Infrared spectroscopy of mass-selected aromatic and diamondoid molecular ions: a laboratory quest for the organic inventory in space

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Citation for published version (APA):
Bucky-bowl Corannulenes* 

The structural transition from planar PAHs to spheroidal fullerene structures involves the incorporation of five-membered carbon rings (pentagonal defects). Therefore, corannulene—with an inner pentagonal ring and inherent curvature—may hold the key to the understanding of the chemistry that takes place towards the formation of C$_{60}$ and other fullerenes in space environments. Here, an IR spectroscopic investigation of the corannulene structure is undertaken in its neutral, radical cationic and protonated forms. Clear differences in the IR activity are seen between the three corannulenes, as well as relative to planar PAHs. The spectral features are rationalized in terms of the corresponding electronic configurations and intramolecular vibronic mechanisms such as the Jahn–Teller distortion (in case of the radical cationic form). Accordingly, while planar PAHs show strong specificity of the IR absorption bands, ionized corannulene exhibits different bands that fall close to the nominal UIR band positions, in particular in the 5–9 µm range. This may relax the need to invoke a mixture of large planar PAHs in different anionic and/or cationic states in order to reproduce, for instance, the different subfeatures of the 7.7 µm UIR complex. The spectra of ionized corannulene suggest that the evolution of the 7.7 µm complex can alternatively be explained by curved PAH ionic structures—which deviate from the pure $sp^2$-hybridized species via the inclusion of pentagonal defects.

*Based on: Héctor Alvaro Galué, Corey A. Rice, Jeffrey D. Steill and Jos Oomens, 2011, The Journal of Chemical Physics, 134, 054310
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7.1 Introduction

Corannulene (C\textsubscript{20}H\textsubscript{10}) is a highly symmetric molecule (C\textsubscript{5v}) that belongs to the family of polycyclic aromatic hydrocarbons (PAHs), and is composed of five perifused aromatic rings around a central five-membered ring. Its molecular structure resembles that of coronene (C\textsubscript{24}H\textsubscript{12}), which is a D\textsubscript{6h}-symmetry PAH molecule consisting of six aromatic rings symmetrically arranged around an inner six-membered ring. As shown by x-ray diffraction (Hanson & Nordman 1976), the bonds between the carbon atoms of the pentagonal ring and the peripheral benzenic rings are significantly out of the plane in corannulene. Therefore, the adopted curved geometry reduces the aromatic character of corannulene as compared to planar coronene. Being the smallest stable PAH adopting a bowl-shaped structure, corannulene resembles a fragment of a fullerene (C\textsubscript{60}) with the outer-perimeter carbons terminated by hydrogen atoms. Figure 7.1 compares the molecular structures of coronene, corannulene and C\textsubscript{60}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{molecular_structures.png}
\caption{Molecular carbon structures of coronene (C\textsubscript{24}H\textsubscript{12}), corannulene (C\textsubscript{20}H\textsubscript{10}), and fullerene (C\textsubscript{60}).}
\end{figure}

The occurrence of corannulene in interstellar environments is conjectured based on its possibly role in the formation of interstellar C\textsubscript{60} (García-Hernández et al. 2010, Cami et al. 2010, Sellgren et al. 2010, Kroto 1997). Owing to its large permanent dipole moment of around 2.1 D, corannulene has been the target of several laboratory and observational microwave studies (Lovas et al. 2005, Pilleri et al. 2009). As compared to planar regular PAHs, corannulene offers an opportunity to detect an individual PAH molecule in space based on its microwave spectrum. Corannulene and other compounds of the fullerene family have been extracted from the Allende meteorite (Becker & Bunch 1997). Thus, detection of interstellar and/or circumstellar corannulene (or derivatives) could help clarifying the origin of these complex hydrocarbon molecules in the Solar System.

Neutral corannulene has a fivefold symmetry axis and the highest occupied molecular orbital (HOMO) is degenerate. Upon removal of an electron, the ion becomes energetically unstable and is subject to Jahn–Teller (JT) distortion (Jahn & Teller 1937). This poses substantial challenges to characterizations of the radical species by quantum-chemical methods. Here we present the first gas-phase IR spectrum of the corannulene radical cation, which is compared directly to spectra predicted using different computational density functional theory (DFT) approaches.

DFT methods have been extensively applied to planar PAH systems (Pauzat et al. 1997) and they have proven to yield calculated harmonic IR frequencies which are in
good agreement with experimental IR vibrational spectra, both for neutral and radical
cation forms (Langhoff 1996, Oomens et al. 2003b) as well as for positively charged PAH
derivatives (see Ch. 6, or Zhao et al. (2009)). These methods have also been applied to
PAHs containing a five-membered ring (Bauschlicher et al. 1999), but the performance of
these methods for nonplanar corannulene in its cationic state has not been verified against
experimental data.

Gas-phase IR spectra of two singly positively charged forms of corannulene, proto-
nated and radical cation, were investigated. Interestingly, the former has a closed shell
electronic structure (\(^{1}A\)) and lowered symmetry, while the latter has an open shell elec-
tronic structure (\(^{2}E_{1}\)) and undergoes JT distortion. This difference is clearly observable
in their spectra. Spectra were measured via resonant IR multiple-photon dissociation
(IRMPD) and characterized using standard DFT calculations at various levels of theory.
For comparison, the IR spectrum of neutral corannulene (\(^{1}A_{1}\)) was also measured and
changes in the IR activity as a consequence of protonation and ionization are discussed.
For the radical cation, the effects of destabilization of the degenerate \(^{2}E_{1}\)-state are ratio-
nalized and two optimized JT-distorted C\(_{s}\) geometries are determined in order to calculate
their vibrational spectra. Finally, to gain further insights into the experimental IR spec-
trum of cationic corannulene, we compare the IR spectra of the coronene and corannulene
radical cations.

### 7.2 Laboratory Methods

#### 7.2.1 Experiments

Corannulene was synthesized via solution-phase chemistry by the Siegel group (Seiders
et al. 1999). The fine dust particles that resulted from the procedure were used without
further preparation. The apparatus employed to record the IRMPD spectrum of the coran-
nulene radical cation is described in Chapter 2 (Ion Trap Machine) and here we describe
the most relevant details. A standard FTIR spectrometer was employed to record the
solid-state IR spectrum of neutral corannulene in a KBr pellet.

The radical cation of corannulene was created by evaporating the solid sample from an
effusive source heated to \(~353\) K. The neutral vapor was photoionized by the absorption
of two 193-nm (6.4 eV) photons of an ArF laser focused into the center of a quadrupole
ion trap. The ionization potential of corannulene is 7.2 eV (Denifl et al. 2006) and the ex-
cess energy induces some dissociation. Shortly after the UV pulse, the RF amplitude was
briefly (2 ms) ramped up, axially ejecting the photodissociation fragments from the trap
thus isolating the precursor corannulene cation. The isolated ions are then spectroscopi-
cally interrogated with the high-power IR radiation of the free electron laser for infrared
experiments, FELIX (Oepts et al. 1995). Each FELIX macropulse of around 60 mJ in en-
ergy is composed of \(~5000\) micropulses. Multiple IR photons are sequentially absorbed
whenever the laser frequency is in resonance with a vibrational transition of the cation,
leading to a population of highly vibrationally excited cations that decay via dissociation.
The parent and fragment ions are detected with a linear time of flight mass spectrom-
eter attached to the ion trap. An IRMPD spectrum is then recorded by monitoring the fragmentation yield (H, H$_2$, and C$_2$H$_x$ loss) as a function of the IR frequency of the laser.

The IRMPD spectrum of protonated corannulene was obtained using a Fourier-transform ion cyclotron resonance mass spectrometer (FTICR-MS) also coupled to the IR beamline of FELIX (Polfer & Oomens 2007). Protonated corannulene cations were produced by electrospray ionization (ESI), and for this purpose, corannulene was dissolved in methanol with a small amount of ammonium acetate added, as was previously used for several PAH species (Knorke et al. 2009). Ions were accumulated in a hexapole trap prior to injection into the ion cyclotron resonance cell, where the ions were mass-isolated and subsequently irradiated for 7 s at each IR frequency. The only observed fragmentation channel was atomic hydrogen loss. An IRMPD spectrum was obtained by monitoring the resulting dissociation yield as a function of wavelength of FELIX.

### 7.2.2 Quantum-Chemical Computations

Optimized ground-state geometries were generated for the radical cation and protonated corannulene using several ab initio (Roothaan 1951), and DFT levels of theory. These include the spin-restricted open-shell Hartree-Fock (ROHF) (Binkley et al. 1974), the Becke electron-exchange (Becke 1988) with Perdew (Perdew 1986), or Lee-Yang-Parr gradient-corrected local-density approximation correlation (Lee et al. 1988) pure functionals: B-P86 and B-LYP; and the three-parameter hybrid functionals: B3-P86 and B3-LYP (Becke 1988). The basis-set functions employed range from double- to triple-ζ split-valence sets of Pople and the correlation-consistent polarized valence double-ζ (cc-pVDZ) set of Dunning (Dunning 1989). For Pople basis sets, d and p polarization functions for C and H atoms were used, respectively. All calculations were performed using the GAUSSIAN 03 suite of programs (Frisch et al. 2004). At each level of theory employed, vibrational modes were computed by solving the Hessian as implemented in GAUSSIAN 03. The frequencies (i.e., Hessian eigenvalues) of the modes were convoluted with a 30 cm$^{-1}$ FWHM Gaussian line-shape function to generate synthetic IR spectra.

In addition to the cations, the C$_{5v}$-symmetry structure of neutral corannulene was investigated at the BP86/6-311G(d,p) and B3LYP/6-311G(p,d) levels, and used as a structural reference for spectral characterization of the cationic systems. Frequencies were convoluted with a 5 cm$^{-1}$ FWHM Gaussian function to simulate the experimental FTIR spectrum of corannulene recorded in a KBr pellet.

For protonated corannulene, the C$_1$-optimized geometry and the Hessian matrix were also computed at BP86/6-311G(d,p) and B3LYP/6-311G(d,p) levels. The calculated adiabatic potential energy surface (PES) of the 1A state has a well-defined global minimum located at the C$_1$ point, and the computed vibrational modes at this point produce no imaginary frequencies and, moreover, reproduce the experimental IRMPD spectrum reasonably well (vide infra). For the corannulene radical cation, C$_{5v}$-geometry optimizations at BP86, B3LYP, and other levels of theory were performed, but did not converge to a stable structure because the C$_{5v}$ symmetry point on the degenerate $^2$E$_1$-state PES is located at a JT conical intersection. JT distortion lifts the degeneracy of the electronic states and produces a lowest energy structure at a lower symmetry geometry (Jahn &
7.3 Results

Symmetry considerations within the JT theorem are borne in mind to find optimized JT-distorted geometries associated with the two electronic states that form the conical intersection. JT-distorted geometries and fundamental frequencies were computed using the four methods mentioned above, and for each one of them, basis sets of different sizes were employed. The results of these computations are evaluated against the experimental IRMPD spectrum of the corannulene radical cation. Calculated energies and frequencies reported throughout this work are obtained using the B3LYP functional with the 6-311G(d,p) basis set unless noted otherwise.

7.3 Results

7.3.1 Electronic and Geometric Structures

Detailed structural parameters are listed in Table 7.1 (and in the inset of Fig. 7.3). For neutral corannulene, the HOMO electron density on the C atoms of the inner pentagonal ring is larger than in any other region of the molecule (Kato & Yamabe 2006). This is evident from the electron density isosurface of the HOMO shown in Fig. 7.2. Therefore, upon ionization (or protonation), changes in CC bond lengths are more significant in the inner ring than in any other part of the molecule, resulting in a very distinct change in the geometry of the pentagonal ring. Thus, the CC bond lengths of the pentagonal ring characterize the most important structural features of the three systems investigated. For neutral corannulene with C$_5$ symmetry, the pentagonal ring evidently has equal sides and hence the five optimized CC bond lengths (X, . . . , X) are equivalent.

As detailed further in Sec. 7.4.2, the JT vibronic interaction in the radical cation gives rise to one compressed and one elongated JT-distorted structure both of C$_s$ symmetry. In this case, the C$_s$ pentagon can be fully described by three of the five CC bond lengths (X, X, and X). The structure will be called “compressed” if X > X > X (see Fig. 7.3), while the elongated structure refers to the situation where X > X > X. For the C$_s$ geometry of protonated corannulene, all five sides of the pentagonal ring are different and all CC bond lengths are required to describe the structure.

7.3.2 IR Spectra

The IRMPD spectra of radical cation and protonated corannulene (corannulene$^+$ and corannuleneH$^+$, respectively) are shown in Fig. 7.3. As described in Sec. 7.2.1, both spectra are recorded in the gas phase and differ essentially in the method of ionization (193-nm UV photoionization for the radical cation and ESI for the protonated species). Furthermore, in the ion trap experiment, the IR beam is focused more sharply than in the FTICR-MS setup. This is necessary because the dissociation threshold of corannulene$^+$ is substantially higher than that of corannuleneH$^+$: neutral C$_{2n}$H$_{2n}$ loss is observed for corannulene$^+$, while the only decay channel observed for corannuleneH$^+$ is loss of atomic hydrogen, forming the radical cation; as was also observed for many protonated PAH molecules (Knorke et al. 2009). Dissociation of the radical cation involves unknown rearrangements, whereas in the protonated form, H-atom loss proceeds via a barrierless
Table 7.1 - Ground-state energies and structural parameters of corannulene (neutral and radical cation) calculated at several ab initio and DFT levels of theory. Energy values in boldface indicate the lower of the two cationic states. The columns list the stationary points as first-order saddle points (imaginary frequency) or minimum ("0").

<table>
<thead>
<tr>
<th>Method</th>
<th>Energy (Hartree Å cm⁻¹)</th>
<th>R₁ (Å)</th>
<th>R₂ (Å)</th>
<th>R₃ (Å)</th>
<th>∆E (Hartree Å cm⁻¹)</th>
<th>∆X₁ (Å)</th>
<th>∆X₂ (Å)</th>
<th>∆X₃ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-31G(d)</td>
<td>-762.652775</td>
<td>1.373</td>
<td>1.43</td>
<td>1.386</td>
<td>0</td>
<td>570i</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6-31G(d,p)</td>
<td>-768.014863</td>
<td>1.451</td>
<td>1.39</td>
<td>1.432</td>
<td>0</td>
<td>3.3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>cc-pVDZ</td>
<td>-767.917621</td>
<td>1.448</td>
<td>1.396</td>
<td>1.43</td>
<td>0</td>
<td>4.9</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

B3LYP-6-31G(d)  1.381  1.435  1.404  7.9  0.059  -0.047  0.018  -770.332212
ROHF-6-31G(d)   1.382  1.438  1.403  8.4  0.06  -0.048  0.018  -770.6537
7.3 Results

![Figure 7.2](image)

**Figure 7.2** – The electron density iso-surfaces of (a) the averaged twofold $e_1$-degenerate HOMO of neutral corannulene, (b) the HOMO of protonated corannulene, the SOMO of the cationic, (c) elongated ($A'$) structure, and (d) compressed ($A''$) structure.

abstraction reaction, for which the activation energy is computed as 276 kJ/mol. The peak positions of the measured IRMPD bands are listed in Table 7.2.

The FT-IR spectrum of neutral corannulene recorded in a KBr pellet is shown in the top panel of Fig. 7.3 for comparison. This spectrum was measured in order to validate the sample, and test the predictability and performance of selected theoretical methods on the corannulene system. Good agreement was found between this FT-IR spectrum and a previously recorded spectrum of neutral corannulene (Rouillé et al. 2008).

Simulated IR spectra are generated using BP86 and B3LYP methods. Figure 7.3 compares the experimental spectra of the neutral and protonated corannulene with the B3LYP calculated spectrum, where the frequencies have been scaled by 0.9679 (Andersson & Uvdal 2005). In addition, the performance of the BP86 method was tested and a comparison is shown in Fig. 7.4. Both methods show good agreement with FT-IR (neutral) and IRMPD (protonated) spectra. Contrary to the B3LYP harmonic calculation, where a scaling factor is necessary in order to match the observed IRMPD band positions, the good agreement of unscaled BP86 harmonic bands with IRMPD bands is due to a partial compensation of understimated harmonic frequencies and ignored vibrational anharmonicity, which is known to be particularly fortunate for this method (Neugebauer & Hess 2003). A systematic analysis of the IR spectrum of corannulene$^+$ based on DFT calculations is presented in the next section.
Figure 7.3 – FTIR KBr-pellet spectrum of neutral corannulene (top), and IRMPD spectra of corannulene$^+$ (middle) and corannuleneH$^+$ (bottom). Scaled harmonic B3LYP spectra are shown for neutral and protonated corannulene in green. The CC bond lengths of the pentagonal ring ($X_i$) shown in the corannulene structures adopt five different values for the protonated system ($C_1$ symmetry), three different values for the radical cation ($C_s$ symmetry) and all values are equivalent for neutral corannulene ($C_{5v}$ symmetry). Refer to text for further explanation.
7.4 Discussion

7.4.1 Singlet Systems: Neutral and Protonated Corannulene

There are $3N-6 = 84$ vibrational degrees of freedom in corannulene spanning the linear combination of irreducible representations $\Gamma_{\text{vib}} = 9A_{1} + 7A_{2} + 16E_{1} + 18E_{2}$ in the $C_{5v}$ point group. Symmetry-derived selection rules determine that modes of $A_{1}$ and $E_{1}$ species are the IR-active molecular vibrations in neutral corannulene. The totally symmetric CH “out-of-plane” $a_{1}$-mode at approximately $840 \text{ cm}^{-1}$ is the most intense (127 km mol$^{-1}$), as observed in the FTIR spectrum and reproduced by the DFT calculation (Fig. 7.3, top).

Similar to regular polyaromatic hydrocarbon molecules (Zhao et al. 2009, Knorke et al. 2009, Hudgins et al. 2001, Ricks et al. 2009) corannulene protonates on one of the peripheral carbon atoms, forming a tetrahedral, $sp^{3}$ hybridized site. Upon protonation, corannulene loses its symmetry completely and the extra H atom adds three new vibrational degrees of freedom. The (closed shell) singlet electronic state is preserved, though the electron density in the HOMO (predominantly localized at the center of the

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1We adopt the nomenclature that is usual for regular, planar PAH molecules.
molecule in the neutral system) is now redistributed away from the ring bearing the extra H atom (see Fig. 7.2). This electronic configuration results in a well-defined $C_1$ symmetry global minimum structure lying 721 kJ/mol lower in energy than the $C_{5v}$-minimum of neutral corannulene. The low symmetry structure is, for instance, revealed by the five nonequivalent CC bond lengths $(X_1, \ldots, X_5)$ of the inner pentagonal ring. As will be further discussed below, this situation is very different from that of the radical cation, where removal of an electron from the degenerate $e_1$-HOMO of the neutral results in two $C_s$-symmetry PESs, which retain an intricate vibronic connection to the neutral $C_{5v}$-PES.

Charge redistribution in corannulene$H^+$ induces substantial asymmetric carbon displacements enhancing the IR intensities of the CC stretching modes, observed in the IRMPD spectrum as two intense bands at 1394 and 1594 cm$^{-1}$ (Fig. 7.3, bottom). Contrary to the cationic structure, where CH “in-plane” bends are predicted to couple strongly to CC stretches (in particular to those involving the five inner carbons), protonation tends to decouple CH in-plane bends from CC stretches. As a result, in the 1000–1250 cm$^{-1}$ region of the experimental IRMPD spectra, the modes in corannulene$H^+$ have much lower intensities than in corannulene$^+$. In general, modes involving a multiple vibrational character are known to feature strong IR intensities in PAHs (Torii 2000).

The strong CH out-of-plane bending $a_1$-mode in the neutral system is considerably influenced by protonation and is found in the corannulene$H^+$ IRMPD spectrum at 850 cm$^{-1}$ with a slightly lower intensity, which at the B3LYP/6-311G(d,p) level of theory amounts to 95 km mol$^{-1}$. The experimental spectra in Fig. 7.3 indeed clearly show the lowest relative CH out-of-plane intensity for the protonated system. As opposed to the neutral and radical, only eight local CH oscillators participate in this normal mode. The CH in-plane bending mode near 1320 cm$^{-1}$ in the IRMPD spectrum, which is better reproduced at the BP86/6-311G(d,p) level of theory, has a strong local H–C–H scissoring character at the protonated site.

The general features in the spectrum of corannulene$H^+$, that is, an isolated band assigned to a strong CH out-of-plane mode located within the 750–850 cm$^{-1}$ range, the 1300–1450 cm$^{-1}$ region featuring medium to strong intensity modes of somewhat mixed CH bending/CC stretching character, and a force constant enhancement in the CC stretching modes (as compared to non-protonated PAHs) yielding a band around 1600 cm$^{-1}$, have also been observed in previously measured IR spectra of protonated PAHs (Knorke...
et al. 2009, Ricks et al. 2009) as well as in protonated PANHs (see Chapter 6), and other protonated PAH species (Zhao et al. 2009, Vala et al. 2009b). The similarity in IR spectral features among the various protonated PAH species suggests that, in general, PAH IR spectra are primarily determined by the charge state and the closed- versus open-shell nature of the PAH.

7.4.2 Doublet Systems: Corannulene Radical Cation

**Jahn–Teller distorted structures** Neutral corannulene with $C_{5v}$ symmetry has a twofold degenerate HOMO of $E_1$ symmetry. Upon ionization, removal of an electron lifts the degeneracy of the two $e_1$ orbitals and according to the JT theorem (Jahn & Teller 1937), vibrations of certain symmetry split the degenerate $2E_1$ state into symmetric and antisymmetric states of $C_s$ symmetry (Herzberg 1945). The $C_{5v}$ geometric structure distorts with respect to a mirror plane ($\sigma_h$) resulting in a compressed and an elongated JT geometry of $A''$ and $A'$ symmetry. Figure 7.5 illustrates the closed-shell HOMO of the neutral system and the two possible (open-shell) singly occupied molecular orbitals (SOMO), which determine the molecular geometry and symmetry of each of the doublet states for the radical cation. The species of a non-totally symmetric vibration, appearing in the symmetry product of the two $e_1$-degenerate electronic wavefunctions, determine the type of molecular vibrations capable of lifting the degeneracy. For the $C_{5v}$ point group, the direct product $E_1 \times E_1$ contains the symmetry species $A_1$, $A_2$, and $E_2$ (Herzberg 1945), and given that $A_1$ and $A_2$ retain the $C_5$ axis, the modes with $E_2$ symmetry are responsible for inducing the JT orbital adjustment. Although the nature of the JT interaction in the corannulene$^+$ system has not been experimentally investigated, it is understood from group theory that vibronic mixing of $E_1$ (electronic) and $E_2$ (vibration) species gives rise to the first order couplings (Herzberg 1945, Barckholtz & Miller 1998), and the interaction strengths have been previously calculated (Kato & Yamabe 2006).

Key structural parameters of the two JT-distorted geometries of corannulene$^+$ are listed in Table 7.1. The lowest energy structure, for which values are shown in boldface, was found by all methods to be the elongated geometry (since $X_2 > X_3 > X_1$). The ab initio ROHF assigns it to the $2A''$ electronic state, whereas all DFT methods assign it to the $2A'$ state. However, the frequency calculations are not always consistent with the assignment of the minimum and saddle-point structures, which is probably a consequence of the small curvature of the potential.

For the lowest energy structure found at a particular level of computation, the Hessian matrix is positive definite (i.e., all frequencies are real) for the ROHF frequency computations, although those employing polarization functions failed to converge. For DFT methods, the Hessian has in some cases (depending on functional and basis set) one imaginary frequency indicating a local maximum in the direction of the relevant normal coordinate (saddle point). For any given DFT method, polarization functions have a strong impact on the assignment of the local minimum. For instance, employing the 6-31G basis set, the BP86 functional yields a small imaginary frequency for the lowest energy $2A'$ structure. In contrast, including polarization functions yields positive definite Hessians for the $2A'$ electronic structures and assigns the saddle point to the $2A''$ structures. The same beha-
Figure 7.5 – The $C_5$ molecular structure of neutral corannulene at the bottom shows the $C_5$ symmetry axis and the five equivalent mirror plane elements ($\sigma_v$). The $e_1$ twofold degenerate HOMO is illustrated and the totally symmetric representation of the $C_{5v}$ point group is the ground electronic state of corannulene termed as $^1A_1$. Upon ionization, the resulting $^2E_1$-ground state of the open-shell corannulene cation is Jahn–Teller active and vibronic interaction (via $E_2$ vibrational modes) lifts the degeneracy leading to two JT distorted $C_s$ structures $^2A'$ and $^2A''$, corresponding to elongated and compressed molecular geometries of the corannulene radical cation, respectively. The geometric distortion due the JT effect is exaggerated for illustration.

Vibrational structure and IRMPD spectrum The IRMPD spectrum of the corannulene radical cation, shown in the top panel of Fig. 7.7, features a number of clearly recognizable, though fairly broad resonances. As compared to the experiment on protonated corannulene, we note that in this case an oven was used to evaporate the sample and that the dissociation threshold of the radical cation is substantially higher than that of the protonated species. The observed bandwidths are primarily a consequence of the IRMPD excitation mechanism, which involves anharmonic shifting and broadening effects in-
Figure 7.6 – Thermal energy distributions of corannulene ions at 0 (273 K), 25 (298 K), 80 (353 K) and 200 (473 K) Celsius. The relative population (%) of ions in the vibrational ground state is shown in parenthesis. The inset shows the steep rise of density of vibrational states of the corannulene cation as compared with the smaller naphthalene cation.

Increasing with internal energy E — in view of eq. 2.30, the IVR lifetimes (governing the spectral broadening) increase via the density of states $\rho_v(E)$ — in combination with the rotational envelope and the appearance of hot bands at the temperature of the oven (353 K). Due to the high internal energy contained in the corannulene ions, anharmonic coupling resonances between vibrational modes likely further influence the band shapes observed (Sadovskii & Zhilinskii 1995). Figure 7.6 shows the energy distributions of corannulene cations at four different temperatures. At 353 K, the average internal energy per corannulene ion is around 3100 cm$^{-1}$ (0.38 eV). At that internal energy, the percentage of ions in the ground state is only 0.011, and the number of vibrational combination levels per cm$^{-1}$ is on the order of $10^6$ (the inset is cut at $10^5$) as estimated from the harmonic frequencies and a direct count using the Beyer-Swinehart algorithm (Stein & Rabinovitch 1973).

Figure 7.7 compares the experimental IRMPD spectrum with spectra calculated at various DFT levels. For a more consistent comparison, no scaling of the harmonic frequencies has been applied. Three out of the eighteen $E_2$ modes in the reference $C_{5v}$ neutral structure, with computed values of 439, 648, and 1498 cm$^{-1}$ at the B3LYP/6-31G(d) level, exhibit the strongest linear vibronic coupling to the $e_1$-HOMO (Kato & Yamabe 2006). By increasing the level of theory to B3LYP/6-311G(d,p), these modes appear at...
440, 650, and 1484 cm\(^{-1}\), and are characterized by having large carbon displacements, as indicated by their computed reduced masses of 7.9, 6.5, and 7.5 amu, respectively. Overall, they involve a substantial deformation of the pentagonal inner ring, where the HOMO electron density is largely localized, thus explaining their strong coupling through significant orbital interactions among neighboring pentagonal carbons (Kato & Yamabe 2006).

The vibrational patterns of the three vibronic JT-active E\(_2\) modes clearly induce nuclear displacements in the direction of the structural change from the C\(_{5v}\) neutral corannulene structure to the cationic C\(_3\) structure(s) (see for instance Fig. 1 of Kato & Yamabe...
7.4 Discussion

In general, $E_2$ modes contain elements of mirror plane symmetry as recognized from the symmetry-descending correlation between $C_{5v}$ and its subgroup $C_5$, that is, the $E_2$ representation converts as $E_2 \rightarrow A' + A''$ (Wilson Jr. et al. 1955). Therefore, the substantial atomic orbital mixing among pentagonal carbons in the direction of the three JT-active $E_2$ modes generates stationary structures having compressed ($A''$) or elongated ($A'$) geometries.

The harmonic vibrational frequencies calculated for both $^2A'$ and $^2A''$ structures are mostly similar, and as a result, the simulated 30 cm$^{-1}$ FWHM IR spectra (Fig. 7.7) of the two states are almost indistinguishable at any particular DFT level. The only variations seen are essentially in relative intensities.

For instance, in the pure DFT methods (BP86 and BLYP) the largest intensity variation is found for the band with CH in-plane bending character computed roughly at 1170 cm$^{-1}$. The intensity of this band is larger in the $^2A''$ state by about 50% (except for the 6-31G basis set calculations where it is about 90% larger). For hybrid-DFT methods (B3LYP and B3P86), the largest intensity variation is seen in the band at roughly 1100 cm$^{-1}$ (this band is predicted at $\sim$ 1090 cm$^{-1}$ for BP86 and BLYP methods). For instance, in the cc-pVDZ basis-set calculations (see Fig. 7.7), its intensity in the $^2A''$ state is 30% larger for both hybrid functionals. We note that this band also has CH bending character.

Other bands in the spectrum appear nearly equal. For each particular DFT method, the main effect of a higher basis set is a correction of the relative intensity of the band at 1100 cm$^{-1}$ (or at 1090 cm$^{-1}$ for pure DFT methods), which is similar for both electronic states. This effect increasingly favors the match with the experimental IRMPD spectrum. At the highest levels of theory used, that is, those combining hybrid functionals with 6-311G(d,p) and cc-pVDZ basis sets, the calculated spectra are virtually identical. As the cc-pVDZ harmonic calculations reproduce the observed relative intensities slightly better, in particular, for the observed 1222 cm$^{-1}$ band, these calculations are used for the spectral comparisons in Fig. 7.7.

It is observed that all intensity variations found among DFT levels involve the CH bending modes in the 1000–1250 cm$^{-1}$ region. In the IRMPD spectrum, three close-lying semi-resolved bands at approximately 1092, 1154, and 1222 cm$^{-1}$ dominate this region. Inspection of the four DFT spectra calculated with the cc-pVDZ basis set (see Fig. 7.7) reveals that there are also three bands with predicted peak positions close to the three experimental bands, although the intensity pattern is clearly different. As already stated, these bands are characterized by symmetric ($A'$) and antisymmetric ($A''$) CH in-plane bending vibrations, although they also involve substantial in-plane stretching displacements of the five central carbons.

The weakest of the three bands, seen in hybrid B3P86 and B3LYP spectra near 1040 cm$^{-1}$, is unnoticeable to the eye in pure BP86 and BLYP spectra. This band, due to a single $a'$-mode, involves a strong CC-stretching character of the pentagonal inner ring. Along this mode, an induced change in electronic structure is expected, since it is known that in addition to $\pi$-orbital interactions among the five central carbons, $\sigma$-orbital interactions occur due to the curved geometry of corannulene; this contrasts planar PAH structures such as coronene, where orbital interactions are exclusively between $\pi$ orbitals of neighboring carbons (Kato & Yamabe 2002, 2006). The discrepancy in intensities as pre-
dicted by pure and hybrid functionals is possibly related to the different SOMO density distributions calculated by these methods, as it has been suggested that the phase patterns of these distributions influence the IR mode intensities Torii et al. (1999). Furthermore, animation of the 1040 cm\(^{-1}\) mode shows that it deforms the cation alternately between compressed and elongated geometries of the JT distorted cation, which possibly relates to the vibronic interaction in corannulene\(^+\). Its peak position calculated with the hybrid functionals, although somewhat redshifted, closely approximates the relatively broad band in the IRMPD spectrum centered at 1092 cm\(^{-1}\). Thus, the 1092, 1154, and 1222 cm\(^{-1}\) IRMPD bands are tentatively assigned to the nominal 1040, 1100, and 1200 cm\(^{-1}\) bands as calculated by the highest-level hybrid-DFT methods employed here (B3LYP and B3P86 spectra in Fig. 7.7).

The IRMPD bands at 835 and 1332 cm\(^{-1}\) appear well resolved in the IRMPD spectrum, and present a FWHM of 25 and 52 cm\(^{-1}\), respectively. The intensity of the 835 cm\(^{-1}\) IRMPD band is, according to theory, chiefly carried by a single symmetric CH out-of-plane bending mode and to a lesser extent, by two neighboring \(a'\) and \(a''\) modes of similar intensity characterized as breathing deformations of the five benzenoid rings. The narrow profile seen in the experiment is best reproduced at the BP86/cc-pVDZ level. In the hybrid-DFT spectra a splitting of this band is predicted owing to the neighboring \(a'\) and \(a''\) modes, which are computed at slightly lower frequencies. The 1332 cm\(^{-1}\) IRMPD band is reproduced by the nominal 1300 cm\(^{-1}\) hybrid-DFT harmonic band, and therefore assigned to an admixture of CH in-plane bending and CC stretching modes. Based on the harmonic band nominally located at 1630 cm\(^{-1}\) in the hybrid functional spectra (or at 1580 cm\(^{-1}\) for the BLYP and BP86 functionals), the very broad IRMPD signal centered around 1663 cm\(^{-1}\) is assigned as being due to CC stretching modes, where the carbons of the pentagonal ring display the largest displacements. Possibly, large anharmonicities of these modes cause the extreme broadening observed in the IRMPD spectrum. The increase in signal around 1760 cm\(^{-1}\) is an artifact that results from the decreasing FELIX power in this range in combination with the linear power-correction applied.

In summary, the calculated spectra give a qualitative match to the experimental spectrum, where the hybrid functionals appear to be slightly better than the pure functionals. The vibrational character of the modes calculated for the corannulene radical cation is consistent with the character of the modes found in other PAH cationic structures investigated before. Nevertheless, all experimental bands are blueshifted compared to the calculated harmonic frequencies, even though no scaling was applied and even though IRMPD bands are typically redshifted compared to linear absorption spectra. In contrast, bands for the neutral and protonated systems were accurately predicted. This outcome further indicates that, contrary to the two singlet systems studied here, the doublet radical cation does not rest on a well-defined single PES, but instead, on an intricate \(^2\)A\(^{\prime\prime}\)\(^–\)\(^2\)A\(^{\prime}\) PES with angular dependence around the JT C\(_5\)v conical intersection, as is the case for the corannulene anion (Sato et al. 2000). In contrast to many cationic PAHs (Oomens et al. (2003b), Chapter 6), where it has been shown that their IRMPD spectra can be successfully analyzed with linear-absorption harmonic DFT spectra, a comprehensive understanding of the observed IRMPD spectrum of the corannulene radical cation requires a more rigorous theoretical approach, which is beyond the scope of this investigation.
7.5 Effects of Curvature in the PAH Skeleton: Corannulene$^+$ versus Coronene$^+$

In Fig 7.8 the IRMPD spectra of corannulene$^+$ and coronene$^+$ (Oomens et al. 2001) are compared. As anticipated, the main distinction is an intensity enhancement of the CH in-plane bending modes around 1000–1250 cm$^{-1}$. This clearly indicates the influence of the inner pentagonal ring in corannulene$^+$, which undergoes pronounced deformations along vibrational modes in this frequency range. These induce charge redistributions that are not present (or that cancel out) in the higher-symmetry planar coronene$^+$, and which modify the dipole derivatives enhancing, in this case, the IR activity of those modes.

![Figure 7.8](image) – Comparison of the IRMPD spectra of corannulene and coronene radical cations.

In general, the strong IR intensities typical of PAH cations are the effect of long and short range charge fluxes among aromatic rings as a consequence of electron-vibration interactions (Torii 1999, Torii et al. 1999). Because of the pentagonal-ring deformations inherent to the warped structure, these charge fluctuations are stronger in corannulene$^+$ than in the planar coronene$^+$. This explains why the computed linear vibronic couplings for corannulene$^+$ are larger than those computed for coronene$^+$ (Kato & Yamabe 2006).

An important implication is that the modes in the 1000–1250 cm$^{-1}$ region featuring substantial intensity enhancement in corannulene$^+$ have a more mixed mode character (Torii 2000) than in coronene$^+$. Dynamic charge polarizations are, therefore, generally larger for corannulene$^+$ giving rise to larger dipole derivatives. Normal modes in this spectral range for corannulene$^+$ involve both CH in-plane bends and CC stretches (mainly within the pentagonal inner ring), while for coronene$^+$ they appear to have more pure CH in-plane character. Interestingly, planar PAH cations having a pentagonal ring also
show an intensity enhancement of CH in-plane bending modes in the same spectral region (Oomens et al. 2001) as compared to regular cationic PAHs of similar sizes.

The strong CH out-of-plane vibration near 840 cm\(^{-1}\) is qualitatively similar in both cationic systems, showing up as a well-resolved band in the far-IR range of the IRMPD spectrum, although in corannulene\(^+\) it appears to be somewhat more intense. The similar position for both species is expected based on the fact that both have only doubly adjacent CH groups (or “duets”) on their periphery (Hudgins & Allamandola 1999). The admixture of CH bends and CC stretches, featured in both corannulene\(^+\) and coronene\(^+\) as an intense well-resolved IRMPD band at 1332 cm\(^{-1}\) and 1330 cm\(^{-1}\), respectively, are virtually identical. To the high-frequency end of the spectral range studied, the IR activity observed in the corannulene\(^+\) and coronene\(^+\) spectra is carried by CC stretching modes. The nonplanar structure in corannulene\(^+\) appears to induce larger force constants, which cause a blueshift of these modes with respect those in coronene\(^+\).

### 7.6 Conclusions

IRMPD spectroscopy was applied to record the gas-phase spectra of protonated corannulene and the corannulene radical cation. Good agreement was found between the experimental IR spectrum of protonated corannulene and the computed spectrum for a structure where one of the peripheral C-atoms is protonated. The spectral features of protonated corannulene are analogous to those recently observed for various protonated PAH species. This similarity is believed to be due to the combined effect of charge (q = +1) and spin (S = 0) states common among protonated PAH species.

The corannulene radical cation undergoes Jahn-Teller distortion as a consequence of the degenerate HOMO in the neutral form. Extensive DFT calculations were performed for the radical cation in its two distorted C\(_s\) geometries. The computed energy difference between \(2\)A\(^{'}\) and \(2\)A\(^{''}\) structures is small, hence suggesting a dynamical Jahn-Teller distortion of the corannulene radical cation. Accordingly, strictly speaking, its doublet ground state cannot be associated with a single optimized local-minimum structure. Thus, while a comparison of the IRMPD spectrum with harmonic DFT spectra gives a qualitative, overall agreement at the highest levels of theory used, a one-to-one assignment of each of the bands remains speculative. Of all computational methods used, the best match was found for B3LYP and B3P86, employing both the cc-pVDZ and 6-311G(d,p) basis function sets.

A comparison between the IRMPD spectra of corannulene\(^+\) and its “planar analog” coronene\(^+\) shows the influence of charge redistribution on relative intensities along certain frequency modes. In particular, modes involving CC stretching vibrations within the pentagonal inner ring are largely affected. Especially in the 1000–1250 cm\(^{-1}\) region, the IR intensities in corannulene\(^+\) are substantially higher than in coronene\(^+\). Spectral comparison was also made with the positively charged corannuleneH\(^+\), where the extra hydrogen changes the structure and symmetry reducing the pentagonal CC stretching character in these modes. In coronene\(^+\) and corannuleneH\(^+\), the modes are characterized mainly by CH in-plane bends, whereas in corannulene\(^+\), they involve both CH bends and CC stretches, chiefly among carbons of the highly vibronically active pentagonal ring.