Infrared Spectrum of Hydrogenated Corannulene \( \text{rim-HC}_2\text{0H}_{10} \)
Isolated in Solid \( \text{para}-\text{Hydrogen} \)

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Abstract

Hydrogenated polycyclic aromatic hydrocarbons have been proposed to be carriers of the interstellar unidentified infrared (UIR) emission bands and the catalysts for formation of H₂; spectral characterizations of these species are hence important. We report the infrared (IR) spectrum of mono-hydrogenated corannulene (HC₂₀H₁₀) in solid para-hydrogen (p-H₂). In experiments of electron bombardment of a mixture of corannulene and p-H₂ during deposition of a matrix at 3.2 K, two groups of spectral lines increased with time during maintenance of the matrix in darkness after deposition. Lines in one group were assigned to the most stable isomer of hydrogenated corannulene, rim-HC₂₀H₁₀, according to the expected chemistry and a comparison with scaled harmonic vibrational wavenumbers and IR intensities predicted with the B3PW91/6-311++G(2d,2p) method. The lines in the other group do not agree with predicted spectra of other HC₂₀H₁₀ isomers and remain unassigned. Alternative hydrogenation was achieved with H-atoms produced photochemically in the infrared-induced reaction Cl + H₂ (v = 1) → H + HCl in a Cl₂/C₂₀H₁₀/p-H₂ matrix. With this method, only lines attributable to rim-HC₂₀H₁₀ were observed, indicating that hydrogenation via a quantum-mechanical tunneling mechanism produces preferably the least-energy rim-HC₂₀H₁₀ regardless of similar barrier heights and widths for the formation of rim-HC₂₀H₁₀ and hub-HC₂₀H₁₀. The mechanisms of formation in both experiments are discussed. The bands near 3.3 and 3.4 μm of rim-HC₂₀H₁₀ agree with the UIR emission bands in position and relative intensity, but other bands do not match satisfactorily with the UIR bands.
I. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) are ubiquitous in the interstellar media (ISM). These molecules, composed primarily of carbon in fused rings, are believed to be the carbon compound of the most common class in the galaxy, meteorites, cometary, and cosmic dust. PAH and their derivatives are considered as possible candidates for the carriers of the interstellar unidentified infrared (UIR) emission bands. The 3.4-μm feature observed in the UIR emission has been postulated to originate from aliphatic CH stretching vibration modes of hydrogenated PAH. Spectral signatures of hydrogenated PAH identified in a laboratory will help to assess this hypothesis and, moreover, enable observers to probe these species in the ISM.

In addition, PAH and their derivatives have been suggested to be able to catalyze the formation of H2. Because H2 is the most abundant molecule in the universe, its formation and evolution in the interstellar space are important in many astrochemical processes. Gaseous reactions involving H-atom recombination, radiative association, and other processes to produce H2 molecules are too slow to account for the abundance of H2 in the ISM. The main route for the formation of H2 is hence generally assumed to occur through the recombination of H-atoms on dust grain surfaces. A physisorbed hydrogen atom can combine with another hydrogen atom to form H2, which eventually evaporates into space, but these processes require very low temperature, 10–20 K. H2 formation via this mechanism cannot occur in the photodissociation regions where dust and gas temperatures are higher. However, high H2 formation rates have been observed in the
photodissociation region. In order to explain the observed rates, we need to consider other mechanisms responsible for the H$_2$ formation, and one proposed mechanism is the H$_2$ formation catalyzed by PAH and their derivatives. The proposed model for H$_2$ formation with PAH involves the capture of a hydrogen atom by a neutral PAH, $H + PAH \rightarrow HPAH$, or by a PAH cation (designated PAH$^+$), $H + PAH^+ \rightarrow H^+PAH$, in which HPAH and H$^+PAH$ denote mono-hydrogenated PAH and mono-protonated PAH, respectively. When a second H-atom extracts an excess hydrogen from HPAH or H$^+PAH$, molecular hydrogen can be formed.

We have recorded the infrared (IR) spectra of several HPAH and H$^+PAH$ in solid $p$-H$_2$ that were produced by electron bombardment on PAH/$p$-H$_2$ mixtures during deposition at 3.2 K. The advantages of our method include negligible fragmentation, narrow spectral lines, true absorption intensity, and wide spectral coverage. This method has been applied to benzene (C$_6$H$_6$), naphthalene (C$_{10}$H$_8$), pyrene (C$_{16}$H$_{10}$), coronene (C$_{24}$H$_{12}$), and ovalene (C$_{32}$H$_{14}$) to obtain IR spectra of their protonated and mono-hydrogenated species. That the reactions $H + PAH \rightarrow HPAH$ can occur via quantum tunneling of H-atom through small reaction barriers even at the low temperatures relevant to astronomical conditions has been demonstrated.

Extending our research to corannulene (C$_{20}$H$_{10}$), a bowl-shaped PAH that is considered to be a fragment of C$_{60}$, we reported recently the IR spectra of protonated corannulene isomers ($hub$-H$^+$C$_{20}$H$_{10}$ and $rim$-H$^+$C$_{20}$H$_{10}$). The IR spectrum of $hub$-H$^+$C$_{20}$H$_{10}$ matches well the UIR emission bands, consistent with the suggestions that H$^+PAH$ and non-planar PAH (and their derivatives) might...
be important contributors to the UIR bands.\textsuperscript{4,29} Hydrogenated corannulene (HC\textsubscript{20}H\textsubscript{10}) might consequently be present also in the ISM. Experiments on protonated corannulene in the gaseous phase\textsuperscript{30} and in solid $p$-H\textsubscript{2}\textsuperscript{28} are known, but, to our knowledge, no experiment on hydrogenated corannulene has been reported. The tentative assignments of a few IR lines of HC\textsubscript{20}H\textsubscript{10} observed in our preliminary experiments were presented recently.\textsuperscript{31} We report here the full IR assignments of the most stable isomer of hydrogenated corannulene ($rim$-HC\textsubscript{20}H\textsubscript{10}) in solid $p$-H\textsubscript{2}.

II. METHODS

Our experimental setup for $p$-H\textsubscript{2} matrix isolation is described elsewhere.\textsuperscript{20,32} In brief, the experiments were performed with a closed-cycle helium-refrigerator system capable of cooling a gold-coated copper substrate to 3.2 K; this copper plate serves also as a mirror to reflect the incident IR beam to the detector. A Fourier-transform infrared (FTIR) spectrometer, equipped with a KBr beam splitter and a Hg-Cd-Te detector (77 K), was used to record IR spectra in a spectral range 400–5000 cm\textsuperscript{-1}. Spectra were recorded with resolution 0.25 cm\textsuperscript{-1} and averaged over 500 scans at each stage of an experiment.\textsuperscript{25}

Two methods were utilized to produce hydrogenated corannulene. In the first method, gaseous mixtures of C\textsubscript{20}H\textsubscript{10}/$p$-H\textsubscript{2} were bombarded with electrons during deposition of a matrix at 3.2 K. The electrons ionized H\textsubscript{2} to produce H\textsubscript{2}$^+$ that readily reacted with another H\textsubscript{2} to form H\textsubscript{3}$^+$ and H-atom;\textsuperscript{33} reactions of H\textsubscript{3}$^+$ and H with corannulene led to protonated and mono-hydrogenated corannulene,
respectively. In the second method, a Cl₂/C₂₀H₁₀/p-H₂ matrix was photolyzed to produce Cl atoms; subsequent irradiation of the matrix with IR light induced the reaction Cl + H₂ (ν = 1) → H + HCl. The H-atom thus produced was mobile and could react effectively with corannulene.

In the electron-bombardment experiment, gaseous mixtures of C₂₀H₁₀/p-H₂ were prepared in situ during deposition. Para-H₂ was passed through a stainless steel tube (outer diameter 6 mm) containing corannulene (C₂₀H₁₀, >94 % purity, Kanto Chemical); the tube was heated to 408 K to increase the vapor pressure of the sample. The gaseous mixture of C₂₀H₁₀/p-H₂ was deposited onto the substrate at 3.2 K over a period of 10 h at a flow rate ~12 mmol h⁻¹. We estimated the mixing ratio of C₂₀H₁₀/p-H₂ in these experiments to be 3.0 ± 0.3 ppm according to the method of Ruzi et al. using the estimated matrix thickness and quantum-chemically predicted IR intensities of some intense lines of corannulene; the error represents only the fitting error from various lines, whereas the actual relative error might be as great as 50 %. The matrix was bombarded with an electron beam during deposition with current 30 µA and kinetic energy 270 eV. To distinguish the hydrogenated species from various species produced after electron bombardment, we maintained the matrix in darkness for 30 h. Secondary photolysis was subsequently performed with light at 520, 445, and 365 nm from light-emitting diodes and at 254 nm from a low-pressure Hg lamp.

In the Cl₂/C₂₀H₁₀/p-H₂ experiments, a C₂₀H₁₀/p-H₂ mixture and a small amount of Cl₂ gas were co-deposited over a period of 8 h with flow rate ~12.5 mmol h⁻¹ of C₂₀H₁₀/p-H₂; the temperature of the corannulene sample was set at 415 K. The flow rate of Cl₂ was adjusted to obtain a matrix with
an approximate mixing ratio \( \text{Cl}_2/\text{C}_{20}\text{H}_{10}/p\text{-H}_2 \approx 50/1/100,000 \). After deposition at 3.2 K, the matrix was irradiated with light at 405 nm from a diode laser (20 mW), followed by irradiation with IR light from a water-cooled Globar source. We employed light at 405 nm instead of the absorbance maximum of Cl\(_2\) near 365 nm to avoid unwanted photolysis of corannulene.\(^{28}\) During photolysis and acquisition of spectra, a long-pass filter (LP-2500 nm, Spectrogon) blocking light above 4000 cm\(^{-1}\) was employed to avoid the reaction between Cl and \( p\)-H\(_2\). Several ratios of Cl\(_2\)/C\(_{20}\)H\(_{10}\) and varied durations of visible and IR irradiations were investigated to achieve a better yield of hydrogenated products. To differentiate the products further, secondary photolysis was performed with light at 460 nm for 30 min and 365 nm for 30 min. \( p\)-Para-hydrogen was prepared in another closed-cycle helium-refrigerator system capable of cooling a 1/8" copper tube, filled with Fe(OH)\(_3\) catalyst, to 10 K. Normal-H\(_2\) (99.9999 %) was typically passed through the tube with a conversion temperature set to 13 K.\(^{32}\)

Quantum-chemical calculations were performed with Gaussian 09 (revisions C.01 and D.01). Geometrical optimization and harmonic vibrational analysis were performed with the B3PW91/6-311++G(2d,2p) method; this method has been applied to several PAH and H\(^+\)PAH investigated in our group; satisfactory agreements between predicted and observed IR spectra have been demonstrated.\(^{31}\) To account for the difference in the extent of anharmonicity between the CH stretching and other vibrational modes, the harmonic vibrational wavenumbers were scaled with factors of 0.958 for values >2500 cm\(^{-1}\) and 0.978 for values <2500 cm\(^{-1}\); these factors are the same
as those used for coronene, ovalene, and corannulene. In calculations of relative energies, correction of zero-point vibrational energy (ZPVE) was performed with unscaled harmonic vibrational wavenumbers.

III. COMPUTATIONAL RESULTS

Corannulene has carbon atoms of three distinct types; one consists of carbon atoms of the inner five-membered ring, one consists of the unfused carbons of the outer benzenoid rings, and the other consists of the fused carbon of these outer rings, to which we refer as hub-, rim-, and spoke-carbons, respectively. The hydrogen atom can attack a carbon of each of these three types. We found four stable isomers of hydrogenated corannulene HC$_{20}$H$_{10}$; representative bond angles and bond lengths are presented in Fig. 1. The spoke-carbon can be hydrogenated from both convex and concave sides of the molecule; the former is designated spoke-HC$_{20}$H$_{10}$ and the latter concave-spoke-HC$_{20}$H$_{10}$. Hydrogenation at the rim-site leads to only one product, rim-HC$_{20}$H$_{10}$. Although, for the hub-carbon, hydrogen atom can attack it from both the convex and the concave sides, we found only one stable isomer, hub-HC$_{20}$H$_{10}$, with hydrogenation from the convex side. All attempts to optimize concave-hub-HC$_{20}$H$_{10}$ resulted in concave-spoke-HC$_{20}$H$_{10}$. The isomer of least energy is rim-HC$_{20}$H$_{10}$, whereas hub-HC$_{20}$H$_{10}$ and spoke-HC$_{20}$H$_{10}$ have energies greater by 17.2 and 64.4 kJ mol$^{-1}$, respectively; all energies are corrected for ZPVE. The energy of concave-spoke-HC$_{20}$H$_{10}$ is 127.3 kJ
mol$^{-1}$ above that of rim-HC$_{20}$H$_{10}$, much greater than energies of the corresponding structures arising from hydrogenation at the convex side.

The potential-energy schemes for the hydrogenation of corannulene and the isomerization of hydrogenated corannulene are presented in Fig. 2. The energies of all four possible isomers of hydrogenated corannulene and the associated transition states (TS) for isomerization are listed in Table I. The formation of hub- or spoke-hydrogenated isomers from H + C$_{20}$H$_{10}$ has a barrier 10.7 or 22.4 kJ mol$^{-1}$, respectively. The barriers for the formation of the rim-isomer via attack from the convex and concave sides are 10.9 and 16.0 kJ mol$^{-1}$, respectively. The barrier for the formation of the concave-spoke-isomer is much greater, 45.8 kJ mol$^{-1}$. The barriers for the interconversion between isomers with neighboring hydrogenation sites are greater than the exothermicities of H + C$_{20}$H$_{10}$; once corannulene is hydrogenated in the tunneling reaction at low temperature, interconversion between them is hence unlikely.

Vibrational wavenumbers and IR intensities of the representative vibrational modes of hub-, rim-, and spoke-HC$_{20}$H$_{10}$, predicted with the B3PW91/6-311++G(2d,2p) method, are listed in Table II; the full lists of predicted values are available in Tables SI and SII. Those predicted for concave-spoke-HC$_{20}$H$_{10}$ are listed in Table SII. The isomers of HC$_{20}$H$_{10}$ have intense vibrational lines associated with the CH out-of-plane bending modes at 827.0 ($v_{54}$) and 835.2 ($v_{53}$) cm$^{-1}$ for rim-HC$_{20}$H$_{10}$, 829.5 ($v_{53}$) cm$^{-1}$ for hub-HC$_{20}$H$_{10}$, and 823.3 ($v_{54}$) and 847.2 ($v_{52}$) cm$^{-1}$ for spoke-HC$_{20}$H$_{10}$. The rim-HC$_{20}$H$_{10}$ has characteristic vibrational modes associated with the CH$_{2}$ moiety, with lines
associated with the CH\textsubscript{2} scissoring (mixed) mode predicted in region 1457.1–1407.2 (\nu\textsubscript{18}–\nu\textsubscript{24}) cm\textsuperscript{−1} and those with the CH\textsubscript{2} stretching modes predicted at 2828.3 (\nu\textsubscript{11}) and 2916.6 (\nu\textsubscript{10}) cm\textsuperscript{−1}. Vibrational lines of the CH stretching mode (\nu\textsubscript{11}) associated with the added H-atom are predicted at 2785.3 cm\textsuperscript{−1} for \textit{hub}-HC\textsubscript{20}H\textsubscript{10}, 2717.0 cm\textsuperscript{−1} for \textit{spoke}-HC\textsubscript{20}H\textsubscript{10}, and 2600.7 cm\textsuperscript{−1} for \textit{concave-spoke}-HC\textsubscript{20}H\textsubscript{10}.

The UV-Vis absorption spectra of \textit{rim}-, \textit{hub}-, \textit{spoke}-, and \textit{concave-spoke}-HC\textsubscript{20}H\textsubscript{10} predicted with the TD-B3PW91/6-311++G(2d,2p) method are shown in Fig. S1. The \textit{rim}-, \textit{hub}-, and \textit{spoke}-HC\textsubscript{20}H\textsubscript{10} isomers have similar absorption profiles with one weak line near 480–500 nm and an intense line near 300 nm. The absorption spectrum of \textit{concave-spoke}-HC\textsubscript{20}H\textsubscript{10} isomer has two features near 480 and 300 nm with similar intensities.

**IV. EXPERIMENTAL RESULTS**

**A. Electron bombardment on C\textsubscript{20}H\textsubscript{10}/p-H\textsubscript{2} mixtures**

Fig. 3(a) shows a partial IR spectrum of an electron-bombarded C\textsubscript{20}H\textsubscript{10}/p-H\textsubscript{2} matrix measured after deposition. The lines of C\textsubscript{20}H\textsubscript{10} are stripped (i.e., the IR lines of the parent molecule are subtracted from the spectrum by using a spectrum of C\textsubscript{20}H\textsubscript{10}/p-H\textsubscript{2} matrix deposited without electron bombardment); lines present in this spectrum are hence all induced by electron bombardment. The spectra in the CH stretching region (3150–2750 cm\textsuperscript{−1}) are shown in Fig. S2. The electron bombardment of C\textsubscript{20}H\textsubscript{10}/p-H\textsubscript{2} mixtures during deposition produces both protonated and hydrogenated corannulene as discussed in our previous work.\textsuperscript{28} To distinguish the protonated and hydrogenated
products, we maintained the matrix in darkness for 30 h during which the neutralization of the protonated corannulene, \( \text{HC}_{20}\text{H}_{10}^+ + e^- \rightarrow \text{HC}_{20}\text{H}_{10} \), and the H-atom addition to corannulene, \( \text{H} + \text{C}_{20}\text{H}_{10} \rightarrow \text{HC}_{20}\text{H}_{10} \), occurred. As a consequence of these reactions, lines of \( \text{HC}_{20}\text{H}_{10} \) are expected to increase in intensity with time. A difference spectrum obtained on subtracting the spectrum measured directly after deposition from one measured after 30 h is shown in Fig. 3(b).

During maintenance of the matrix in darkness for 30 h, lines marked A increased in intensity by ~20 % and those marked B increased by ~50 %. Group A consists of 26 lines with the most intense line at 827.1 cm\(^{-1}\) and lines with intensities \( \geq 10 \% \) of this most intense line, at 3051.2, 3048.1, 2908.2, 2792.3, 788.9, 768.3, 652.4, 638.6, 627.5, and 536.4 cm\(^{-1}\), as listed in Table III. Group B consists of 15 lines with this most intense line at 822.7 cm\(^{-1}\); these lines are also listed in Table III for comparison. Secondary photolysis was conducted at wavelengths 520, 445, 365, and 254 nm. At 365 and 445 nm, lines in groups A and B decreased to the same extent whereas no changes were observed upon irradiation at 520 and 254 nm. To be discussed in Sec. V-A, lines in group A are assigned to \( \text{rim-HC}_{20}\text{H}_{10} \) and those in group B might be due to some fragments.

**B. Photolysis of Cl\(_2/C_{20}H_{10}/p-H_2\) matrices**

After co-deposition of Cl\(_2\) and C\(_{20}H_{10}/p-H_2\), the matrix was subjected to photolysis at 405 nm for 1.5 h followed by IR irradiation for 3 h. The partial IR spectrum in the CH out-of-plane bending regions 860–750 and 680–600 cm\(^{-1}\), with lines of C\(_{20}H_{10}\) stripped, is shown in Fig. 4(a) and compared with the spectrum of an electron-bombarde\(d\) C\(_{20}H_{10}/p-H_2\) matrix shown in Fig. 4(b).
comparison for region 1510–500 cm\(^{-1}\) is presented in Fig. S3. These comparisons indicate that, in a visible- and IR-irradiated Cl\(_2/\text{C}_{20}\text{H}_{10}/p-\text{H}_2\) matrix, only one product (lines in group A) was produced. The wavenumbers and relative intensities of these lines are listed in Table III for comparison. This result allowed us to discriminate further lines in groups A and B.

V. DISCUSSION

A. Assignment of lines in group A to rim-HC\(_{20}\text{H}_{10}\)

As discussed in Sec IV-A, the increased intensity of lines in groups A and B during maintenance of the electron-bombarded matrix in darkness indicates that they might be associated with hydrogenated corannulene. Grouping of lines to A and B was achieved based on their behavior in darkness, the secondary photolysis, and the presence or absence in the Cl\(_2/\text{C}_{20}\text{H}_{10}/p-\text{H}_2\) experiments. The IR spectrum of a Cl\(_2/\text{C}_{20}\text{H}_{10}/p-\text{H}_2\) matrix measured after visible- and IR-irradiations is compared with quantum-chemically predicted IR spectra of rim-, hub-, and spoke-HC\(_{20}\text{H}_{10}\) in Fig. 5; these predicted spectra were simulated according to the scaled harmonic vibrational wavenumbers and IR intensities calculated with the B3PW91/6-311++G(2d,2p) method. The spectrum of an electron-bombarded C\(_{20}\text{H}_{10}/p-\text{H}_2\) matrix measured after deposition is also compared with these predicted spectra in Fig. S4.

According to the theoretical predictions (Table II), these three isomers of HC\(_{20}\text{H}_{10}\) show distinct patterns in the spectral region 1500–500 cm\(^{-1}\), with the most intense line in region 850–500 cm\(^{-1}\). In
this region, for \textit{rim-HC}_{20}H_{10}, six intense lines with IR intensities \(>10 \text{ km mol}^{-1}\) are predicted near 835.2, \textbf{827.0}, 786.1, 651.0, 638.4, and 537.2 cm\(^{-1}\); lines with intensities greater than 80 \% of that of the most intense line are listed in bold face. For \textit{hub-HC}_{20}H_{10}, six intense lines are predicted near \textbf{829.5}, 788.8, 775.4, 668.0, 642.3, and 529.0 cm\(^{-1}\) with IR intensities \(>10 \text{ km mol}^{-1}\). For \textit{spoke-HC}_{20}H_{10}, seven intense lines are predicted near 979.6, \textbf{847.2}, \textbf{823.3}, 801.5, 660.6, 635.1, and 549.7 cm\(^{-1}\) with IR intensities \(>10 \text{ km mol}^{-1}\).

Five intense lines in group A with wavenumbers \textbf{827.1}, 788.9, 652.4, 638.6, and 536.4 cm\(^{-1}\), with the most intense line in bold face, agree with those predicted for \textit{rim-HC}_{20}H_{10}; the line predicted at 835.2 cm\(^{-1}\) was unobserved because of severe interference from the most intense line of \textit{C}_{20}H_{10} near 837 cm\(^{-1}\). In addition to these lines, 8 lines in group A with moderate intensities at 1299.4, 1128.4, 1124.7, 947.5, 807.8, 768.3, 627.5, and 528.5 cm\(^{-1}\) were observed; their wavenumber and relative intensities agree satisfactorily with lines predicted at 1297.4, 1128.4, 1125.1, 947.5, 811.7, 763.8, 624.7, and 526.0 cm\(^{-1}\), as compared in Table III. For the CH stretching modes above 3030 cm\(^{-1}\) (Fig. S5), because of spectral congestion, we provide only tentative assignments. The CH\(_2\) stretching modes, which are characteristic of \textit{rim-HC}_{20}H_{10}, were predicted at 2916.6 (\(\nu_{10}\)) and 2828.3 (\(\nu_{11}\)) cm\(^{-1}\) and observed at 2908.2 and 2792.3 cm\(^{-1}\). The 26 lines in group A are hence assigned to \textit{rim-HC}_{20}H_{10} with mean absolute deviation 4.3 \(\pm\) 1.4 cm\(^{-1}\).

The spectrum of lines in group B observed in an electron-bombarded \textit{C}_{20}H_{10}/\(p\)-\textit{H}_2 matrix is compared in Fig. S4 with quantum-chemically predicted IR spectra of \textit{rim-}, \textit{hub-}, and \textit{spoke-}.
Below 1500 cm$^{-1}$, four intense lines in group B at 822.7, 777.6, 761.7, and 656.4 cm$^{-1}$ were observed. In addition to these lines, eleven lines were identified, as listed in Table III. These lines in group B do not agree with the predicted spectrum of $rim$- or $hub$- or $spoke$-HC$_{20}$H$_{10}$, indicating that the spectral carrier of lines in group B is not an isomer of HC$_{20}$H$_{10}$.

Depletion fractions upon secondary photolysis at 365 and 465 nm were similar for lines in groups A ($rim$-HC$_{20}$H$_{10}$) and B (unassigned product). According to the TD-DFT calculations with the B3PW91/6-311++G(2d,2p) method, $rim$-HC$_{20}$H$_{10}$ has absorption maxima near 300 and 480–500 nm (Fig. S1). The similarity between groups A and B upon secondary photolysis indicates that the spectral carrier of lines in group B might have a chromophore similar to that of $rim$-HC$_{20}$H$_{10}$.

We compared IR stick spectra of hydrogenated coronene ($rim$-HC$_{24}$H$_{12}$)$^{23}$ and hydrogenated corannulene ($rim$-HC$_{20}$H$_{10}$) in Fig. S6. The number of lines of $rim$-HC$_{24}$H$_{12}$ is smaller than that of $rim$-HC$_{20}$H$_{10}$ because of higher symmetry. The $rim$-HC$_{20}$H$_{10}$ has four intense lines in region 850–750 cm$^{-1}$ corresponding to CH out-of-plane bending modes, but $rim$-HC$_{24}$H$_{12}$ possesses only two intense lines. In addition, for $rim$-HC$_{24}$H$_{12}$, the vibrations associated with ring deformation and combination modes in region below 700 cm$^{-1}$ are unobserved due to small intensities except for the line observed at 541.0 cm$^{-1}$ due to the combination of CH out-of-plane bending and CH$_2$ rocking modes.

**B. Comparison with UIR emission bands**

The UIR emission spectra typically exhibit bands near 3.3 μm (CH stretching modes, with a weak feature at 3.4 μm), 6.2 and 7.7 μm (CC stretching modes of aromatic ring), 8.6 μm (CH in-plane
bending modes), and 11.2 μm (CH out-of-plane bending modes). The hydrogenated PAH are of astronomical significance especially in studying the 3.3 and 3.4 μm bands of the UIR emission, which correspond to the aromatic and aliphatic CH stretching modes, respectively. Several theoretical modelling and experimental studies have demonstrated that a PAH with an aliphatic side group could indeed contribute to the 3.4 μm band. Fig. 6 presents a comparison of the IR spectra of rim-HC20H10 and the most stable protonated isomer hub-H+C20H10 with the UIR bands from the Orion Bar PDR. Because experimental spectra are IR absorption spectra of matrix-isolated species, they might differ slightly from the UIR bands originating from UV-induced emission. For rim-HC20H10, the aromatic CH stretching mode is located at 3.28 μm and aliphatic CH stretching modes are located at 3.44 and 3.58 μm. The lines of the rim-HC20H10 at 3.28 and 3.44 μm are in close resemblance with the 3.3 and 3.4 μm bands of the UIR emission in terms of line positions and relative intensities.

The position of the CH stretching modes of the most stable protonated isomer, hub-H+C20H10, is red-shifted to 3.62 μm, close to the weak 3.74-μm line of the UIR emission. Compared with the spectrum of rim-HC20H10, the laboratory spectrum of hub-H+C20H10 is in close agreement with the UIR bands in the region 6–12 μm as discussed in our previous work. When we compare the spectra of protonated and hydrogenated species, the enhancement of intensities of features in the protonated isomer (hub-H+C20H10) near 6.2, 7.7, and 8.6 μm is evident, in general accordance with the argument that the 6.2, 7.7, and 8.6 μm bands are dominated by cationic/protonated PAH and the 3.3 and 11.2 μm are dominated by neutral PAH. However, the lines of CH out-of-plane bending modes in
hydrogenated corannulene \( \textit{rim-} \text{HC}_2\text{H}_{10} \) extending from 11.8–13.5 \( \mu \text{m} \) agree poorly with the intense UIR band near 11.2 \( \mu \text{m} \), but the corresponding line of the protonated species \( \textit{hub-} \text{H}^+\text{HC}_2\text{H}_{10} \) agrees well with the UIR band.

C. \underline{Mechanism of formation}

As discussed previously, in electron-bombardment experiments, \( \text{HC}_2\text{H}_{10} \) was produced either via reaction of corannulene with an H-atom or on neutralization of protonated corannulene \( \text{H}^+\text{HC}_2\text{H}_{10} \),\(^{28}\) whereas, in the Vis/IR irradiation experiments of \( \text{Cl}_2/\text{C}_2\text{H}_{10}/p-\text{H}_2 \), \( \text{HC}_2\text{H}_{10} \) was produced only via hydrogenation.

Because H-atom addition reactions to corannulene have small barriers (Fig. 2), these reactions can occur at low temperatures only through tunneling. According to calculations with the B3PW91/6-311++G(2d,2p) method, barrier heights for the formation of \( \textit{rim-} \), \( \textit{hub-} \), \( \textit{spoke-} \), and \( \textit{concave-spoke-} \text{HC}_2\text{H}_{10} \) are 10.9, 10.7, 22.4, and 45.8 kJ mol\(^{-1}\), respectively; the barriers for \( \textit{rim-} \) and \( \textit{hub-} \)-isomers are nearly identical, within computational accuracy. Calculations of the intrinsic reaction coordinate indicate that the widths of the barrier for the formation of \( \textit{rim-} \) and \( \textit{hub-} \)-isomers are also practically the same, but, as discussed in Sec IV-B, the H-atom addition preferably favors the formation of \( \textit{rim-} \text{HC}_2\text{H}_{10} \) that has the least energy. Intuitively, the greater density of states for the formation of \( \textit{rim-} \text{HC}_2\text{H}_{10} \) might be the reason for this preference. In our previous experiments on \( \text{H} + \text{ovalene (C}_{32}\text{H}_{14} \), we observed the formation of isomer 7-C\(_{32}\)H\(_{15}\) of least energy that has a barrier \( \sim 10 \) kJ mol\(^{-1}\); the next feasible channel producing 1-C\(_{32}\)H\(_{15}\) has a barrier \( \sim 13 \) kJ mol\(^{-1}\) and
energy 31 kJ mol$^{-1}$ above 7-C$_{32}$H$_{15}$, but was unobserved.$^{26}$

In one experiment with the Vis/IR irradiation of Cl$_2$/C$_{20}$H$_{10}$/p-H$_2$, the mixing ratio of C$_{20}$H$_{10}$ decreased from 10.5 to 9.4 ppm (a decrease of 1.1 ppm) upon IR irradiation and the mixing ratio of rim-HC$_{20}$H$_{10}$ was estimated to be 1.3 ppm; three most intense lines of rim-HC$_{20}$H$_{10}$ and their predicted IR intensities were used for the estimation. The decreased amount of parent and the amount of reaction product agree with each other within errors in mixing ratio estimation; in other words, the quantum yield of the hydrogenation reaction, H + C$_{20}$H$_{10}$ $\rightarrow$ rim-HC$_{20}$H$_{10}$ seems to be high. The mixing ratio of HCl produced upon IR irradiation was estimated to be ~50 ppm. If we assume that the mixing ratio of H atoms thus produced was comparable to that of HCl, it was much larger than the mixing ratio of the hydrogenated product (i.e., the amount of H atoms reacted), indicating that most H-atoms were consumed in the H$_2$ recombination reactions.

In one experiment with electron-bombarded C$_{20}$H$_{10}$/p-H$_2$, the mixing ratio of rim-HC$_{20}$H$_{10}$ after deposition was estimated to be 1.7 ppm. After maintenance of the matrix in darkness for 30 h, the mixing ratio of rim-HC$_{20}$H$_{10}$ increased to 2.0 ppm (an increase of 0.3 ppm), corresponding to relative increase ~20 %. In contrast, the mixing ratio of C$_{20}$H$_{10}$ decreased from 3.0 to 2.2 ppm (a decrease of 0.8 ppm). This decrease (0.8 ppm) is much greater than the increase of rim-HC$_{20}$H$_{10}$ (0.3 ppm), even though the errors in the estimation of mixing ratios based on theoretically predicted IR intensities might be as large as a factor of two. One possibility for the decrease of C$_{20}$H$_{10}$ might be due to side reactions leading to other products such as a carrier of lines in group B. However, it is difficult to
elucidate the exact mechanism and to estimate the contribution from \( \text{H} + \text{C}_{20}\text{H}_{10} \rightarrow \text{rim-HC}_{20}\text{H}_{10} \) reaction in darkness because, in our experiments, we observed only the time-integrated variation of species.

For protonated species \( \text{hub-H}^+\text{C}_{20}\text{H}_{10} \) and \( \text{rim-H}^+\text{C}_{20}\text{H}_{10} \), the mixing ratios after deposition were 0.14 and 0.10 ppm, respectively; after 30 h in darkness, the mixing ratios decreased to 0.03 ppm (a decrease of 0.11 ppm) and 0.02 ppm (a decrease of 0.08 ppm), respectively. The absence of \( \text{hub-HC}_{20}\text{H}_{10} \) in electron bombardment experiments indicated that this isomer was not produced by the neutralization of \( \text{hub-H}^+\text{C}_{20}\text{H}_{10} \). The increase of \( \text{rim-HC}_{20}\text{H}_{10} \) (0.3 ppm) after 30 h in darkness is significantly more than the decrease of \( \text{rim-H}^+\text{C}_{20}\text{H}_{10} \) (0.08 ppm), but is comparable to the sum of decreases of \( \text{hub-} \) and \( \text{rim-H}^+\text{C}_{20}\text{H}_{10} \) (0.19 ppm), considering the possible errors in the estimates. These results indicate two possibilities: (i) Neutralization of \( \text{hub-H}^+\text{C}_{20}\text{H}_{10} \) involves isomerization from \( \text{hub-} \) to \( \text{rim-} \)-isomer, though neutralization-induced isomerization has not been identified for other \( \text{H}^+\text{PAH} \) in solid \( p-\text{H}_2 \). (ii) Neutralization reaction proceeds via dissociation followed by recombination; i.e., \( \text{hub-H}^+\text{C}_{20}\text{H}_{10} + e^- \rightarrow \text{H} + \text{C}_{20}\text{H}_{10} \rightarrow \text{rim-HC}_{20}\text{H}_{10} \). This mechanism is consistent with the preferential formation of \( \text{rim-HC}_{20}\text{H}_{10} \) from \( \text{H} + \text{C}_{20}\text{H}_{10} \) in the \( \text{Cl}_2/\text{C}_{20}\text{H}_{10}/p-\text{H}_2 \) experiment and the absence of \( \text{hub-HC}_{20}\text{H}_{10} \) after deposition in the electron bombardment experiment.

So far, we are unable to provide a definitive assignment for lines in group B. These lines in group B were observed when a \( \text{Cl}_2/\text{C}_{20}\text{H}_{10}/p-\text{H}_2 \) matrix was irradiated with UV light (365 nm) followed by IR light; in contrast, visible (405 nm) and IR irradiation led to the formation of lines only in group A.
Furthermore, the lines in group B were observed only after IR irradiation. These results indicate that these lines in group B should originate from the hydrogenation reaction of fragments of C_{20}H_{10} produced via photolysis at 365 nm.\textsuperscript{28} From Table III, lines in group B show some similarity to those in group A.

VI. CONCLUSION

Electron bombardment during the deposition at 3.2 K of a mixture of C_{20}H_{10} and excess p-H\textsubscript{2} produced hydrogenated species \textit{rim}-HC_{20}H_{10}, in addition to protonated species \textit{hub}-H\textsuperscript+\textsubscript{C_{20}}H_{10} and \textit{rim}-H\textsuperscript+\textsubscript{C_{20}}H_{10}. IR lines in two groups (A and B) were identified according to the fractional increase of intensity when the matrix was maintained in darkness. The lines in group A are assigned to \textit{rim}-HC_{20}H_{10} based on the expected chemistry and comparison with the scaled harmonic vibrational wavenumbers and IR intensities predicted with the B3PW91/6-311++G(2d,2p) method. In experiments with a Cl\textsubscript{2}/C_{20}H_{10}/p-H\textsubscript{2} matrix, irradiated with light at 405 nm followed by IR light to generate H-atoms for reaction with C_{20}H_{10}, only \textit{rim}-HC_{20}H_{10} was observed. Although the bands near 3.3 and 3.4 \textmu{}m of \textit{rim}-HC_{20}H_{10} agree with the UIR bands, other bands do not match satisfactorily with the UIR bands.

The quantum-chemical computations predicted that barrier heights (10.7 and 10.9 kJ mol\textsuperscript{-1}, respectively) for the formation of \textit{hub}-HC_{20}H_{10} and \textit{rim}-HC_{20}H_{10} are similar, but only the formation of \textit{rim}-HC_{20}H_{10} in the reaction H + C_{20}H_{10} was observed. This preference in the tunneling
hydrogenation reaction might originate from the greater density of states for the formation of rim-\(\text{HC}_{20}\text{H}_{10}\), whose energy is lower than hub-\(\text{HC}_{20}\text{H}_{10}\) by \(\sim 17\) kJ mol\(^{-1}\).

The mechanisms for the formation of rim-\(\text{HC}_{20}\text{H}_{10}\) in electron-bombarded \(\text{C}_{20}\text{H}_{10}/p\text{-H}_{2}\) matrices were discussed according to its estimated mixing ratio at each stage of the experiments. Stoichiometric considerations on rim-\(\text{HC}_{20}\text{H}_{10}\), hub-\(\text{H}^+\text{C}_{20}\text{H}_{10}\), and rim-\(\text{H}^+\text{C}_{20}\text{H}_{10}\) identified in the matrix and especially the absence of hub-\(\text{HC}_{20}\text{H}_{10}\) indicate that, upon neutralization of hub-\(\text{H}^+\text{C}_{20}\text{H}_{10}\), isomerization of hub-\(\text{HC}_{20}\text{H}_{10}\) to rim-\(\text{HC}_{20}\text{H}_{10}\) and/or a dissociative recombination reaction followed by a hydrogenation reaction to form rim-\(\text{HC}_{20}\text{H}_{10}\) might occur.

**SUPPLEMENTAL MATERIAL**

Predicted absorption spectra of hub-\(\text{HC}_{20}\text{H}_{10}\), rim-\(\text{HC}_{20}\text{H}_{10}\), spoke-\(\text{HC}_{20}\text{H}_{10}\), and concave-spoke-\(\text{HC}_{20}\text{H}_{10}\) in the UV-Vis region (Fig. S1). Infrared spectra of the electron-bombarded \(\text{C}_{20}\text{H}_{10}/p\text{-H}_{2}\) matrix in region 3150–2750 cm\(^{-1}\) (Fig. S2). Comparison of infrared spectra in the 1510–500 cm\(^{-1}\) region measured in a hydrogen-addition experiment and in an electron-bombardment experiment (Fig. S3). Comparison of lines in groups A and B produced upon electron bombardment with simulated spectra in regions 1500–500 cm\(^{-1}\) (Fig. S4) and 3150–2750 cm\(^{-1}\) (Fig. S5). Comparison of infrared stick spectra of rim-\(\text{HC}_{24}\text{H}_{12}\) and rim-\(\text{HC}_{20}\text{H}_{10}\) (Fig. S6). Comparison of experimental vibrational wavenumbers and relative IR intensities of lines in group A with corresponding predicted
values for rim-HC$_{20}$H$_{10}$ (Table SI). Calculated vibrational wavenumbers and IR intensities of hub-HC$_{20}$H$_{10}$, spoke-HC$_{20}$H$_{10}$, and concave-speak-HC$_{20}$H$_{10}$ (Table SII).

ACKNOWLEDGEMENTS

This work was supported by Ministry of Science and Technology, Taiwan (grant No. MOST106-2745-M009-001-ASP and MOST107-3017-F009-003) and the Center for Emergent Functional Matter Science of National Chiao Tung University from The Featured Areas Research Center Program within the framework of the Higher Education Sprout Project by the Ministry of Education (MOE) in Taiwan. Japan Society for the Promotion of Science (JSPS KAKENHI grant No. JP18K03717) partially supported this work. The National Center for High-Performance Computation of Taiwan and the Information Initiative Center of Hokkaido University provided computer time.
<table>
<thead>
<tr>
<th>Isomer&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Relative energy / kJ mol&lt;sup&gt;−1&lt;/sup&gt;</th>
<th>Barrier for formation&lt;sup&gt;c&lt;/sup&gt; / kJ mol&lt;sup&gt;−1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>rim</td>
<td>0.0</td>
<td>10.9, 16.0&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>hub</td>
<td>17.2</td>
<td>10.7</td>
</tr>
<tr>
<td>spoke</td>
<td>64.4</td>
<td>22.4</td>
</tr>
<tr>
<td>concave-spoke</td>
<td>127.3</td>
<td>45.8</td>
</tr>
<tr>
<td>TS1 (spoke-rim)</td>
<td>170.6</td>
<td></td>
</tr>
<tr>
<td>TS2 (hub-spoke)</td>
<td>198.1</td>
<td></td>
</tr>
<tr>
<td>TS3 (rim-concave-spoke)</td>
<td>188.4</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Zero-point vibrational energies are corrected using unscaled harmonic vibrational wavenumbers.

<sup>b</sup>See Fig. 1 for hydrogenation sites.

<sup>c</sup>Energy of the transition state relative to that of H + C<sub>20</sub>H<sub>10</sub>.

<sup>d</sup>Hydrogen atom approaching from the convex side.

<sup>e</sup>Hydrogen atom approaching from the concave side.
TABLE II. Representative vibrational wavenumbers (cm$^{-1}$) and relative IR intensities of *rim*-, *hub*-, and *spoke*-HC$_{20}$H$_{10}$ predicted with the B3PW91/6-311++G(2d,2p) method.$^{a,b}$

<table>
<thead>
<tr>
<th>Mode</th>
<th>$rim$-HC$<em>{20}$H$</em>{10}$ cm$^{-1}$ (Int.$^c$)</th>
<th>$hub$-HC$<em>{20}$H$</em>{10}$ cm$^{-1}$ (Int.$^c$)</th>
<th>$spoke$-HC$<em>{20}$H$</em>{10}$ cm$^{-1}$ (Int.$^c$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH stretch</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_2$</td>
<td>3052.5 (68)</td>
<td>3054.1 (44)</td>
<td>3053.2 (72)</td>
</tr>
<tr>
<td>$v_3$</td>
<td>3052.1 (19)</td>
<td>3053.4 (48)</td>
<td>3052.3 (17)</td>
</tr>
<tr>
<td>$v_4$</td>
<td>3051.0 (26)</td>
<td>3052.9 (16)</td>
<td>3046.2 (76)</td>
</tr>
<tr>
<td>$v_{10}$</td>
<td>2916.6 (24)</td>
<td>2785.3 (14)</td>
<td>3035.6 (11)</td>
</tr>
<tr>
<td>$v_{11}$</td>
<td>2828.3 (29)</td>
<td></td>
<td>2717.0 (24)</td>
</tr>
<tr>
<td>CC stretch, CH$_2$ Scissor, CH in-plane bend</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_{18}$</td>
<td>1457.1 (12)</td>
<td>$v_{38}$ 1143.7 (11)</td>
<td>$v_{19}$ 1472.1 (10)</td>
</tr>
<tr>
<td>$v_{19}$</td>
<td>1449.7 (10)</td>
<td></td>
<td>$v_{20}$ 1440.5 (10)</td>
</tr>
<tr>
<td>$v_{23}$</td>
<td>1413.6 (8)</td>
<td></td>
<td>$v_{29}$ 1301.4 (19)</td>
</tr>
<tr>
<td>$v_{24}$</td>
<td>1407.2 (8)</td>
<td></td>
<td>$v_{30}$ 1274.6 (19)</td>
</tr>
<tr>
<td>$v_{30}$</td>
<td>1297.4 (11)</td>
<td></td>
<td>$v_{40}$ 1125.5 (13)</td>
</tr>
<tr>
<td>CH out-of-plane bend, Ring deform</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_{53}$</td>
<td>835.2 (22)</td>
<td>$v_{53}$ 829.5 (100)</td>
<td>$v_{45}$ 976.6 (19)</td>
</tr>
<tr>
<td>$v_{54}$</td>
<td>827.0 (100)</td>
<td>$v_{55}$ 806.3 (9)</td>
<td>$v_{52}$ 847.2 (87)</td>
</tr>
<tr>
<td>$v_{57}$</td>
<td>786.1 (16)</td>
<td>$v_{57}$ 788.8 (13)</td>
<td>$v_{54}$ 823.3 (100)</td>
</tr>
<tr>
<td>$v_{63}$</td>
<td>651.0 (23)</td>
<td>$v_{58}$ 775.4 (11)</td>
<td>$v_{56}$ 801.5 (31)</td>
</tr>
<tr>
<td>$v_{64}$</td>
<td>638.4 (14)</td>
<td>$v_{59}$ 744.8 (9)</td>
<td>$v_{57}$ 798.4 (9)</td>
</tr>
<tr>
<td>$v_{66}$</td>
<td>624.7 (10)</td>
<td>$v_{63}$ 668.0 (23)</td>
<td>$v_{58}$ 786.7 (10)</td>
</tr>
<tr>
<td>$v_{71}$</td>
<td>537.2 (22)</td>
<td>$v_{64}$ 642.3 (14)</td>
<td>$v_{63}$ 660.6 (30)</td>
</tr>
<tr>
<td>$v_{72}$</td>
<td>529.0 (23)</td>
<td>$v_{65}$ 635.1 (44)</td>
<td></td>
</tr>
<tr>
<td>$v_{71}$</td>
<td>549.7 (35)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Vibrational modes with relative intensities ~10 % and higher are listed. Tables SI (*rim*) and SII (*hub* and *spoke*) present lists of all vibrational modes.

$^b$Harmonic vibrational wavenumbers are scaled with factors 0.958 and 0.978 for regions above and below 2500 cm$^{-1}$, respectively.

$^c$The predicted IR intensities in parentheses are normalized to the listed intensity of the most intense line in each species: *rim* ($v_{54}$), 72.3 km mol$^{-1}$; *hub* ($v_{53}$), 93.6 km mol$^{-1}$; *spoke* ($v_{54}$), 52.7 km mol$^{-1}$. 

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TABLE III. Comparison of experimental vibrational wavenumbers (cm\(^{-1}\)) and relative IR intensities of \(\text{rim-HC}_{20}\text{H}_{10}\) (group A) with corresponding values predicted with the B3PW91/6-311++G(2d,2p) method. Lines of group B are also listed for comparison.

<table>
<thead>
<tr>
<th>Mode(^a)</th>
<th>Calculated(^b)</th>
<th>Group A</th>
<th>Group B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(\text{C}<em>{20}\text{H}</em>{10}/p-\text{H}_2) (e(^-) bombardment)</td>
<td>(\text{Cl}<em>2/\text{C}</em>{20}\text{H}_{10}/p-\text{H}_2) (Vis/IR)</td>
</tr>
<tr>
<td>(\nu_2)</td>
<td>3052.5 (68)(^c)</td>
<td>3051.2??d (47)(^e)</td>
<td>3051.2??d (51)(^e)</td>
</tr>
<tr>
<td>(\nu_3)</td>
<td>3051.0 (26)</td>
<td>3048.1 (15)</td>
<td>3048.1 (15)</td>
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<tr>
<td>(\nu_7)</td>
<td>3035.6 (4)</td>
<td>3030.1 (5)</td>
<td>3030.1 (5)</td>
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<tr>
<td>(\nu_{10})</td>
<td>2916.6 (24)</td>
<td>2908.2 (10)</td>
<td>-(^f)</td>
</tr>
<tr>
<td>(\nu_{11})</td>
<td>2828.3 (29)</td>
<td>2792.3 (11)</td>
<td>2792.3 (10)</td>
</tr>
<tr>
<td>(\nu_{19})</td>
<td>1311.6 (7)</td>
<td>1311.3(^g) (7)</td>
<td>1311.3 (6)</td>
</tr>
<tr>
<td>(\nu_{20})</td>
<td>1297.4 (11)</td>
<td>1299.4 (5)</td>
<td>1299.4 (8)</td>
</tr>
<tr>
<td>(\nu_{31})</td>
<td>1280.9 (6)</td>
<td>1277.8 (2)</td>
<td>1277.8 (2)</td>
</tr>
<tr>
<td>(\nu_{32})</td>
<td>1225.3 (4)</td>
<td>1223.3 (3)</td>
<td>1223.3 (3)</td>
</tr>
<tr>
<td>(\nu_{36})</td>
<td>1166.2 (3)</td>
<td>1155.9 (3)</td>
<td>1155.9 (2)</td>
</tr>
<tr>
<td>(\nu_{40})</td>
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<td>1128.4 (7)</td>
<td>1128.4 (8)</td>
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<tr>
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<td>1125.1 (8)</td>
<td>1124.7 (7)</td>
<td>1124.7 (7)</td>
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<tr>
<td>(\nu_{47})</td>
<td>947.5 (9)</td>
<td>947.5 (9)</td>
<td>947.5 (9)</td>
</tr>
<tr>
<td>(\nu_{53})</td>
<td>835.2 (22)</td>
<td>-(^h)</td>
<td>-(^h)</td>
</tr>
<tr>
<td>(\nu_{54})</td>
<td>827.0 (100)</td>
<td>827.1 (100)</td>
<td>827.1 (100)</td>
</tr>
<tr>
<td>(\nu_{55})</td>
<td>811.7 (8)</td>
<td>807.8 (9)</td>
<td>807.8 (8)</td>
</tr>
<tr>
<td>(\nu_{56})</td>
<td>805.0 (3)</td>
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<td>788.9 (17)</td>
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<tr>
<td>(\nu_{58})</td>
<td>763.8 (6)</td>
<td>768.3 (11)</td>
<td>768.3 (10)</td>
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<tr>
<td>(\nu_{59})</td>
<td>748.9 (3)</td>
<td>734.1 (3)</td>
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<tr>
<td>(\nu_{63})</td>
<td>651.0 (23)</td>
<td>652.4 (24)</td>
<td>652.4 (24)</td>
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<tr>
<td>(\nu_{64})</td>
<td>638.4 (14)</td>
<td>638.6 (14)</td>
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<tr>
<td>(\nu_{71})</td>
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<td>536.4 (10)</td>
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</tr>
<tr>
<td>(\nu_{72})</td>
<td>532.9 (4)</td>
<td>534.0 (6)</td>
<td>534.4 (5)</td>
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<tr>
<td>(\nu_{73})</td>
<td>526.0 (7)</td>
<td>528.5 (8)</td>
<td>528.5 (7)</td>
</tr>
</tbody>
</table>

\(^a\)Table S1 presents a list of all vibrational modes.

\(^b\)Harmonic vibrational wavenumbers are scaled with factors 0.958 and 0.978 for regions above and below 2500 cm\(^{-1}\), respectively.

\(^c\)The predicted IR intensities in parentheses are normalized to the intensity of the most intense line (\(\nu_{54}\)) with IR intensity 72.3 km mol\(^{-1}\).


\textsuperscript{d}Assignments are tentative because of spectral congestion in the CH stretching region.

\textsuperscript{e}Integrated IR intensities as a percentage of the most intense line at 826.4 cm\(^{-1}\) are listed in parentheses.

\textsuperscript{f}Unobserved because of severe interference from \((\text{HCl})_n\).

\textsuperscript{g}The increase of this line in darkness was unidentified because of severe interference from \(\text{H}^+\text{C}_{20}\text{H}_{10}\) and \(\text{C}_{20}\text{H}_{10}\).

\textsuperscript{h}Unobserved because of the interference with the most intense line of \(\text{C}_{20}\text{H}_{10}\) near 837 cm\(^{-1}\).
FIG. 1. Geometries of (a) rim-HC$_{20}$H$_{10}$, (b) hub-HC$_{20}$H$_{10}$, (c) spoke-HC$_{20}$H$_{10}$, and (d) concave-spoke-HC$_{20}$H$_{10}$ optimized with the B3PW91/6-311++G(2d,2p) method. The ZPVE-corrected relative energies (in kJ mol$^{-1}$) are listed in parentheses. Bond lengths and angles are in Å and degree, respectively.

(Single column)
FIG. 2. Calculated relative energies of hydrogenated corannulene isomers (rim-, hub-, spoke-, and concave-spoke-HC$_{20}$H$_{10}$) and transition states connecting them. Calculations were performed with the B3PW91/6-311++G(2d,2p) method; zero-point vibrational energies were corrected with unscaled harmonic vibrational energies. Blue traces indicate hydrogen-addition reaction and red traces indicate isomerization. The values in parentheses are barrier heights relative to C$_{20}$H$_{10}$ + H. The formation of the rim-isomer can occur either via hydrogen atom approaching from the convex side (marked as a) and from the concave side (marked as b).
FIG. 3. Infrared spectra of electron-bombardment experiments on C$_{20}$H$_{10}$/p-H$_2$ in region 1510–500 cm$^{-1}$. (a) IR spectrum of the electron-bombarded matrix with lines of C$_{20}$H$_{10}$ subtracted using an IR spectrum of C$_{20}$H$_{10}$/p-H$_2$ matrix deposited without electron bombardment; (b) difference spectrum of the electron-bombarded matrix after maintenance in darkness at 3.2 K for 30 h; lines pointing upward indicate production and those pointing downward indicate destruction. The lines in groups A and B are indicated with red and blue arrows, respectively. Tentative assignments are indicated with "?". The lines near 1100 and 1392 cm$^{-1}$ due to HO$_2$, which originated from the hydrogenation of O$_2$ impurity, are also indicated. Negative lines in trace (b) are due to C$_{20}$H$_{10}$ or H'C$_{20}$H$_{10}$ for which spectral assignments were presented in our previous work.$^{28}$ The regions suffering from extensive interference are indicated with grey rectangles.

(Double column)
FIG. 4. Comparison of IR spectra in regions 860–750 and 680–600 cm$^{-1}$ measured for a hydrogen-addition experiment and an electron-bombardment experiment. (a) The IR spectrum of Cl$_2$/C$_{20}$H$_{10}$/p-H$_2$ matrix after visible (405 nm) and IR irradiation. (b) The spectrum of the electron-bombarded C$_{20}$H$_{10}$/p-H$_2$ matrix after maintenance in darkness at 3.2 K for 30 h. From both traces, the lines of C$_{20}$H$_{10}$ were stripped. The lines in groups A and B are indicated with red and blue arrows, respectively.

(Single column)
FIG. 5. Comparison of an experimental IR spectrum with simulated spectra in region 1500–500 cm$^{-1}$. (a) The IR spectrum of a Cl$_2$/C$_{20}$H$_{10}$/p-H$_2$ matrix after visible (405 nm) and IR irradiation; the lines of C$_{20}$H$_{10}$ were stripped and lines in group A are indicated by red dots. Infrared stick spectra of (b) rim-HC$_{20}$H$_{10}$, (c) hub-HC$_{20}$H$_{10}$, and (d) spoke-HC$_{20}$H$_{10}$ simulated according to scaled harmonic vibrational wavenumbers and IR intensities predicted with the B3PW91/6-311++G(2d,2p) method; see text. In (a), the regions suffering from extensive interference are indicated with grey rectangles.

(Double column)
FIG. 6. Comparison of UIR bands with experimental IR spectra of hydrogenated and protonated corannulene in solid $p$-H$_2$. Experimental spectra of (a) $\text{hub-}H\text{C}_{20}\text{H}_{10}^2$ and (b) $\text{rim-}H\text{C}_{20}\text{H}_{10}$; (c) the UIR emission spectrum from Orion Bar PDR (Ref. 39). Experimental spectra are presented with sticks of which the heights represent integrated intensities. Solid red lines represent spectra convoluted with Gaussian profiles of full-width at half-maximum 30 cm$^{-1}$.

(Single column)
REFERENCES