



Research paper

Spectroscopic characterization of vinylidene formed from isomerization of acetylene on Pd(111)

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ABSTRACT

Acetylene on the Pd(111) surface was studied with reflection absorption infrared spectroscopy (RAIRS). Upon adsorption of acetylene at 90 K, no vibrational peaks are observed. However, after annealing the surface to 300 K, peaks at 1095 and 1327 cm^{-1} due to the CC stretch and CH_3 deformation modes of ethylidyne (CCH_3) are observed. These peaks are accompanied by a peak at 1425 cm^{-1} that is assigned to the CC stretch mode of vinylidene. The experimental spectrum is in good agreement with a simulated spectrum from DFT calculations of vinylidene on a Pd_{19} cluster model of the Pd(111) surface.

1. Introduction

The surface chemical reactions that underlie catalytic hydrogenation and dehydrogenation of simple hydrocarbons have been extensively studied for many decades [1–7]. One goal of many of these studies has been to establish the elementary steps of the reactions and hence the mechanism. As part of this goal, vibrational spectroscopies are frequently used to identify stable surface intermediates [8–10]. Yet definitive identification of surface moieties is often elusive for a variety of reasons. These include multiple possible species having similar vibrational spectra, insufficient sensitivity to detect all the expected modes, the lack of suitable reference spectra for analogous well-characterized organometallic species, and the difficulty of accurately simulating the spectra of hypothesized species from theoretical calculations [11]. These issues pertain even to the relatively simple C_2H_x intermediates in catalytic reactions of C_2 hydrocarbons. Here we focus on the spectroscopic characterization with reflection absorption infrared spectroscopy (RAIRS) of vinylidene, CCH_2 , on the Pd(111) surface, which several studies have indicated is a stable surface species that forms from the isomerization of adsorbed acetylene. Similar C_2H_x surface chemistry occurs on the Pt(111) surface. However, there are conflicting reports in the literature regarding the vibrational spectrum and stability of vinylidene on Pd(111). As a relatively small molecule, vinylidene possesses only a few normal modes of vibration, so a detailed assessment of its vibrational spectrum should be possible.

An early study with low energy electron diffraction (LEED) suggested that a CCH_2 intermediate might form from acetylene interaction with a

Pt(111) surface [12]. Other LEED studies indicated that the same stable surface moiety formed from acetylene and ethylene to give a (2×2) pattern on Pt(111) [13,14]. In an early surface vibrational study using high resolution electron energy loss spectroscopy (HREELS), Ibach and Lehwald proposed that vinylidene was the stable intermediate that formed on Pt(111) from acetylene and ethylene adsorption [15]. Similarly, vinylidene was identified as the stable intermediate that forms from acetylene at room temperature on Pd(111) [16]. Latter LEED studies identified ethylidyne, CCH_3 , as the stable intermediate on Pt(111) [17,18], a conclusion also reached in a subsequent HREELS study [19]. Numerous studies since then have confirmed this assignment. Nevertheless, vinylidene is a plausible intermediate in the surface chemistry of C_2H_x hydrocarbons on metal surfaces. For example, the first step in the formation of ethylidyne from adsorbed acetylene is likely the isomerization of C_2H_2 to CCH_2 with subsequent hydrogenation from residual hydrogen to form CCH_3 .

To identify surface vinylidene with vibrational spectroscopy requires careful consideration of the frequencies and intensities of the vibrational modes of the adsorbed molecule. Various theoretical studies indicate that vinylidene bonds to both Pd(111) and Pt(111) as an $\eta^2\mu_3$ species in which the end carbon bonds at a metal three-fold site and the second carbon also bonds to one of the metal atoms of the three-fold site [20–27]. The $\text{C}=\text{C}$ bond is tilted from the surface normal, but the molecule retains a plane of symmetry such that four modes have symmetry allowed fundamentals by the surface selection rule. These modes are composed largely of four internal coordinates, the symmetric C-H stretch, the $\text{C}=\text{C}$ stretch, the CH_2 scissors mode, and a CH_2 wagging

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mode. The two normal modes with fundamentals in the 1100 to 1500 cm^{-1} range both contain substantial contributions from the C=C stretch and the CH_2 scissors coordinates, which has led to some ambiguity in the labelling of the vibrations. Evans and McNulty [28] reported the vibrational spectrum of $\eta^2\mu_3$ -vinylidene in an Os_3 complex and performed normal mode calculations and concluded that of the CH_2 scissor and C=C stretch modes, the former has the higher wavenumber value, which also agrees with an earlier study of this Os_3 complex [29]. However, from our DFT calculations we calculate frequencies of 1467 and 1304 cm^{-1} for the pair, with the higher frequency mode better described as the CC stretch with the lower one best described as the CH_2 scissors mode.

Kesmodel and coworkers have published several studies using HREELS on the adsorption and reactions of acetylene with the Pd(111) surface [30–32]. In the most recent of these studies, they identified vinylidene as an intermediate in the formation of ethylidyne from acetylene through the appearance of a set of peaks over a narrow temperature range of 203 to 233 K. They report the CH_2 scissors mode at 1415 to 1420 cm^{-1} , depending on acetylene exposure. The intensity of this peak reaches a maximum at 213 K. Other peaks attributed to vinylidene show a similar temperature dependence and were plausibly assigned to vinylidene, although there is considerable overlap with peaks assigned to acetylene or ethylidyne. In contrast, in a RAIRS study of acetylene exposed to Pd(111) at 300 K, Kaltchev et al. observed a peak at 1268 cm^{-1} , which they assigned to vinylidene [33]. In a later paper, the same research group stated that the most intense RAIRS peak for vinylidene on Pd(111) is at 1267 cm^{-1} [34]. RAIRS was used to identify vinylidene on Pt(111) formed from the thermal decomposition of vinyl halides, where it was found to be stable over the range of 130–170 K [35]. In that case, a peak at 1440 cm^{-1} was assigned to the CH_2 scissors mode of vinylidene, with peaks at 1306, 1071, and 921 cm^{-1} also assigned to vinylidene [35].

The discrepancies in the previous surface vibrational studies of vinylidene on the Pd(111) surface motivated the present study. We show through comparison of simulated and experimental spectra that vinylidene gives rise to a single vibrational peak at 1425 cm^{-1} with sufficient intensity to be observed with RAIRS and that vinylidene is stable over a narrow temperature range before it is hydrogenated by background hydrogen to ethylidyne. The results largely confirm the HREELS results of Jungworthová and Kesmodel [36]. However, our results imply that some of the peaks that they assign to vinylidene may be associated with either acetylene or ethylidyne.

2. Experimental

All experiments were carried out in a stainless steel ultra-high vacuum (UHV) chamber with a base pressure of 1×10^{-10} Torr. The chamber is equipped with an ion gun for Ar^+ sputtering (Physical Electronics, PHI 04–161), a Fourier transform infrared (FTIR) spectrometer (Mattson Instruments, RS-10,000), a hemispherical electron energy analyzer (VG Microtech, CLAM 2) with a dual Mg/Al anode X-ray source for X-ray photoelectron spectroscopy (XPS), and reverse view LEED optics (Princeton Research Instruments, RVL 8–120SH) [37]. All RAIR spectra were obtained with 1024 scans at a resolution of 4 cm^{-1} , unless otherwise noted.

The Pd(111) single crystal is spot-welded to two tantalum wires mounted on a liquid nitrogen cooled sample holder. A type K thermocouple was spot-welded to the edge of the crystal for temperature measurement. The sample can be resistively heated to 1200 K and cooled with liquid N_2 to 90 K. For the annealing experiments, a background RAIR spectrum was obtained at the measurement temperature of 90 or 298 K followed by heating the crystal to the target temperature for 60 s. The crystal was then cooled back to the measurement temperature where the sample spectrum was acquired. The Pd(111) surface was prepared by Ar^+ bombardment (1 keV, 5 μA) and annealing to 1200 K in UHV. The cleanliness of the surface was examined by XPS, LEED and O_2

TPD [37]. Acetylene (99.6%) was purchased from BOC Gases and further purified by several freeze–pump–thaw cycles before use. Hydrogen (99.9999%) was purchased from Matheson Gas Products and was used without further purification.

3. Computational method

Density functional theory (DFT) calculations of vinylidene and ethylidyne bonded to a palladium cluster (Pd_{19}) model of the Pd(111) surface were performed with the Gaussian 09 program [38]. Geometry optimizations and harmonic frequency calculations of the molecules on the Pd_{19} cluster were performed with the B3LYP functional and 6-311G(d,p) basis set for the carbon and hydrogen atoms. Visualization of the vibrations were performed with the GaussView Program [39]. For the Pd atoms of the Pd_{19} cluster, we used the frozen core option with the LanL2DZ basis set. The computations were conducted with the tight geometry optimization and the ultrafine integration grid. The DFT calculation includes an extra step called numerical integration of the functional to improve the accuracy of the calculation. The intensities of the RAIRS peaks were taken as the square of the component of the dipole moment derivatives along the surface normal. To assign the experimentally observed frequencies, the computed frequencies were scaled by a factor of 0.9668.

4. Results and discussion

Fig. 1 shows a series of RAIR spectra from 1000 to 1600 cm^{-1}

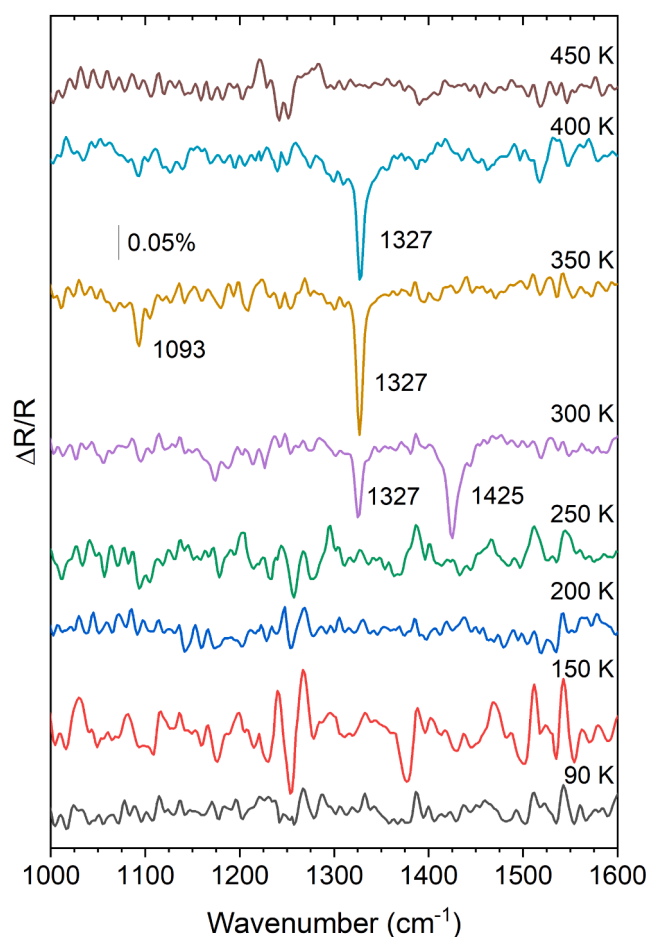


Fig. 1. RAIR spectra obtained after the Pd(111) surface at 90 K was exposed to 5.0 L of acetylene at 90 K, followed by annealing to the indicated temperature. These spectra were recorded at 90 K with 2 cm^{-1} resolution.

obtained after exposing the surface to 5.0 L of acetylene at 90 K and then annealing to the indicated temperatures. Essentially the same results (Fig. S1, Supporting Information) were obtained following a 100 L acetylene exposure indicating that 5 L is more than sufficient to saturate the surface, which occurs for a 1.0 L exposure. Unlike RAIRS studies of acetylene on other surfaces, no peaks attributable to adsorbed acetylene are visible in the 90 K spectrum, nor in the full spectral region from 800 to 4000 cm^{-1} . On Cu(111), we observed strong peaks at 1288 and 2921 cm^{-1} after acetylene adsorption at 90 K [40], in good agreement with a previous RAIRS study where the two peaks were assigned to the CC and CH stretches [41]. On Ag(111), acetylene is not rehybridized and the RAIR spectrum features a single sharp peak at 776 cm^{-1} assigned to the CH bending mode, consistent with a linear molecule oriented parallel to the surface [42]. In HREELS studies of acetylene on Pd(111), following adsorption at 120 K the most intense peak is at 675 cm^{-1} due to the CH bending mode [36]. This is just below the spectral range available with the RAIRS setup used here. It is therefore not surprising that no peaks due to adsorbed acetylene are observed in Fig. 1.

The temperature interval from 250 to 400 K in Fig. 1 shows two prominent peaks of ethylidyne, one at 1327 cm^{-1} assigned to the symmetric methyl deformation, $\delta(\text{CH}_3)_{\text{sym}}$, and the other at 1093 cm^{-1} assigned to the CC stretch, $\nu(\text{CC})$. The peak at 1425 cm^{-1} is assigned to the CC stretch mode of vinylidene and is only visible in the 300 K spectrum, whereas the ethylidyne peak at 1327 cm^{-1} is present after annealing to 300, 350, and 400 K. No peaks are visible after the 450 K anneal indicating that ethylidyne dissociation has occurred by this temperature. In agreement with a previous study [16], temperature programmed reaction spectroscopy (TPRS) results (Fig. S2) for acetylene adsorption on Pd(111) reveal an H_2 desorption peak at 441 K, which is at a higher temperature than H_2 desorption from the clean Pd(111) surface, indicating that it is due to ethylidyne decomposition. Ethylidyne decomposition is reported to produce the ethynyl species (CCH) [36], which has also been detected on Pt(111) with RAIRS from ethylidyne decomposition [43]. The observation of the 1425 cm^{-1} peak for vinylidene is in good agreement with the HREELS results of Jungwirthová and Kesmodel [36]. However, they also assigned to vinylidene peaks at 770, 875–880, 1100, and 2995 cm^{-1} , none of which we were able to detect. One of the challenges is that their resolution was 48–56 cm^{-1} , making it difficult to resolve vinylidene peaks from those of acetylene or ethylidyne. Although they list a peak at 770 cm^{-1} in their Table 3 and in their text, a peak at this position is not apparent in their Figs. 1 and 2 nor is its temperature dependence given in their Figs. 3 and 4. Their 875–880 cm^{-1} peak does reach a maximum intensity at 213 K, the temperature of maximum intensity for the 1415–1420 cm^{-1} peak. However, there is also a peak at this position for acetylene adsorption at 120 K. The peak at 1100 cm^{-1} overlaps strongly with the ethylidyne peak at 1095 cm^{-1} . In the C–H stretch region, the evolution from acetylene to vinylidene to ethylidyne to ethynyl is manifested by a peak shape indicative of unresolved components. Given that our RAIRS sensitivity was insufficient to observe the C–H stretch of acetylene, it is not surprising that we also do not detect the C–H stretch at 2985–2995 cm^{-1} that they assigned to vinylidene. Thus, the only peak clearly in common is the one at $\sim 1420 \text{ cm}^{-1}$. The two studies agree that this peak reaches its maximum intensity in a narrow temperature interval between where adsorbed acetylene and ethylidyne are the stable surface species, although they found this interval to be significantly lower than we did. Although the vinylidene peak is visible only in the 300 K spectrum, exposure of the surface to acetylene at room temperature yields only peaks due to ethylidyne (Fig. S5). Annealing the ethylidyne covered surface prepared this way yields the same results as observed in Fig. 1. When acetylene exposures to the Pd(111) surface at 298 K were varied from 0.5 to 15 L (Fig. S6), there was little variation in the ethylidyne intensities although the maximum was for a 1.0 L exposure.

Fig. 2 shows spectra analogous to those of Fig. 1 except the surface was dosed with 1.0 L of H_2 followed by 1.0 L of C_2H_2 at 90 K. The temperature interval from 250 to 400 K shows only the $\delta(\text{CH}_3)_{\text{sym}}$ and

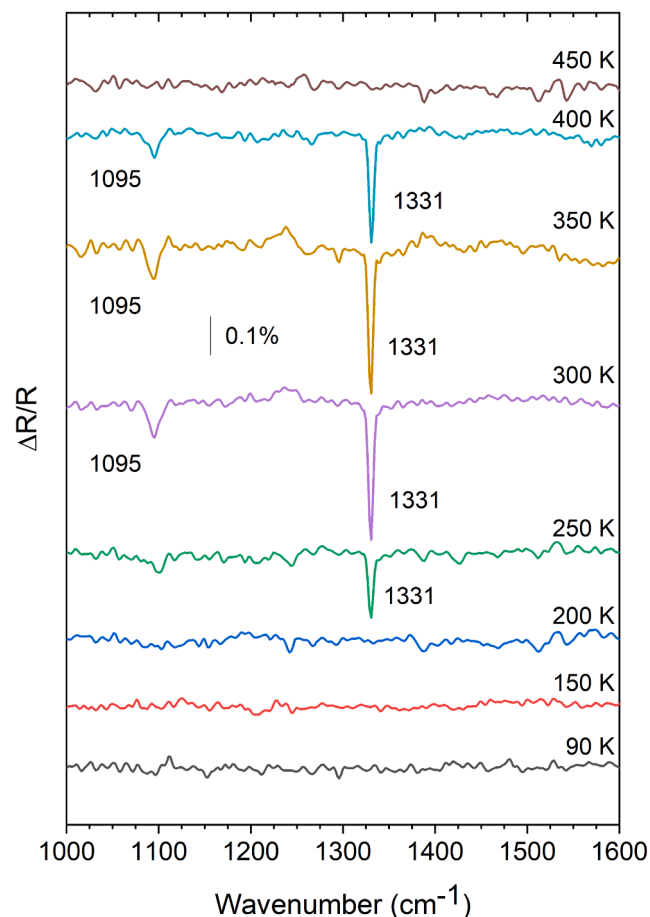


Fig. 2. RAIRS spectra after first exposing the Pd(111) surface at 90 K to 1.0 L of H_2 and then to 1.0 L of C_2H_2 followed by annealing to the indicated temperatures.

$\nu(\text{CC})$ peaks of ethylidyne, now at 1331 and 1095 cm^{-1} , respectively. The vinylidene peak is not seen. Increasing the initial hydrogen exposure to 10 L produced the same result (Fig. S3), indicating that a 1.0 L H_2 exposure was sufficient to convert all the vinylidene to ethylidyne. In contrast, in experiments in which the surface was first exposed to 1.0 L of acetylene, followed by 1.0 L of H_2 (Fig. S4), the vinylidene peak appears with comparable intensity as seen in Fig. 1. This indicates that pre-adsorption of acetylene suppresses hydrogen adsorption. Comparison of the results of Figs. 1 and 2 indicates that if there is a sufficient coverage of hydrogen on Pd(111), the conversion of vinylidene to ethylidyne is rapid enough that vinylidene does not accumulate on the surface. Because the surface hydrogen needed to form the ethylidyne seen in Fig. 1 presumably came from the chamber background, the H_2 partial pressure will determine the coverage ratio of vinylidene to ethylidyne. Since the background H_2 pressure will vary from one UHV system to another, the vinylidene to ethylidyne coverage ratio would be expected to also vary from one system to another. Thus, in cases with very low H_2 background pressures, it may be possible for vinylidene to be the dominant stable surface species formed from the exposure of acetylene to Pd(111) at room temperature, as reported by Omerod et al. [16].

To account for the observation of only one peak attributable to vinylidene, we have simulated the spectrum based on the results of our DFT calculations. Fig. 3 shows the simulated spectrum of vinylidene along with its optimized structure on the Pd_{19} cluster model of the Pd(111) surface. This shows that the 1467 cm^{-1} peak completely dominates the spectrum. The other calculated peaks that are allowed by the surface selection rule, such as the symmetric C–H stretch at 3009 cm^{-1} ,

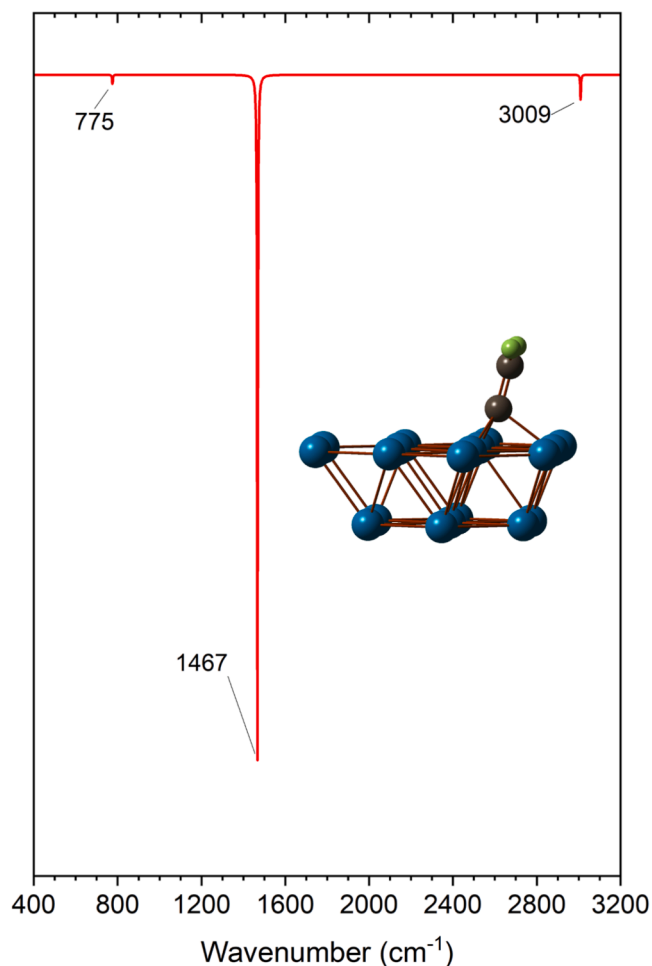


Fig. 3. Simulated RAIR spectrum of vinylidene on a Pd₁₉ cluster model of the Pd(111) surface.

the CH₂ scissors mode at 1304 cm⁻¹, and the wagging mode at 775 cm⁻¹, have much reduced intensity. For example, the 1467 cm⁻¹ peak is calculated to have an intensity greater than that of the 1304 cm⁻¹ peak by almost a factor of 10⁶. Clotet et al. calculated the structure and vibrational frequencies of vinylidene at the fcc and hcp sites of a Pd₉ cluster model of the Pd(111) surface and obtained frequencies of the most intense modes of 2954–2958, 1481–1491, 786–801, and 638–663 cm⁻¹ [21]. In agreement with our calculations, they described the 1481–1491 cm⁻¹ mode as the CC stretch. Although they also calculated intensities, there is no indication that they accounted for the surface selection rule so their intensities cannot be directly compared to our results. For the Pt(111) surface, Zhao et al. used a periodic five-layer slab model of the Pt(111) surface and calculated vibrational frequencies for η²_{μ3} vinylidene at coverages of 1/3 and 1/9 of a monolayer and obtained values of 3033–3043, 1413–1415, 1263–1256, and 980–973 cm⁻¹, but without calculated intensities [25]. They describe their 1413–1415 cm⁻¹ frequency as due to the CH₂ scissors mode, with the 1263–1256 cm⁻¹ one as the CC stretch [25], which is the opposite of what we and Clotet et al. [21] found. Corresponding to the 980–973 cm⁻¹ frequencies calculated by Zhao et al., [25] we calculated a frequency of 913 cm⁻¹, but with negligible intensity as this mode would be forbidden by symmetry. To demonstrate the reliability of our method of simulating RAIR spectra, we also show the simulated spectrum for ethylidyne and its structure in Fig. 4. The two most intense peaks in the simulated spectrum at 1073 and 1326 cm⁻¹ are in good agreement with the experimental peaks at 1095 and 1327 cm⁻¹. The simulation also predicts that the C–H

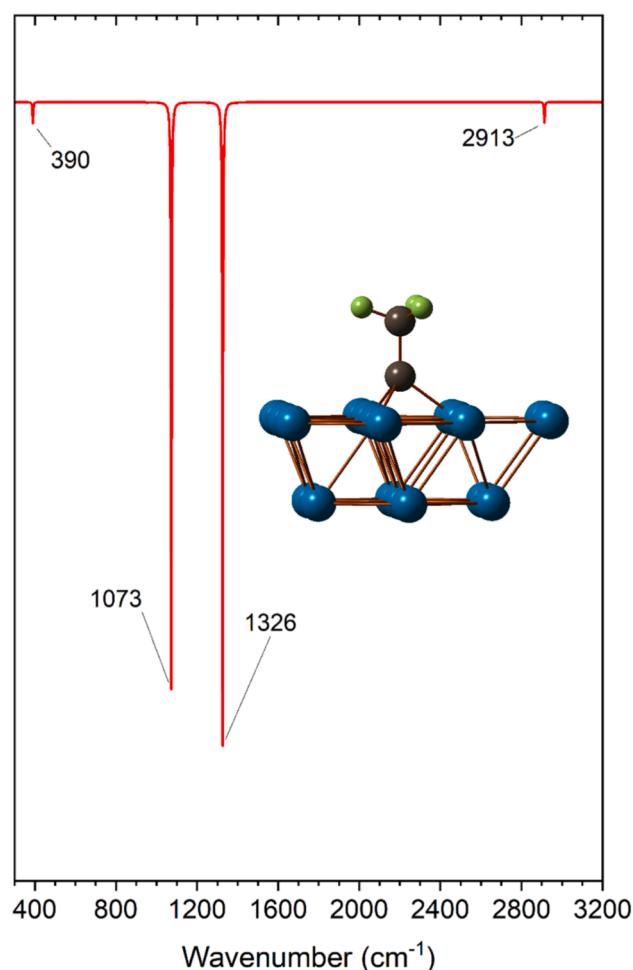


Fig. 4. Simulated RAIR spectrum of ethylidyne on a Pd₁₉ cluster model of the Pd(111) surface.

stretch would have a much lower intensity, making it unobservable given the noise level in the experimental spectra. On the Pt(111) surface, the C–H stretch of ethylidyne is readily observable with RAIRS [43–45]. The carbon–metal stretch of ethylidyne is also allowed by the surface selection rules and was observed with HREELS at 430 cm⁻¹ [19]. Our calculations indicate that this vibration occurs at 390 cm⁻¹ on Pd(111), which is below our low wavenumber cutoff and is calculated to be so weak that it would not be observable if our spectral range extended that low with the same noise levels seen at higher wavenumbers.

5. Conclusions

The results presented here support the conclusion of Jungwirthová and Kesmodel that acetylene converts to ethylidyne via a vinylidene intermediate [36]. Although annealing to 300 K after adsorbing acetylene at 90 K produces both vinylidene and ethylidyne, exposure of Pd(111) to acetylene at room temperature produces only ethylidyne. Vinylidene on Pd(111) is difficult to detect with RAIRS for three reasons: 1) It is stable only in a narrow temperature range; 2) In the presence of pre-adsorbed hydrogen, it is hydrogenated to ethylidyne as fast as it forms so that it never reaches a high enough coverage to give a measurable spectrum. The extent of the hydrogenation of vinylidene to ethylidyne will depend on the background H₂ partial pressure, a quantity that is both difficult to control and will vary from one UHV system to another; and 3) There is only a single peak, at 1425 cm⁻¹, with sufficient intensity to be observable above the noise in the spectrum. Nevertheless,

the 1425 cm⁻¹ peak provides a unique signature for vinylidene and could provide a means for further characterizing its role in the reactions of C₂ hydrocarbons on metal surfaces.

CRedit authorship contribution statement

Ravi Ranjan: Validation, Investigation, Data curation, Writing – original draft, Visualization. **Michael Trenary:** Conceptualization, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cplett.2023.140763>.

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