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Article

Heat of Adsorption of Propyne on Cu(111) from Isotherms Measured by Reflection Absorption Infrared Spectroscopy

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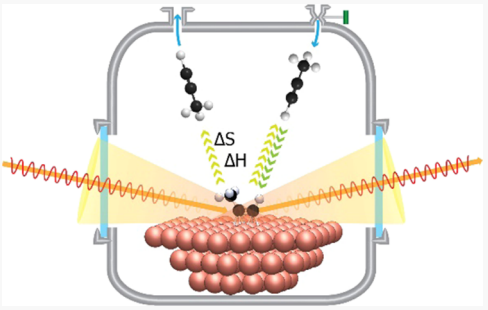
ABSTRACT: Reflection absorption infrared spectroscopy (RAIRS) has been used to show that under pressures of 5−100 nTorr, propyne adsorbs reversibly at room temperature on the Cu(111) surface. The pressure dependence of the propyne coverage, based on RAIRS peak areas, was found to follow a Langmuir isotherm. From fits of the isotherms, the equilibrium constants for the adsorption were determined at temperatures from 300.0 to 307.5 K. From van't Hoff plots of the temperature dependence of the equilibrium constant, a heat of adsorption of −120 ± 27 kJ mol^{-1} and an entropy change of adsorption of −171 ± 88 J mol^{-1} K^{-1} were determined. These values are consistent with the corresponding literature values of similar systems.



INTRODUCTION

The measurement of adsorption isotherms—plots of coverage versus equilibrium pressure—is a classic way to characterize gas adsorption on surfaces and is most often used for high-area powder samples. From fittings of the isotherms, equilibrium constants can be determined and from the temperature dependence of the equilibrium constants, heats of adsorption (ΔH) can be obtained. A recent study describes applications of gas adsorption in metal−organic frameworks, where it was noted that the measurements should be made over a narrow temperature range of no more than 20 K to avoid complications from the temperature dependence of ΔH.[1] However, it is difficult to gain precise atomic-scale information on powder surfaces, which is possible using well-characterized single crystals and ultrahigh vacuum (UHV) surface science techniques. Furthermore, computational studies often report heats of adsorption using models of surfaces based on specific crystallographic planes. Experimental benchmarks for such computational results should ideally be obtained on the same crystal surfaces assumed in these models. Because reflection absorption infrared spectroscopy (RAIRS) can be used to study adsorbates on single crystals under both UHV and ambient pressure conditions, it can provide data on the same models assumed in the theoretical calculations. Here, we use RAIRS to measure the surface coverage of propyne ($CH_3C{\equiv}CH$) reversibly adsorbed on a Cu(111) surface that is in dynamic equilibrium with gas-phase propyne. This allows us to determine the heat of adsorption of propyne, which we compare to the corresponding computational results. This method of determining ΔH_{ads} is complementary to the alternative experimental method of microcalorimetry.[2−6] While the latter is broadly applicable to a range of atomic and molecular adsorbates on the surfaces of metals and metal oxides, the use of RAIRS as described here has the advantage of providing structural information on the adsorbate in addition to ΔH_{ads}. For example, the C−O stretch frequency is different for CO adsorption at threefold hollow sites, twofold bridge sites, and atop sites on metal surfaces.[7] Therefore, correlations between heats of adsorption and adsorption site can, in principle, be obtained from RAIRS under dynamic equilibrium with gas-phase CO. For example, in a study similar to the present one, Truong et al. used RAIRS to obtain isotherms of CO on Cu(100).[8] Their spectra clearly revealed that their heats of adsorption were for CO bound to atop sites at both terraces and steps. In the present case, the RAIR spectra imply a specific bonding structure for propyne on Cu(111). The method used here also provides the entropy change for adsorption (ΔS), which can be related to the degree of order for the adsorbed molecule. Although the values we obtain for ΔH and ΔS in the present case have large error bars, it should be possible to improve the accuracy in future experiments and thereby use this method to obtain experimental values for thermodynamic quantities of central importance in gas−surface interactions.

EXPERIMENTAL METHODS

All experiments were performed in a stainless steel UHV system. Briefly, the system consisted of two main components separated by a manual gate valve: an upper UHV analysis

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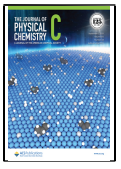

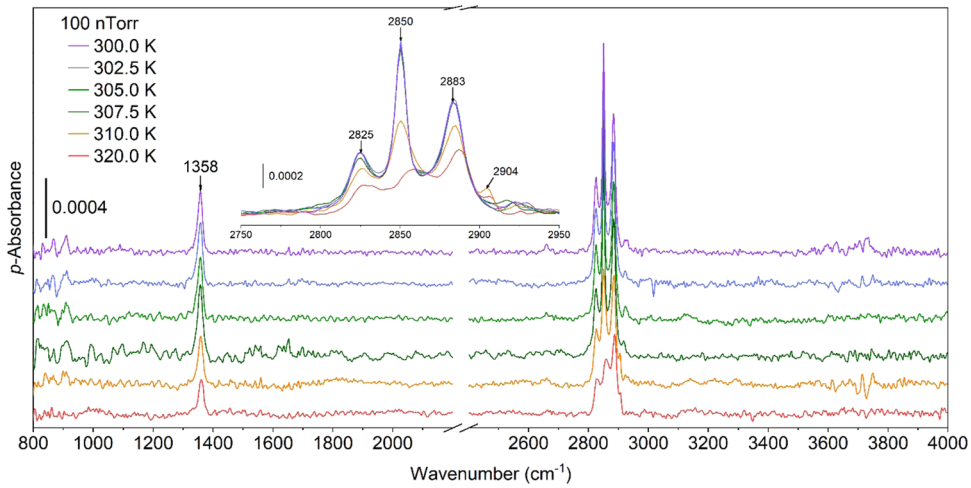

Figure 1. RAIR spectra of adsorbed propyne on the Cu(111) surface in the 300−320 K range in the presence of 100 nTorr of propyne. Four peaks in the C−H stretch region are enlarged in the inset. Peaks at 1358, 2825, 2850, and 2883 cm^{-1} are assigned to the following modes: a mix of C_1-C_2 stretch and CH_3 deformation, first overtone of asymmetric CH_3 deformation, alkynic C−H stretch, and symmetric CH_3 stretch. The peak at 2904 cm^{-1} is assigned to the coupling products at temperatures higher than 307.5 K.

chamber equipped for low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), and temperature-programmed desorption (TPD) and an ion gun for Ar^+ sputtering and a lower ambient pressure cell for RAIRS. The sample was transferred into the infrared (IR) cell through a set of spring-loaded Teflon seals, which then isolated the IR cell from the analysis chamber when the transfer rod was in place. During the IR experiments, the pressure in the IR cell was increased up to atmospheric pressure from its base pressure of 5.0×10^{-10} Torr, while the pressure in the main chamber was maintained at 5.0×10^{-10} Torr. In its current configuration, the system does not allow for cooling the crystal below room temperature.

The Cu(111) crystal was supplied by the Surface Preparation Laboratory and was in the shape of a disc, 15 mm in diameter and 2.5 mm thick. The tungsten support and heating wires passed through spark-eroded holes along the edges of the crystal. The type-K thermocouple was tightly wedged into a 0.3 mm diameter, 3 mm deep hole spark-eroded into the top edge of the crystal. The crystal surface was prepared in the upper chamber. The sample was annealed at 950 K by resistive heating for 10 min followed by argon ion sputtering at room temperature for 50 min (Ar pressure, 5×10^{-5} Torr; energy, 1500 eV). After 3 to 4 cycles of annealing and sputtering, the sample was treated with H_2 (5×10^{-5} Torr) at 1073 K for 3 h followed by annealing at the same temperature for 10 min. The additional hydrogen treatment was carried out to remove residual oxygen. Surface cleanness was verified by AES after cooling down to 300 K. The crystal was then translated into the lower chamber for RAIRS measurements.

The p-polarized RAIR spectra were collected using a Bruker Vertex 70v FTIR spectrometer with an external MCT detector with 1024 scans and a resolution of 4 cm^{-1} for an acquisition time per spectrum of 4 min. A constant current power supply controlled with a Watlow EZ-Zone PID controller provided direct heating to the Cu(111) crystal and maintained the temperature within 0.1 K. Propyne was introduced to the IR cell, open to the turbopump, with a precision leak valve, which was used to maintain the desired dynamic pressure for the duration of the data acquisition. Propyne (≥99%) was purchased from Millipore Sigma and used without further purification. Except where noted otherwise, the propyne pressures are given as uncorrected ion gauge readings.

RESULTS AND DISCUSSION

Figure 1 shows RAIRS spectra in the presence of 1×10^{-7} Torr (100 nTorr) of propyne for Cu(111) temperatures of 300.0 to 307.5 K. In previous studies using RAIRS,[9] photoelectron diffraction,[10] and density functional theory (DFT) calculations,[11−14] it was concluded that propyne is bound to Cu(111) in a di-σ/di-π fashion with the C_1-C_2 bond parallel to the surface, with the methyl group carbon denoted as C_3. The adsorbed geometry is highly distorted with the alkynic hydrogen and methyl groups both tilted away from the surface.[9] Chesters and McCash established that under UHV conditions, propyne desorbs without reaction from Cu(111) at 270 K. We find that at a slightly higher temperature of 300 K, propyne reversibly adsorbs on Cu(111) for propyne pressures above a few nTorr (Figure S1) to yield the same RAIR spectrum as under UHV conditions at lower temperatures.[9] The results shown in Figure S1 also reveal that at a pressure of 10 nTorr, the maximum propyne coverage is reached within the measurement time as no increase in coverage is seen for higher pressures of 15 and 20 nTorr. Saturation coverages of propyne were reached for propyne pressures of 10−100 nTorr, depending on the temperature (Figure S2). In accord with the study of Chesters and McCash,[9] we assign the three major peaks at 2825, 2850, and 2883 cm^{-1} (enlarged spectra in the inset of Figure 1) to the first overtone of the asymmetric CH_3 deformation, the alkynic C−H stretch, and the symmetric CH_3 stretch, respectively. In a previous study,[15] we assigned the peak at 1358 cm^{-1} to a normal mode with mixed C_1-C_2 stretch and $\delta(CH_3)$ character, as confirmed by the DFT calculations of Valcárcel et al.[14] In the presence of 100 nTorr of propyne, the peak intensities shown in Figure 1 were constant up to 307.5 K but were lower at 310 and 320 K. At these higher temperatures, coupling reactions occur, leading to irreversible adsorption. The development of the peak at 2904 cm^{-1} was likely associated with a coupling product. It was not included in the peak areas used to measure the coverage of adsorbed propyne.

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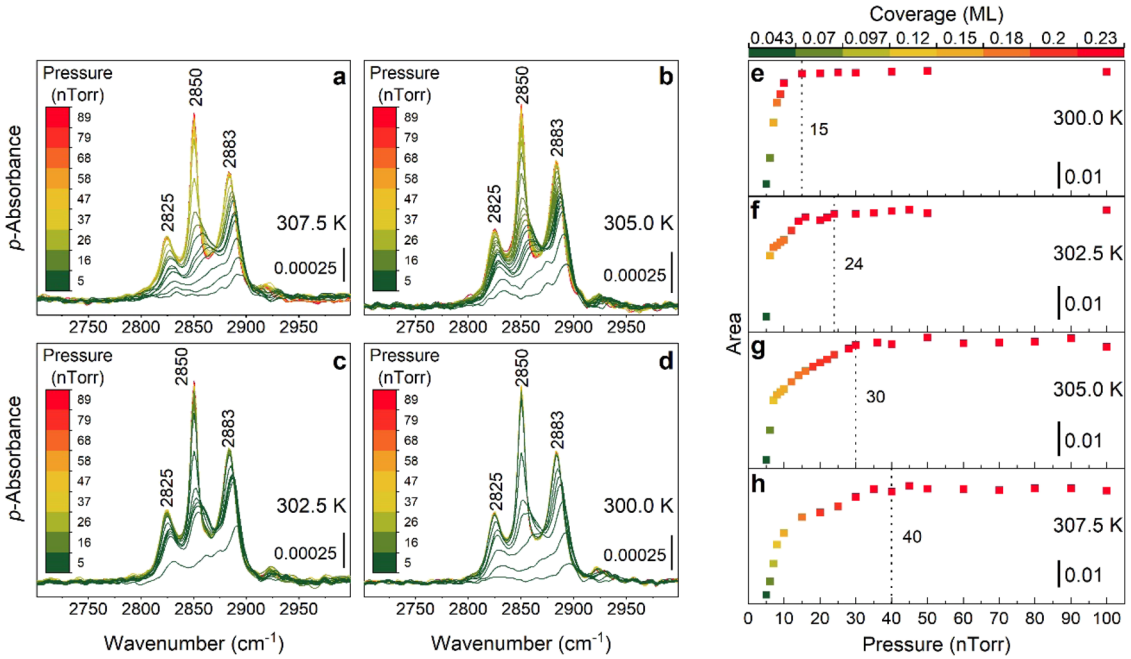

Figure 2. (a–d) RAIR spectra of adsorbed propyne on Cu(111) from 300 to 307.5 K as a function of equilibrium pressure. Three peaks in the C–H stretch region (2825, 2850, and 2883 cm^{-1}) were integrated separately and their total area was plotted versus pressure (e–h). The dotted vertical lines indicate the pressure at which propyne saturates the Cu(111) surface.

Figure 2a–d shows spectra in the C–H stretch region as a function of increasing pressure at 300.0, 302.5, 305.0, and 307.5 K. Figure 2e–h shows the total C–H stretch peak area versus pressure. These peaks were used rather than the peak at 1358 cm^{-1} as the former ones are more intense allowing their areas to be measured more accurately. Similar plots were obtained based on the 1358 cm^{-1} peak (Figure S3), but there was more scatter in the data. The relative intensity of the peaks in the C–H stretch region changes with coverage such that at the lowest coverage, the most intense one is just below 2900 cm^{-1}, whereas at the highest coverage, the 2850 cm^{-1} peak is the most intense. Through peak fitting, we deconvoluted three peaks in the C–H stretch region (Figure S4) and found that while two of them increase monotonically with the total C–H stretch area at each temperature, the third one either decreases, increases, or stays the same depending on the temperature. This indicates that there is an exchange in intensity among the modes in the C–H stretch region as the coverage changes. This observation and the smooth trend seen in the plots of Figure 2e–h suggest that the total C–H peak area is proportional to the coverage. This is also indicated by the plots of the total C–H stretch intensity versus intensity of the 1358 cm^{-1} peak, which display a linear relationship (Figure S5). This shows that if the 1358 cm^{-1} peak area is proportional to propyne coverage, then so is the total C–H stretch peak area.

A possible origin of the changes in the C–H stretch region with coverage can be found in the DFT studies of Valcárcel et al. of the structure, adsorption energy, and IR spectrum of propyne on Cu(111).[12,14] They concluded that the alkynic carbon (C_1) could be placed above either the hcp or fcc hollow site and they labeled these two forms as P (propyne) and t–P (twisted-propyne). They calculated frequencies and intensities for P and t–P for two cases. In the first case, two molecules, P and t–P, were placed in one unit cell of the $4 \times \sqrt{3}$ structure. In the second case, one molecule, either P or t–P, was placed in the smaller unit cell of a $2 \times \sqrt{3}$ structure. The coverage was the same in both cases, but the results with two molecules per unit cell provided some indication of how adsorbate–adsorbate interactions could affect frequencies and intensities. The frequencies of the two molecules in the two cases differed by no more than 10 cm^{-1} but the calculated intensities varied by as much as 40% for the symmetric C–H stretch among the cases. As Valcárcel et al. acknowledged,[14] their calculations ignored anharmonic effects, which are significant in the C–H stretch region. Thus, their results did not consider the overtone of the asymmetric CH_3 deformation, which is prominent in the experimental spectrum due to a Fermi resonance interaction with the symmetric C–H stretch fundamental. Although the calculation results cannot provide a quantitative understanding of the observed changes in relative intensity with coverage, they do reveal how sensitive the intensities are to subtle changes in the structure, even when these structural differences have no significant effect on adsorption energies.

The plots in Figure 2 show that the peak areas reach a constant value as the pressure increases. The dashed vertical lines indicate the pressures at which the peak areas saturate (i.e., the pressures above which the peak areas no longer increase). These are 15, 24, 30, and 40 nTorr for temperatures of 300.0, 302.5, 305.0, and 307.5 K, respectively. Toomes et al. concluded that the saturation coverage of propyne on Cu(111) is 0.25 monolayer (ML) based on the C 1s/Cu 3s peak area ratio in the photoemission spectra.[10] This coverage is also consistent with their observation of a $(4 \times \sqrt{3})$-rect LEED pattern with two molecules per unit cell. The solid lines shown in Figure 3a–d are fits of the data to Langmuir isotherms, where the dependence of coverage, θ, on pressure, P, is given by

$$\theta = \frac{K_{eq}P}{1 + K_{eq}P}$$

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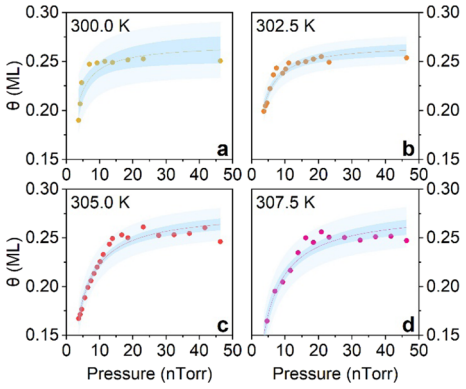

Figure 3. (a–d) Nonlinear fits to Langmuir isotherms of the propyne coverage on Cu(111) versus pressure at temperatures in the range of 300.0 to 307.5 K. The equilibrium constants at each temperature were calculated from the fitting parameters. The dark blue shading represents the 95% confidence interval, and the lighter blue shading represents the 95% prediction interval.

where K_{eq} is the equilibrium constant, which has units of inverse pressure in this equation. At the low pressures used here, the mean free path of the propyne molecules is long relative to the cell dimensions such that the molecules will have equilibrated with the cell walls before striking the Cu(111) surface. This means that the temperature of the gas had a constant value of room temperature as the surface temperature was varied. In the derivation of the Langmuir isotherm, it is assumed that equilibrium is reached when the rate of desorption equals the rate of adsorption; there is no requirement that the gas and the surface be at the same temperature. The temperature dependence of the equilibrium constant will then reflect the variation of the desorption rate and possibly the sticking coefficient with temperature.

Masel has considered the features of various isotherms and notes that the Langmuir isotherm can be derived by assuming that (1) adsorbates are immobile, (2) all sites are equivalent, (3) there is one adsorbate at each site, and (4) there are no interactions between adsorbates.[16] The first three assumptions likely hold for propyne on Cu(111), whereas assumption (4) is generally not valid although the saturation coverage of 0.25 ML is lower than the coverages where strong adsorbate–adsorbate interactions are known to occur. As reported by Masel, the Langmuir isotherm has the advantage that there is only one fitting parameter, the equilibrium constant.[16] Better fits to experimental coverage versus pressure plots can be obtained with other isotherms that explicitly consider adsorbate–adsorbate interactions as they contain more than one fitting parameter. By fitting our data to a Langmuir isotherm, we are assuming that the heat of adsorption is dominated by the propyne-surface bonding and is independent of coverage.

Although the data points in Figure 3a–d qualitatively follow the Langmuir isotherm, there is considerable scatter in the data. The temperature dependence of the equilibrium constants obtained from the fits in Figure 3a–d should follow the van't Hoff relation

$$\ln K_{eq} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$

such that a plot of ln K_{eq} versus $1/T$ should yield a straight line of slope $-\Delta H^0/R$ and intercept of $\Delta S^0/R$. The superscripts on ΔH^0 and ΔS^0 signify that these quantities are at standard pressure conditions of 1 bar. Numerically, expressing pressure in bar is equivalent to using a unitless pressure relative to 1 bar, that is, $K_{eq} = \left(\frac{P(\text{bar})}{1\ \text{bar}}\right)^{-1}$. Since ΔH^0 is based on the slope of the van't Hoff plot, the same value would be obtained regardless of the pressure units used and the accuracy of the absolute pressure will not affect the accuracy of ΔH^0 if the measured pressure is precisely proportional to the actual pressure. However, the numerical value of the intercept and hence of ΔS^0 will depend on the pressure units. Furthermore, any error in the absolute pressure measurement will affect the accuracy of ΔS^0. For this reason, the propyne pressures used to calculate K_{eq} have been corrected based on a reported ion gauge sensitivity of 2.16 for propyne.[17] From the fit of the data points in Figure 4 to the van't Hoff equation, we obtain $\Delta H^0 = -120 \pm 27$ kJ mol^{-1} and $\Delta S^0 = -171 \pm 88$ J mol^{-1} K^{-1}.

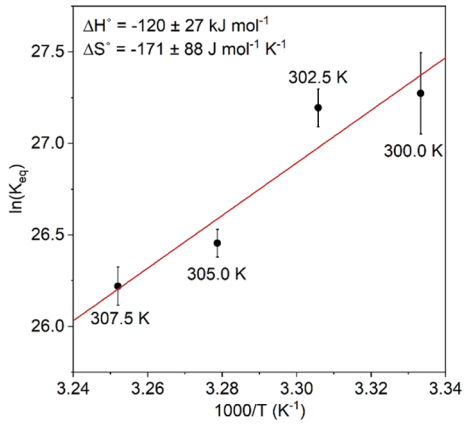

Figure 4. van't Hoff plot and its linear fit. The slope and intercept of the line are proportional to ΔH^0 and ΔS^0, respectively.

From the isotherm plots, it is possible in principle to extract the equilibrium pressures that give the same coverage at different temperatures. Then, according to the Clausius–Clapeyron equation, a plot of ln P versus $1/T$ should yield a straight line with a slope equal to the isosteric (constant coverage) heat of adsorption. The coverage dependence of ΔH would then provide information on adsorbate–adsorbate interactions as Truong et al. showed in their RAIRS study of CO on Cu(100).[8] Just as we use the total C–H stretch peak area as a measure of coverage, Truong et al. argued that the total CO peak area should be proportional to coverage. Obtaining isosteric heats of adsorption from a family of temperature-dependent isotherms requires accurate measurements of the equilibrium pressure for a wide range of coverages. Although we attempted to obtain isosteric heats by this method (Figure S6), any variation of ΔH with coverage was less than the experimental uncertainty.

There are several ways to compare the values for ΔH^0 and ΔS^0 determined here with other estimates for these quantities for propyne adsorption on Cu(111). Valcárcel et al. used DFT calculations to arrive at a binding energy for propyne on Cu(111) in the limit of zero coverage.[12] They showed that the value was highly dependent on the exchange-correlation functional used (B3LYP vs GGA) and whether the surface was modeled as finite Cu_{18} or Cu_{22} clusters or as an infinite two-dimensional three-layer slab. For some calculations, adsorption was found to be endothermic. The strongest

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exothermic binding of 83.0 kJ mol^{-1} was found for the GGA exchange-correlation functional and the slab model, which was taken as the basis for the reported value. Once repulsive adsorbate−adsorbate interactions were considered, they estimated the zero-coverage adsorption energy to be 89.7 ± 33.8 kJ mol^{-1}. The strong dependence of the calculated binding energy on the details of the calculation illustrates the need for reliable experimental benchmarks.

To make the comparison precise, it needs to be recognized that a calculated binding energy such as given by Valcárcel et al. is the internal energy difference (ΔU) at 0 K.[18] To obtain the value of ΔU at temperature T, translational, rotational, and vibrational contributions to the internal energy of gas-phase propyne need to be included as well as the vibrational contributions to U of adsorbed propyne. Although the large uncertainties in the present case make these contributions insignificant, the distinction will be more important if more accurate experimental measurements can be made. For propyne on Cu(111), the surface saturates at fairly low pressures making it difficult to characterize the adsorption at very low coverages. For more favorable systems, it should be possible to carry out isotherm measurements over a wider range of pressures, coverages, and temperatures, which should lead to more accurate thermodynamic quantities. Therefore, we consider the corrections in detail here.

At a finite temperature, translations and rotations each contribute $3/2RT$ to the internal energy.[18] Since $H = U + PV$, which equals $U + RT$ for an ideal gas, neglecting vibrational contributions, $H_{298.1}$ is higher than U_0 for gas-phase propyne (or any gas-phase nonlinear molecule) at 298.1 K by $4R(298.1\ K) = 9.91$ kJ/mol. Vibrational contributions are potentially significant only for the lowest frequency normal modes. For gas-phase propyne, the lowest frequency modes are ν_5 (A_1), ν_9 (E), and ν_{10} (E), with wavenumbers of 931, 633, and 328 cm^{-1}, respectively. Using the standard equation relating vibrational frequency to U,[19] these modes contribute 0.126, 0.374, and 1.01 kJ/mol, respectively. Therefore, the total vibrational contribution to the internal energy of gas-phase propyne at 298.1 K is: 0.126 + 2(0.374) + 2(1.01) = 2.89 kJ/mol, where the contributions from the degenerate E modes are doubled. Thus, H at 298.1 K for $CH_3CCH(g)$ is U_0 + 12.8 kJ mol^{-1}.

Although adsorbed propyne does not have translational and rotational degrees of freedom, it has low-frequency frustrated translations and rotations. In their Supporting Information, Valcárcel et al. provide calculated values for the 42 modes corresponding to two-propyne molecules per unit cell.[14] The lowest frequencies are 79 and 90 cm^{-1}. The contribution from the 25 modes with frequencies below 1000 cm^{-1} is 21.3 kJ/mol for two-adsorbed propyne molecules or 10.7 kJ mol^{-1} per molecule. The PV term for the adsorbed molecule should be negligible, so $H \approx U$ for an adsorbed molecule. Therefore, $\Delta H_{298.1} = \Delta U + 10.7 - 12.8 = \Delta U - 2.1$ kJ mol^{-1}. This shows that temperature contributions to the internal energy of the gas phase and adsorbed molecule almost cancel out because the low-frequency modes of the latter contribute almost as much to the internal energy as the translations and rotations contribute to the gas-phase molecule. Furthermore, this will generally be the case, so that except in the most precise study, experimental ΔH^0 values at elevated temperatures can be compared directly to calculated ΔU values at 0 K.

A common way to estimate binding energies is by using TPD. Although there do not appear to be any TPD results for propyne on Cu(111), Chesters and McCash state that propyne desorbs at around 270 K.[9] Toomes et al. noted that their LEED pattern for propyne on Cu(111) became sharper after annealing to 275 K,[10] suggesting that desorption had not occurred by that temperature. If we take 280 K as the peak desorption temperature that would be observed in a TPD experiment with a linear heating rate of 1 K/s, then Redhead's method[20] would give an activation energy for desorption of 75 kJ/mol, assuming a pre-exponential factor of 10^{13} s^{-1}. Although this is within the uncertainty of the value calculated by Valcárcel, it is below the lower range we obtain for ΔH^0.

The value of ΔS^0 of −171 ± 88 J mol^{-1} K^{-1} can be compared to Trouton's rule that ΔS^0 for vaporization is 88 ± 5 J mol^{-1} K^{-1}, which generally applies to nonpolar liquids.[21,22] Propyne vaporization follows Trouton's rule quite closely with ΔS^0 = 86.4 J mol^{-1} K^{-1}.[23] Because an ordered layer of propyne on Cu(111) would surely have a lower entropy than liquid propyne, we would expect the ΔS^0 value for adsorption to be more negative than the value of −84.6 J mol^{-1} K^{-1} for condensing propyne from vapor to liquid. In contrast, Onida et al., using IR spectroscopy in a way similar to ours, obtained an estimated value of −47.9 J mol^{-1} K^{-1} for propyne adsorption on a silica surface through interactions with OH sites.[23] However, they made measurements only at room temperature and estimated ΔS^0 from their ΔG^0 value and an estimated value of ΔH^0. They did not provide any uncertainty in their estimated ΔS^0 values. Onida et al. concluded that because only about half the surface sites were occupied, the disorder and hence entropy of the adsorbed propyne was higher than that of liquid propyne.[23] At the other limit, the standard entropy for propyne is 248.47 J mol^{-1} K^{-1}.[24] Thus, for the formation of a perfect crystal of propyne at 0 K from propyne gas, the entropy change would be −248 J mol^{-1} K^{-1} since the entropy of the final state, in this case, would be 0 according to the third law. Therefore, we expect in our case for ΔS^0 to be between −86.4 and −248 J mol^{-1} K^{-1} as it is. If a more precise value of ΔS^0 could be obtained from an experiment such as ours, this could provide information on the degree of order in the adsorbed state under dynamic equilibrium with the gas phase.

CONCLUSIONS

Propyne reversibly adsorbs on Cu(111) in the temperature range of 300.0 to 307.5 K. The pressure dependence of the propyne coverage, as measured in situ with RAIRS, was found to follow a Langmuir isotherm. From fits of the isotherms, the equilibrium constant for adsorption was obtained at each temperature. From the temperature dependence of the equilibrium constant, a standard heat of adsorption of −120 ± 27 kJ mol^{-1} and a standard entropy of adsorption of −171 ± 88 J mol^{-1} K^{-1} were obtained. The experimental heat of adsorption agrees with that obtained from DFT calculations within the large uncertainties of both values. The entropy of adsorption is in the range expected for adsorption from the gas phase into an ordered adsorbate phase.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c06750.

Additional RAIR spectra, isotherms based on the 1358 cm^{-1} peak, plots of the total C−H stretch peak area

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versus area of the 1358 cm^{-1} peak, and Clausius–Clapeyron plots (PDF)

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Notes

The authors declare no competing financial interest.

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