possible confusion, we emphasize here that the differences in the calculated normal modes properties, especially the differences in intensities, are mainly due to differ-

TABLE II. All b_{2g} and e_{2u} harmonic frequencies (ω , cm^{-1}), infrared (I, km/mole), and Raman (Raman, $\text{\AA}^4/\text{AMU}$) intensities calculated at B3LYP/TZP($\alpha_d=0.6$)/ D_{6h} level compared with the corresponding a_g and paired a_u , b_u normal modes properties calculated at B3LYP/TZP($\alpha_d=0.6$)/ C_{2h} . The table is a numerical illustration of how the calculated b_{2g} and e_{2u} normal modes defer in frequency and/or intensity upon symmetry reduction.

b_{2g} (D_{6h})		a_g (C_{2h})		e_{2u} (D_{6h})		a_u , b_u pairs (C_{2h}) ^a	
ω	Raman	ω	Raman	ω	I	ω	I
228	f ^b	226	f	87	f	87 ^b	f,
679i	f	648	65.2	300	f	302	f, f
709	f	866	361.2	526	f	543	0.2
991	f	993	2.6	739	f	762	f, f
				815	f	823	f
						821	f
				987	f	988	vw ^b
						989	vw

^aAn a_g , b_g pair is considered degenerate if the difference in the wave number is $\leq 0.5 \text{ cm}^{-1}$.

^bf stands for forbidden; vw stands for very weak.

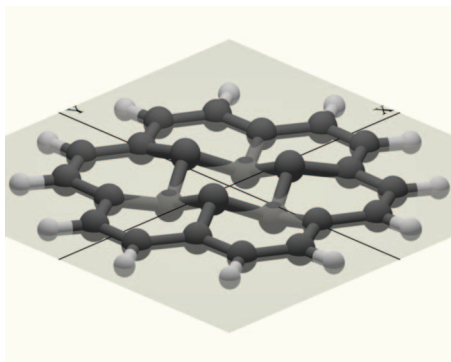


FIG. 1. A short movie that visualizes one period of the imaginary b_{2g} normal mode (D_{6h} symmetrical stationary point) calculated at the B3LYP/TZP($\alpha_d=0.6$) level (enhanced online). [URL: <http://dx.doi.org/10.1063/1.3282331.1>]

ences in the molecular geometry/symmetry rather than being a basis set artifact. For instance, when the molecule is restricted to the D_{6h} point group, no appreciable disparities in infrared/Raman intensities calculated with either TZP($\alpha_d=0.5$) or TZP($\alpha_d=0.6$) are observed. Note that b_{2g} (e_{2u}) modes are symmetry forbidden, whereas a_g (a_u and b_u) modes are symmetry allowed in one-photon Raman (infrared) spectroscopy.

To further substantiate the importance of geometry/symmetry, we used GAMESS-UK (Ref. 13) to carry out illustrative RHF calculations. Changing the electronic structure method from DFT to RHF does not change the picture of Sec. I. When restricted to the D_{6h} point group, the molecular geometry optimized with the RHF/TZP($\alpha_d=0.5$) and RHF/TZP($\alpha_d=0.6$) method represents a minimum and a first order transition state respectively according to the Hessian calculations. On D_{6h} to C_{2h} symmetry reduction, the changes in molecular geometry and normal modes properties follow the same pattern as described for the DFT calculations (Table II and *vide infra* Fig. 6). Now, we performed a non-conventional vibrational analysis at the C_{2h} symmetrical stationary point identified as a minimum at RHF/TZP($\alpha_d=0.6$) level of theory using the RHF/TZP($\alpha_d=0.5$) method. The positive definite Hessian matrix in combination with small gradients suggests that the imposed geometry is not very far from the D_{6h} symmetrical minimum at

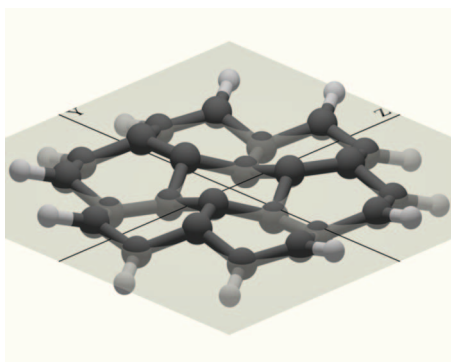


FIG. 2. A short movie that visualizes one period of the real a_g normal mode (C_{2h} symmetrical stationary point) calculated at the B3LYP/TZP($\alpha_d=0.6$) level (enhanced online). [URL: <http://dx.doi.org/10.1063/1.3282331.2>]

TABLE III. Harmonic frequencies (ω in cm^{-1}) and Raman intensities (Raman in $\text{\AA}^4/\text{AMU}$) of the two normal modes that depended on the basis set: RHF/TZP($\alpha_d=0.5$) or RHF/TZP($\alpha_d=0.6$). Both calculations were conducted at the C_{2h} symmetrical minimum obtained at RHF/TZP($\alpha_d=0.6$) level of theory.

Irrep.	TZP($\alpha_d=0.6$)		TZP($\alpha_d=0.5$)	
	ω	Raman	ω	Raman
b_{2g}	405 ^a	337.9	889	207.1
b_{2g}	798	67.1	680	97.1

^aThe b_{2g} normal mode with an imaginary harmonic frequency of $127i \text{ cm}^{-1}$ at RHF/TZP($\alpha_d=0.6$) level of theory and D_{6h} symmetry constrained geometry.

RHF/TZP($\alpha_d=0.5$) level of theory. More importantly, the normal modes properties calculated with either the RHF/TZP($\alpha_d=0.5$) or RHF/TZP($\alpha_d=0.6$) method at the RHF/TZP($\alpha_d=0.6$) C_{2h} symmetrical geometry are nearly identical. Two b_{2g} modes are exceptional (see Table III) in the way their frequencies depended on the basis set, however, it is clearly seen from Table III that both modes gain comparable intensity in the Raman spectrum regardless of the basis set used. Thus the change in normal mode properties is a geometry effect and not due to basis set effects.

III. VIBRATIONAL SPECTROSCOPY

Previous theoretical work¹⁰ reported Raman and infrared spectra of D_{6h} coronene. The authors used a scaled quantum mechanical force field approach, based on density functional calculations at the B3LYP/6-31G* level. The calculated spectra were compared with experiment. Although the gas-phase infrared spectrum of coronene was well understood, several unresolved features, the so-called phantom bands were found in both solid-state Raman and solid-state infrared spectra of coronene.

Before we proceed with the spectra interpretation, it is noteworthy that all theoretical frequencies are calculated within the harmonic approximations and they do not directly compare with the experimental fundamentals.

A. Infrared spectroscopy

Wave numbers and intensities of the calculated harmonic frequencies and the experimental infrared active fundamentals are compiled in Table IV.

The most remarkable feature of all solid-state infrared spectra of coronene is the unexpected medium-strong band at about 960 cm^{-1} . Cyvin *et al.*⁷ reported a doublet at 958 cm^{-1} (medium) and 962 cm^{-1} (weak). Joblin *et al.*⁸ did not analyze the $900\text{--}1100 \text{ cm}^{-1}$ range, although a medium-strong band at approximately 960 cm^{-1} is also clearly visible in their solid-state spectrum (cf. Fig. 2a in Ref. 8). This phantom band could not be understood in terms of planar D_{6h} symmetrical coronene. The calculated spectrum has no infrared active modes in the $900\text{--}1100 \text{ cm}^{-1}$ region. However, in our B3LYP/TZP($\alpha_d=0.6$) spectrum calculated for the slightly corrugated coronene (the out-of-plane C_{2h} minimum), we see a very weak a_u , b_u doublet with disproportional intensities at approximately 988 cm^{-1} (see Table IV).

TABLE IV. Experimental (fundamental) wave numbers (ν in cm^{-1}), theoretical (harmonic) frequencies (ω in cm^{-1}) and the corresponding experimental/calculated infrared intensities (I in km/mole).

Expt. ^a (gas-phase)		Calc. B3LYP/TZP($\alpha_d=0.6$)						Expt. ^b (solid-state)	
		D _{6h} symmetry			C _{2h} symmetry				
I	ν	I	ω	Irrep.	Irrep. ^c	ω	I	ν	I
44.4	545	7.4	124	a _{2u}	b _u	125	7.3	151	m
		3.9	384	e _{1u}	b _u	384	3.9	379	m
					a _u	385	4.0		
		0.0	526	e _{2u}	a _u , b _u	543	0.1		
		45.6	560	a _{2u}	b _u	562	44.4	544 ^d	s
26.9	767	0.0	565	b _{1u}	b _u	565	0.5	549 ^e	m
		6.3	784	e _{1u}	a _u , b _u	784	6.3	764 ^f	w
								769	m
		0.0	824	e _{1u}	b _u	821	0.0	811	m
					a _u	823	0.0		
112.2	848	173.1	876	a _{2u}	b _u	878	173.1	847 ^g	vs
		0.0	987	e _{2u}	a _u	988	0.0 ^h	959 ^e	w
					b _u	989	0.1	962 ^e	m
								1125	w
14.8	1136	10.7	1155	e _{1u}	a _u	1156	10.5	1125	m
					b _u	1157	10.5	1136	m
		0.9	1235	e _{1u}	a _u , b _u	1236	0.9	1184	vw
29.9	1308	21.6	1337	e _{1u}	a _u , b _u	1337	21.6	1314	s
		0.4	1426	e _{1u}	a _u , b _u	1427	0.4	1411	vw
		3.4	1531	e _{1u}	a _u , b _u	1532	3.4	1494	w
								1525 ^e	w
13.6	1599	7.3	1652	e _{1u}	a _u , b _u	1653	7.2	1606	m
40.2	3017	2.8	3166	e _{1u}	b _u	3166	2.9	1614	m
					a _u	3167	3.1	3017	m
					a _u	3182	0.9		
120.6	3051	66.2	3185	e _{1u}	a _u	3185	64.9	3045 ^e	m
					b _u	3185	65.9	3050	m

^aReference 8.^bReference 7.^cAn a_g, b_g pair is considered degenerate if the difference in the wave number and/or intensity is $\leq 0.5 \text{ cm}^{-1}$.^dJoblin *et al.* (Ref. 8) reported a multiplet between 540 and 550 cm^{-1} .^ePreviously not assigned as a fundamental.^fJoblin *et al.* (Ref. 8) reported a doublet at 764 and 770 cm^{-1} .^gA doublet at 845 and 849 cm^{-1} .^hThe actual calculated intensity is 0.0002 km/mole for the a_g mode and 0.053 km/mole for the b_g mode.

This quasidegenerate a_u, b_u doublet corresponds to an infrared forbidden e_{2u} mode in D_{6h} symmetry. The experimentally observed band around 960 cm^{-1} would not appear if coronene were planar and D_{6h} symmetrical.

Another typical feature of the solid-state infrared spectra is the multiplet at approximately 545 cm^{-1} . Cyvin *et al.*⁷ reported two bands—a medium one at 549 cm^{-1} and a strong one at 544 cm^{-1} . Joblin *et al.*⁸ reported a strong quadruplet (540, 543, 545, and 550 cm^{-1}). This band was previously assigned to an a_{2u} fundamental of the D_{6h} symmetrical coronene. The calculated spectrum of the slightly corrugated (C_{2h}) coronene has a strong a_u fundamental (562 cm^{-1} ; a_{2u} in D_{6h}), an infrared active b_u mode (565 cm^{-1} ; silent b_{1u} mode in D_{6h} symmetry) and an infrared active quasidegenerate a_u, b_u doublet (543 cm^{-1} ; silent e_{1u} mode in D_{6h} symmetry). Hence, symmetry reduction is supported. These most unique regions (500–600 and

900–1000 cm^{-1}) in the solid-state infrared spectra of coronene are illustrated in Fig. 3.

The majority of the e_{1g} modes of the D_{6h} symmetrical coronene were assigned to experimental doublets (cf. Table IV). Consider now a weakly corrugated coronene. All e_{1g} fundamentals are nearly (but not exactly) degenerate pairs, e.g., a_u and b_u pairs in C_{2h} symmetry. Thus the abundance of experimentally degenerate e_{1g} modes points to molecular symmetry reduction. The experimental doublet at about 847 cm^{-1} remains a bit obscure since it was assigned to a b_u mode (calculated at 878 cm^{-1} ; a_{2u} in D_{6h} symmetry). We can only argue that the nearby a_u, b_u pair (calculated at 823 and 821 cm^{-1}) splits significantly (in fact this e_{1g} mode shows the most profound degeneracy lifting of 2 cm^{-1}) so that the a_u fundamental (calculated at 823 cm^{-1}) joins the strong b_u fundamental (calculated at 878 cm^{-1}) to form the experimental doublet. The b_u fundamental (calculated at 821 cm^{-1}) then matches the experimental band at 811 cm^{-1} .

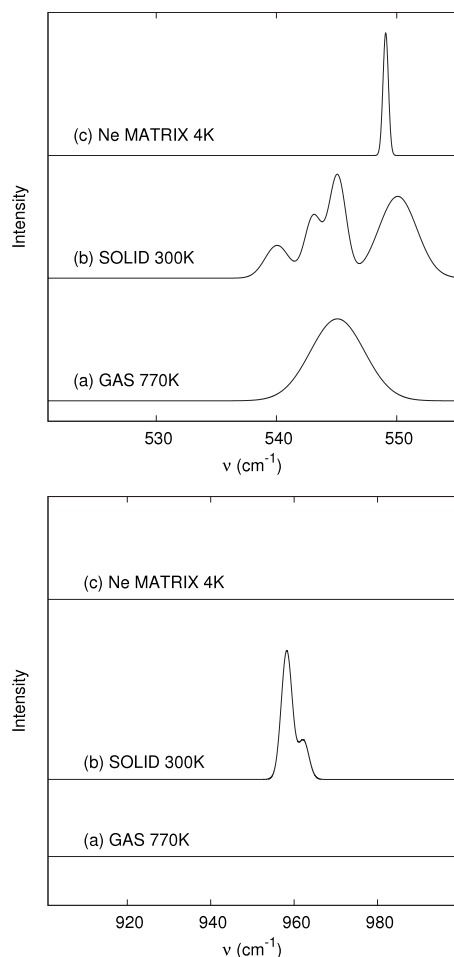


FIG. 3. Illustration of two of the most distinguishing features of the solid-state infrared spectrum of coronene (b) [derived from Table II, Figs. 2a and 2g in Ref. 8] compared with the gas-phase infrared spectrum (a) [derived from Table II, Figs. 2a and 2g in Ref. 8] and its infrared spectrum in low temperature Ne Matrix (c) [derived from Table II, Figs. 2a and 2g in Ref. 8]. The bands' positions are exactly as presented in Ref. 8. The shapes of the bands are qualitatively modeled with Gaussian functions to match the experimentally observed bands (Ref. 8) as closely as possible. The band at approximately 540 cm^{-1} represents four-frequency absorptions in the solid state, whereas in the gas-phase and the low temperature Ne matrix spectrum this band represents a one-frequency absorption. The band at approximately 960 cm^{-1} is present only in the solid-state spectrum and represent a two-frequency absorption. See Table IV for the exact band positions.

The B3LYP/TZP($\alpha_d=0.6$) spectrum calculated at the C_{2h} stationary point (qualitatively) explains all the unresolved features¹⁰ of the experimental solid-state spectra^{7,8} of coronene.

B. Raman spectroscopy

The calculated Raman spectra are compared with experiment in Table V. A couple of unresolved features of the experimental Raman spectrum of crystalline coronene⁹ have been pointed out.¹⁰ The most puzzling ones are (i) the band at 571 cm^{-1} with medium intensity and (ii) the weak band at 828 cm^{-1} . These experimental lines did not appear in the calculated (Raman) spectrum of the D_{6h} symmetrical coronene.¹⁰ To date, they are not considered as fundamentals. However, our theoretical work based on the C_{2h} symmetry optimized coronene sheds new light on these unresolved as-

signments. The imaginary b_{2g} fundamental (D_{6h} symmetry: $679i$ cm^{-1}) shows up as real and Raman active in the C_{2h} calculated spectrum (the a_g mode at 648 cm^{-1}) to match the experimental line at 571 cm^{-1} . The other mysterious experimental band at 828 cm^{-1} is also readily discernable in our C_{2h} calculated spectrum. In fact, there are two experimental lines in the region: a weak one at 828 cm^{-1} and a strong one at 840 cm^{-1} previously assigned to one of the e_{1g} modes. Our C_{2h} symmetry based calculations predict a weak degenerate a_g , b_g doublet at 859 cm^{-1} (the e_{1g} mode at 857 cm^{-1} in D_{6h} symmetry). We assign this a_g , b_g doublet to the experimentally weak peak at 828 cm^{-1} . The strong a_g mode (a silent b_{2g} mode in D_{6h} symmetry) with calculated frequency of 866 cm^{-1} is then assigned to the strong experimental line at 840 cm^{-1} .

A series of theoretical studies¹⁻⁵ on Raman spectroscopy of large polycyclic aromatic hydrocarbons (including coronene) were devoted to the band at approximately 1350 cm^{-1} and the band at approximately 1600 cm^{-1} . These two bands have enjoyed a considerable attention ever since it was realized that they map the most characteristic features of all graphitic materials with some degree of disorder and/or defects in the perfect sp^2 crystalline structure.

The experimental doublet (1625 and 1633 cm^{-1}) is to date associated with an e_{1g} mode (1652 cm^{-1} in our D_{6h} symmetry spectrum). The picture improves a bit by assigning this experimental band to the quasidegenerate a_g , b_g doublet as present at approximately 1653 cm^{-1} in our C_{2h} spectrum. The very strong experimental doublet (1354 and 1369 cm^{-1}) has been persistently considered to be an a_{2g} mode (1375 cm^{-1} in our D_{6h} calculated spectrum). This a_{2g} mode corresponds to a slightly less intensive a_g mode in C_{2h} symmetry (cf. Table V). On the other hand, the nearby e_{1g} fundamental at 1423 cm^{-1} (a quasidegenerate a_g , b_g doublet in C_{2h} symmetry) gained some intensity upon symmetry reduction. The e_{1g} and a_{2g} modes are in-plane vibrations, hence, they will be most strongly affected by changes in the in-plane force field, i.e., in-plane molecular distortions. The computational D_{6h} to C_{2h} symmetry reduction mimics qualitatively well the experimentally observed out-of-plane molecular deformation. The in-plane deformations as experimentally documented by single crystal x-ray structure measurement¹¹ will change the in-plane force field and consequently the in-plane normal modes properties. It is plausible that the intensity of the a_{2g} mode at 1375 cm^{-1} and e_{1g} modes at 1423 cm^{-1} are inverted in sufficiently in-plane distorted coronene (Fig. 4).

IV. MOLECULAR GEOMETRY

We have established that the phantom bands in the experimental solid-state infrared and Raman spectra of coronene can be accounted for by a minute out-of-plane molecular deformation. That this may occur in the solid state is confirmed by x-ray single crystal structure measurement.¹¹ Coronene crystallizes in $P2(1)/n$ space group, i.e., C_i crystal symmetry, with half of the molecule as an independent part

TABLE V. Experimental (fundamental) wave numbers (ν in cm^{-1}) in solid state, theoretical (harmonic) frequencies (ω in cm^{-1}), and their corresponding experimental/calculated Raman intensities (Raman in $\text{\AA}^4/\text{AMU}$).

B3LYP/TZP($\alpha_d=0.6$) D_{6h} symmetry			Expt. ^a (solid-state)		B3LYP/TZP($\alpha_d=0.6$) C_{2h} symmetry		
Irrep.	ω	Raman	ν	Raman	Raman	ω	Irrep. ^b
e_{1g}	291	1.7			1.8	294	a_g, b_g
e_{2g}	370	16.9	369	m	16.7	370	a_g, b_g
e_{1g}	453	1.2	435	m	1.4	455	a_g, b_g
a_{1g}	485	107.2	487	vs	100.7	485	a_g
e_{2g}	496	0.0			0.0	497	a_g, b_g
b_{2g}	679 <i>i</i>	0.0	571	m	65.2	648	a_g
e_{1g}	668	0.7			1.1	672	b_g
					1.2	673	a_g
e_{2g}	690	1.0			1.0	690	a_g, b_g
e_{1g}	857	3.2	828	w	3.2	859	a_g, b_g
b_{2g}	709	0.0	840	s	361.2	866	a_g
e_{1g}	976	3.8			3.8	977	a_g, b_g
b_{2g}	991	0.0			2.3	993	a_g
e_{2g}	1009	12.6			12.5	1009	a_g, b_g
a_{1g}	1047	40.4			37.1	1048	a_g
e_{2g}	1179	0.8			0.8	1180	a_g, b_g
a_{1g}	1242	42.5			43.6	1243	a_g
e_{2g}	1248	7.4			7.4	1249	a_g, b_g
a_{1g}	1375	1283.4	1354	vs	1276.4	1375	a_g
			1369	vs			
e_{2g}	1423	3.7			3.8	1423	a_g, b_g
e_{2g}	1464	0.0			0.1	1465	a_g, b_g
e_{2g}	1479	27.7			27.8	1480	a_g, b_g
a_{1g}	1638	207.1	1584	w	205.3	1638	a_g
e_{2g}	1652	223.6	1625	w	223.0	1653	a_g, b_g
			1633	w			
a_{2g}	3165	0.0			1.7	3165	b_g
e_{2g}	3168	124.6			129.9	3168	b_g
					125.7	3168	a_g
e_{2g}	3183	231.1			223.5	3183	a_g, b_g
a_{1g}	3186	1062.9			1056.3	3186	a_g

^aOhno *et al.* (Ref. 9); crystalline coronene at 77 K.^bAll a_g, b_g pairs are considered to be degenerate since the differences in the wave numbers and intensities are $\leq 0.5 \text{ cm}^{-1}$.

of the unit cell.¹¹ Carbon-carbon bond distances of the experimentally determined molecular geometry¹¹ are shown on Fig. 5.

The accuracy of the carbon nuclear coordinates in the x-ray experiment is approximately $0.001 \text{ \AA}$ (approximately 0.002 a.u.). Hence, the differences in the carbon-carbon bond distances are numerically significant and the D_{6h} to C_i symmetry reduction is experimentally observed.

The change in the calculated carbon-carbon bond distances upon symmetry reduction (D_{6h} to C_{2h}) is insignificant, as shown on Fig. 6. The geometry was slightly altered in an out-of-plane direction (*vide infra*, Table VII).

The scale and type of the molecular corrugation are further studied by inspection of the Cartesian coordinates (see Table VI and Fig. 7). A symmetry unique part of the carbon skeleton is formally divided in three semirings: inner (C_{1-3i}), middle (C_{1-3m}) and outer (C_{1-6o}). The origin of the coordinate system is in the inversion centre of the molecule and the Z-axis passes through the central carbon atom of the inner semiring (see Fig. 7). The adopted coordinate system and the formal semiring division eased the quantitative study of the D_{6h} symmetry deviation. For instance, in D_{6h} symmetry, σ_{yz}

constitutes the molecular plane, i.e., all X-coordinates are zero. Thus the distortion from planarity of each atom in the observed C_i symmetrical coronene is represented by the atom's X-coordinate. In D_{6h} symmetry, σ_{xy} and σ_{xz} are symmetry planes, hence, not only C_{1i} but also C_{1m} lies on the Z-axis and the Y- and Z-coordinates of the $\{C_{2i}, C_{3i}\}$, $\{C_{2m}, C_{3m}\}$, $\{C_{1o}, C_{2o}\}$, $\{C_{3o}, C_{4o}\}$, $\{C_{5o}, C_{6o}\}$, $\{H_1, H_2\}$, $\{H_3, H_4\}$, and $\{H_5, H_6\}$ pairs are exactly the same. Thus the Z-coordinate of C_{1m} , as well as differences in the Y-coordinates and differences in the Z-coordinates within each pair represent in-plane deviations from D_{6h} symmetry.

After inspection of the X-coordinates in Table VI we conclude that the out-of-plane distortion is experimentally observed. The disparities in the Y- and Z-coordinates within each semiring demonstrated the in-plane distortion. On average, each coronene molecule in the crystal is uniformly distorted in- and out-of-plane within each (semi)-ring. In addition, we note that in going from the inner core to the outer perimeter a gradual increase in the molecular distortion is discernable.

The computational out-of-plane distortion is smaller compared with the experimentally observed one (compare

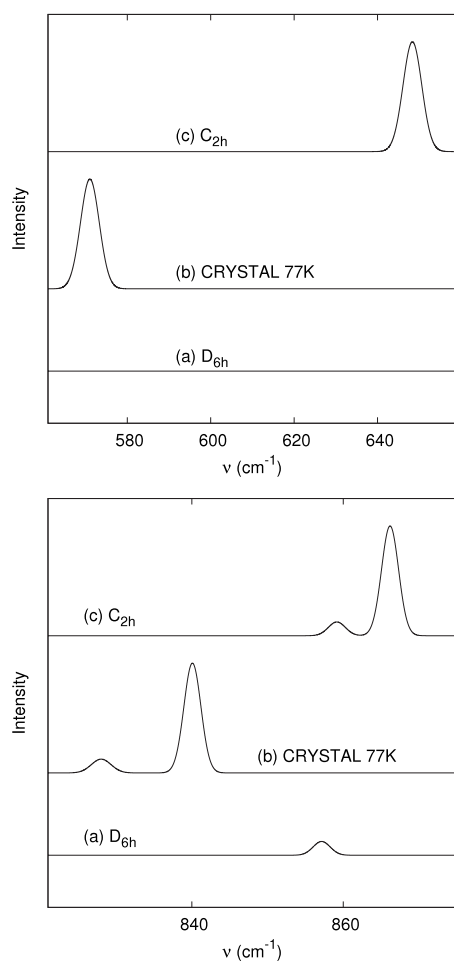


FIG. 4. Illustration of two of the most distinguishing features of solid-state Raman spectrum of coronene (b) (see Table I in Ref. 9; also included in Table V) compared with the B3LYP/TZP($\alpha_d=0.6$) calculated spectrum at the D_{6h} symmetrical stationary point (a) (see also Table V) and the B3LYP/TZP($\alpha_d=0.6$) calculated spectrum at the C_{2h} symmetrical stationary point (c) (see Table V). The shapes of the bands are qualitatively modeled with Gaussian functions. The experimental band at approximately 550 cm^{-1} as present in the experimental Raman spectrum of crystalline coronene is only visible in the C_{2h} calculated spectrum but it is not visible in the D_{6h} calculated spectrum. The strong experimental line at approximately 840 cm^{-1} as present in the crystalline coronene spectrum is visible only in the C_{2h} calculated spectrum but is absent from the D_{6h} calculated spectrum.

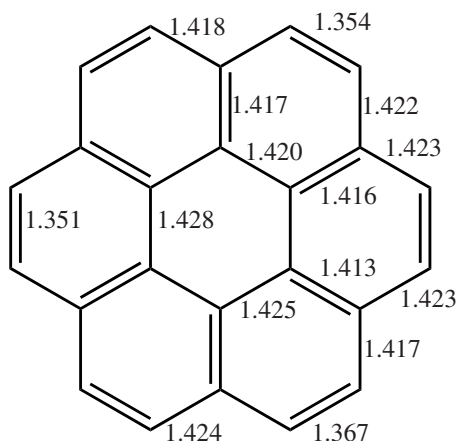
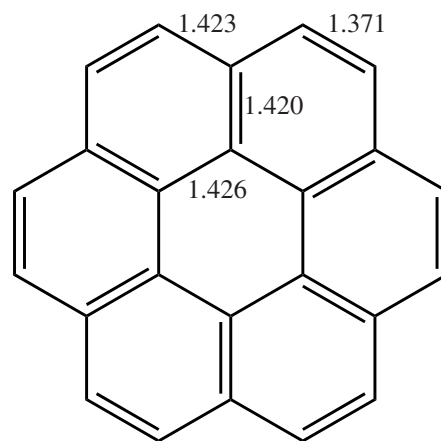
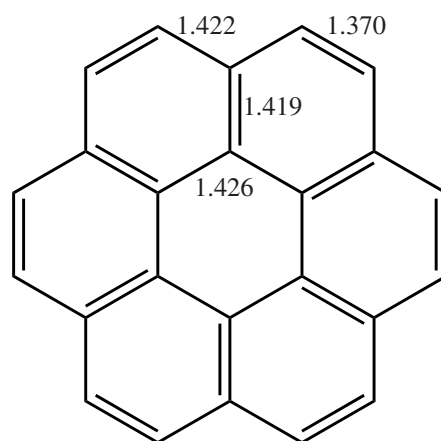


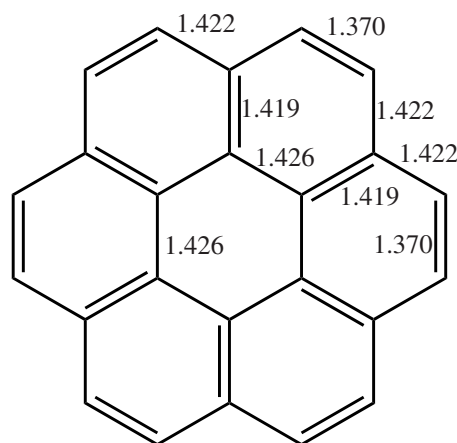
FIG. 5. X-ray measured (Ref. 11) carbon-carbon bond distances (in angstroms).



TZP($\alpha_d = 0.5$)/ D_{6h}



TZP($\alpha_d = 0.6$)/ D_{6h}



TZP($\alpha_d = 0.6$)/ C_{2h}

FIG. 6. Carbon-carbon bond distances (in angstroms) for the B3LYP/TZP($\alpha_d=0.5$) and B3LYP/TZP($\alpha_d=0.6$) optimized neutral coronene restricted to either D_{6h} or C_{2h} symmetry.

the X-coordinates in Tables VI and VII). Moreover, our C_{2h} coronene is computationally in-plane unperturbed. This observation explains the faint change in frequency and intensity of the in-plane e_{1u} modes which had to be assigned to experimental features clearly visible in the solid-state infrared

TABLE VI. Cartesian coordinates (angstrom) (C_i symmetry unique atoms) of neutral coronene from Ref. 11 (coordinates of the hydrogen atoms not published). The choice of the coordinate system and the nuclei labels are depicted in Fig. 7.

Label	X	Y	Z
C _{1i}	0.0000	0.0000	1.4248
C _{2i}	0.0006	1.2338	0.7111
C _{3i}	0.0032	-1.2356	0.7093
C _{1m}	-0.0032	-0.0062	2.8377
C _{2m}	0.0053	2.4571	1.4258
C _{3m}	0.0047	-2.4639	1.4138
C _{1o}	-0.0164	1.2338	3.5228
C _{2o}	0.0105	-1.2586	3.5122
C _{3o}	-0.0031	2.4196	2.8428
C _{4o}	0.0227	-2.4278	2.8359
C _{5o}	0.0122	3.6721	0.6833
C _{6o}	-0.0144	-3.6767	0.6707

spectrum while the out-of-plane b_{2g} modes gained considerable Raman intensity in agreement with the experimental Raman spectrum.

V. POTENTIAL ENERGY SURFACE

The analysis of the infrared and Raman spectra have demonstrated that coronene is expected to be corrugated in the solid-state and D_{6h} symmetrical in the gas-phase. Our calculations considered a single molecule in vacuum, thus, coronene should be computationally D_{6h} symmetrical. The DFT and RHF calculations with the TZP($\alpha_d=0.5$) basis set comply with this conclusion. The calculations with TZP($\alpha_d=0.6$) seem to propose coronene to be out-of-plane distorted. At the DFT/TZP($\alpha_d=0.6$) level of theory, the D_{6h} to C_{2h} symmetry reduction is accompanied by a total energy lowering of approximately $10^{-5} E_h$. However, the zero-point vibrational energy at C_{2h} symmetry is approximately $10^{-3} E_h$ larger than the zero-point vibrational energy at D_{6h} symmetry. As the ground state molecular geometry at zero temperature and zero pressure is determined by the minimum of the

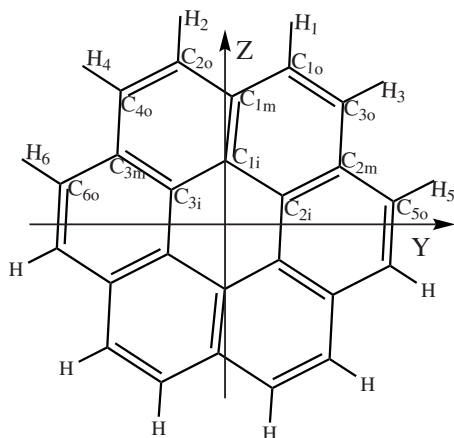


FIG. 7. Coordinate system, carbon and hydrogen labels used to present the Cartesian coordinates in Tables VI and VII.

TABLE VII. Cartesian coordinates (angstrom) (C_i symmetry unique atoms) of the B3LYP/TZP($\alpha_d=0.6$)/ C_{2h} optimized coronene for comparison to the x-ray data (Table VI). The coordinate system and the nuclei labels are depicted on Fig. 7.

Label	X	Y	Z
C _{1i}	0.0000	0.0000	1.4256
C _{2i}	0.0045	1.2345	0.7127
C _{3i}	0.0045	-1.2345	0.7127
C _{1m}	0.0051	0.0000	2.8443
C _{2m}	0.0037	2.4632	1.4222
C _{3m}	0.0037	-2.4632	1.4222
C _{1o}	0.0069	1.2466	3.5291
C _{2o}	0.0069	-1.2466	3.5291
C _{3o}	0.0061	2.4329	2.8442
C _{4o}	0.0061	-2.4329	2.8442
C _{5o}	0.0017	3.6795	0.6850
C _{6o}	0.0017	-3.6795	0.6850
H ₁	0.0094	1.2443	4.6139
H ₂	0.0094	-1.2443	4.6139
H ₃	0.0070	3.3735	3.3848
H ₄	0.0070	-3.3735	3.3848
H ₅	0.0025	4.6179	1.2292
H ₆	0.0025	-4.6179	1.2292

Free Energy, the DFT/TZP($\alpha_d=0.6$) calculations also predict coronene to be flat and D_{6h} symmetrical.

For the purpose of aiding further investigation, we present the Mulliken population analyses from RHF/TZP($\alpha_d=0.6$) calculations conducted with GAMESS-UK (Ref. 13) at the D_{6h} (in Table VIII) and the C_{2h} (in Table IX) stationary points. A slight charge transfer of approximately $0.001 e/\text{atom}$ from the middle to the inner ring (see Fig. 7) is implied. Interestingly, the charge shift occurs through the σ -bonds.

VI. CONCLUSIONS

All previously designated phantom infrared/Raman spectral features¹⁰ of crystalline coronene are now properly assigned. The rationalization comes after considering a small

TABLE VIII. Mulliken gross population of atomic orbitals condensed to the implied core, σ -bonding, π -bonding, polarization and total electron density on each atom of coronene. The raw data is extracted from a RHF/TZP($\alpha_d=0.6$) calculation conducted with GAMESS-UK (Ref. 13) at the D_{6h} stationary point. The coordinate system and the nuclei labels are depicted on Fig. 7.

	Core	Valence		Polarization	Total
		σ	π		
Carbon	1s	2s+2p _y +2p _z	2p _x	3d	
C _{1-3i}	1.9383	3.0846	0.9732	0.0902	6.0863
C _{1-3m}	1.9384	2.8683	0.9525	0.0912	5.8504
C _{1-6o}	1.9383	3.1520	0.9884	0.0748	6.1535
Hydrogen	1s			2p	
H ₁₋₆		0.84989		0.02819	0.87808

TABLE IX. Mulliken gross population of atomic orbitals condensed to the implied core, σ -bonding, π -bonding, polarization, and total electron density on each atom of coronene. The raw data is extracted from a RHF/TZP($a_d=0.6$) calculation conducted with GAMESS-UK (Ref. 13) at the C_{2h} stationary point. The coordinate system and the nuclei labels are depicted on Fig. 7.

	Core	Valence		Polarization	Total
		σ	π		
Carbon	1s	2s+2p _y +2p _z	2p _x	3d	
C _{1i}	1.9383	3.0856	0.9731	0.0902	6.0872
C _{2-3i}	1.9383	3.0852	0.9732	0.0902	6.0869
C _{1-3m}	1.9384	2.8669	0.9525	0.0912	5.8490
C _{1-6o}	1.9383	3.1524	0.9884	0.0748	6.1539
Hydrogen	1s			2p	
H ₁₋₆		0.84989		0.02819	0.87808

symmetry reduction, which is indeed, documented by the available x-ray single crystal structure measurements. Each molecule in the crystal is exposed to the weak C_i symmetry crystal field and it has to relax into a C_i symmetrical conformation. However, the difficulty is to realize the scale of the deformation. The weak crystal field competes with the much stronger intramolecular interactions and alters noticeably the molecular properties of coronene as seen by the infrared and Raman spectroscopy.

Apparently, the molecular structure and vibrational motion of aromatic hydrocarbons still pose considerable theoretical challenges.

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- ¹C. Mapelli, C. Castiglioni, G. Zerbi, and K. Müllen, *Phys. Rev. B* **60**, 12710 (1999).
- ²A. C. Ferrari and J. Robertson, *Phys. Rev. B* **61**, 14095 (2000).
- ³M. Rigolio, C. Castiglioni, G. Zerbi, and F. Negri, *J. Mol. Struct.* **563–564**, 79 (2001).
- ⁴F. Negri, C. Castiglioni, M. Tommasini, and G. Zerbi, *J. Phys. Chem. A* **106**, 3306 (2002).
- ⁵C. Mapelli, C. Castiglioni, E. Meroni, and G. Zerbi, *J. Mol. Struct.* **480–481**, 615 (1999).
- ⁶G. Mulas, G. Mallocci, C. Joblin, and D. Toubanc, *Astron. Astrophys.* **460**, 93 (2006).
- ⁷S. J. Cyvin, B. N. Cyvin, J. Brunvoll, J. C. Whitmer, and P. Klæboe, *Z. Naturforsch. Teil A* **37**, 1359 (1982).
- ⁸C. Joblin, L. d'Hendecourt, A. Léger, and D. Défourneau, *Astron. Astrophys.* **281**, 923 (1994); **299**, 835 (1995).
- ⁹K. Ohno, T. Kajiwar, and H. Inokuchi, *Bull. Chem. Soc. Jpn.* **45**, 996 (1972).
- ¹⁰U. Fleischer and P. Pulay, *J. Raman Spectrosc.* **29**, 473 (1998).
- ¹¹T. M. Krygowski, M. Cyrański, A. Ciesielski, B. Świrski, and P. J. Leszczyński, *Chem. Inf. Comput. Sci.* **36**, 1135 (1996).
- ¹²M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 98, Revision A.9, Gaussian, Inc., Pittsburgh, PA, 1998.
- ¹³M. F. Guest, I. J. Bush, H. J. J. Van Dam, P. Sherwood, J. M. H. Thomas, J. H. van Lenthe, R. W. A. Havenith, and J. Kendrick, *Mol. Phys.* **103**, 719 (2005).
- ¹⁴T. H. J. Dunning, *Chem. Phys.* **55**, 716 (1971).
- ¹⁵R. Bauernschmitt and R. Ahlrichs, *J. Chem. Phys.* **104**, 9047 (1996).
- ¹⁶D. Moran, A. C. Simmonett, F. E. Leach III, W. D. Allen, P. v. Rague Schleyer, and H. F. Schaefer III, *J. Am. Chem. Soc.* **128**, 9342 (2006).