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Positron annihilation spectroscopy of methane monolayers adsorbed on graphite

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Positron annihilation lifetime and Doppler-broadening energy spectra have been measured between 13 and 95 K for 0, 0.50, and 0.81 submonolayers of methane adsorbed on graphite. Both the surface positron lifetimes (~0.31 ns) and S parameter (central) of the Doppler-broadening energy spectra are sensitive to the solid-solid, solid-liquid, and liquid–hypercritical-fluid phase transitions. Activation energies of 0.017±0.002 eV and 0.007±0.002 eV were obtained for surface-defect formation for $n = 0.5$ and 0.81, respectively, in two-dimensional methane on graphite surfaces. Applications of positron annihilation spectroscopy to study physisorption phenomena are discussed.

I. INTRODUCTION

In recent years, phase-transition phenomena associated with physisorption have been the most interesting systems in condensed-matter research. The physisorbed surface constitutes a simple two-dimensional (2D) system where the long-range interaction does not interfere. The weak van der Waals force dominates the 2D interactions among substrate and adsorbate molecules. Among these physisorbed systems, methane on graphite has been extensively studied by theoretical and experimental methods.

Experimental studies of methane on a graphite surface have been made by using neutron scattering,[1–6] nuclear-magnetic-resonance,[7–9] calorimetric,[10–13] vapor-pressure,[14–16] and low-energy electron diffraction methods. The detailed phase diagram has been reported at temperatures between 20 and 100 K and at fractional monolayer coverages from $n = 0$ to $n = 1.2$ by using high-resolution heat-capacity and vapor-pressure isotherm measurements. Neutron and heat-capacity studies have provided a complete 2D phase diagram. A commensurate $\sqrt{3}\times\sqrt{3}$ solid (CS) exists at low coverage ($n < 0.7$) and below 47.6 K and an expanded solid (ES) exists between 47.6 K and the 2D melting temperature (56.2 K). The critical temperature for two dimensions is 68.8 K. For the nearly complete monolayer ($n > 0.75$) region, the transition temperature shifts to higher temperatures according to the fraction of coverage. For example, at $n = 0.8$ coverage, the CS$\rightarrow$ES transition and melting temperatures are at 65.6 and 71 K, respectively. Detailed understanding of these phases and transition mechanisms is of high interest, particularly by using an alternative surface probe.

The positron (the antielectron)[17] is a powerful probe for materials research in condensed matter. The positron-electron annihilation photons contain information about the electronic density and momentum distribution in the condensed matter under study. In the past two decades, positron annihilation spectroscopy (PAS) has been used to probe the electronic structure and defects of solids. In the recent years, the development of slow positron beams has indicated that the positron can provide some new surface information which escapes detection by other techniques. In many solids, the positron and positronium work functions have been known to be negative. Consequently, the PAS signals are enhanced from the surface states of solids.

In this paper we wish to present the first result of using PAS in the study of methane-monolayer-adsorbed graphite surfaces. We have chosen $n = 0$, 0.5, and 0.81, where various 2D phase transitions are known to occur at different temperatures.

II. EXPERIMENTS

A. Submonolayer CH_4 on graphite

The substrate used in this study was Grafoil (from Union Carbide Co.), an exfoliated recompressed sheet of graphite powder, which has a density of 1.1 g/cm^3 and a specific surface area 17.3 m^2/g similar to those previously reported.[18,19] Grafoil samples (34.2 g) were first baked at 650 °C under 10^{-5} Torr vacuum (continuously pumping) for 24 h. Then the samples were transferred to a cell made of Al under a dry high-purity He atmosphere. A 25-μCi-of-^{22}Na (New England Nuclear-Dupont) positron source was deposited on a thin Al foil (0.8 mg/cm^2) and sandwiched between Grafoil samples. The assembled sample cell was connected to a closed-cycle He refrigerator (Displex, Air Product) and to a gas-handling setup.

The submonolayer isotherm adsorptions were performed at 77 K. Three temperature sensors (Au-Fe versus chromel, Pt resistor, and Ge resistor) were employed to monitor the temperature, which was controlled at ±0.1 K. Research-grade methane gas (99.99% purity from Matheson Gas Co.) was passed through a gas purifier (Matheson model 6406) in order to remove the residual impurity gases before it was introduced to the Grafoil sample. The vapor pressure was measured by using two absolute pressure gauges (mks transducer, Baratron).

The volume-pressure isotherm was obtained at 77 K and a monolayer coverage corresponds to a jump of adsorbed volume in the isotherm. The monolayer capacity was found to be 146 cm^3 standard temperature and pressure (STP) by extrapolating the line in the Henry's-law region (low coverage) and the line from the first plateau region. Following the convention of other methane studies, we defined the coverage to be $n=1$ at this amount of coverage. Thus $n=0.87$ corresponds to a coverage of a $\sqrt{3}\times\sqrt{3}$ commensurate solid overlayer at 77 K (see Fig. 1). Two volumes of CH_4, 73 and 118.4 cm^3, were physisorbed at 77 K. They correspond to $n=0.50$ and 0.81 submonolayer adsorptions. The adsorbed samples were gradually cooled down from 77 to 10 K in 24 h so that a more uniform surface was obtained. The experiments were performed from low to high temperature. In order to maintain a constant coverage, the gas pressure of the cell was monitored and adjusted at each temperature based on the logarithmic pressure and $1/T$ relationship.

B. Positron annihilation spectroscopy

Two positron annihilation methods, positron lifetime and Doppler-broadening energy spectroscopies, were utilized in this study. The positron lifetime measurements were performed by using a fast-fast coincident method. The resolution of the positron lifetime spectrometer was measured to be 260 ps from a ^{60}Co source. The actual resolution was obtained in computer analysis by using a program (PATFIT).[20] Source corrections in Al foils have been also made in the data analysis. Three positron lifetimes were resolved for the spectra obtained in this study. The short component ($\tau_1=0.18\pm0.02$ ns), the intermediate component ($\tau_2=0.32\pm0.03$ ns), and the long component ($\tau_3=2.5\pm0.5$ ns) were assigned to be positron annihilation in the bulk graphite, positron annihilation on the surface, and ortho-Ps annihilation, respectively, as previously discussed.[18,21]

The Doppler broadening in annihilation photon-energy spectra due to electronic motion was measured by using a coaxial Ge(Li) solid-state detector (Ortex EG&G, efficiency 15% at 1.3 MeV). A ^{103}Ru radioisotope (generated at the Research Reactor, University of Missouri) was used to monitor the detector resolution (which was found to be 1.5 keV at 497 keV peak) and the electronic stability. The electronic setup was similar to that previously reported.[22] The energy spectrum was processed and stabilized digitally using the method described elsewhere.[23] The Doppler-broadening results are expressed in terms of the S parameter, which is the ratio of the total counts near the central region of 511-keV peak to the total counts of the whole energy spectra after the background has been subtracted.

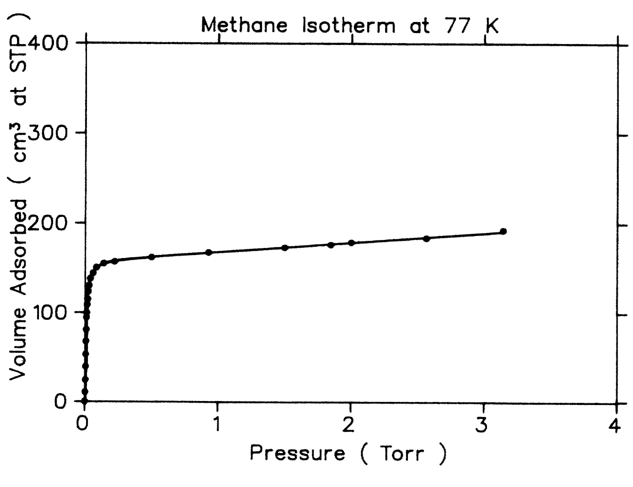

FIG. 1. Monolayer methane adsorption on Grafoil at 77 K. The abscissa and the ordinate represent the equilibrium gas pressure and the amount of CH_4 adsorbed (cm^3) at STP.

III. RESULTS AND DISCUSSION

The positron lifetime and Doppler-broadening experiments were performed as a function of temperature at a fixed fraction of coverage. Positron lifetime spectra were resolved in three components, i.e., short-, intermediate-, and long-lived components. Each component is contributed from positrons annihilated in a particular state. The positron can also pick up an electron and forms a positronium (Ps) atom. Therefore, the observed lifetime spectra contain the annihilation from both positron and Ps. The possible states for the positron and Ps are in the bulk, on the surface, and in the interfacial spaces and voids. It is not possible to distinguish all these states from our lifetime spectra: each state contributes a certain fraction to each of the three resolved lifetime components. The assignment of these states into three components can be made according to the electron and momentum density distribution in the materials under study.

First, we observe a long-lived component with $\tau_3=2.5\pm0.5$ ns and $I_3=0.4\pm0.1$ % in the systems under study. The τ_3 and I_3 are nearly constant and are independent of surface adsorption. This long-lived component is easily identified to be due to ortho-Ps (triplet Ps) annihilation. There are three possible sites for Ps annihilation, namely in the lattice, on the surface, and in the interfacial void. Recently, two-dimensional angular correlation measurements[24] have shown Ps formation in potassium-intercalated graphite with an intensity of 0.30 ± 0.05 % at higher temperature. Although it is still possible that Ps is confined along the c axis of graphite as these authors suggested, we believe that another possible site in the interfacial voids is responsible for this component. According to the known universal correlation between ortho-Ps lifetime and free-volume size,[25] 2.5 ns ortho-Ps lifetime corresponds to a void size of 7.2 Å. In ordinary graphite this size is much too large for the c-c distance (3.4 Å) along the c axis between two basal planes. A systematic lifetime measurement[21] as a function of surface area in graphite systems showed a direct correlation between I_3 and surface area. Oxygen chemical-quenching results[21] further confirm that this component is due to ortho-Ps annihilation in the interfacial voids. The constant value of I_3 and τ_3 with respect to adsorption can be understood that chemical quenching due to CH_4 molecule is insignificant in the monolayer region.

The short-lived component results were found to be $\tau_1=0.18\pm0.02$ ns and $I_1=69\pm2$ %. Besides a very small contribution from para-Ps (singlet Ps), where $\tau=0.125$

ns, this component is mainly due to positron annihilation in the bulk graphite. This assignment also agrees with results reported by authors.[26] The τ_1 and I_1 results do not vary with the presence of adsorbates or temperature. The significant variation of lifetime with respect to the adsorption and temperature is observed in the intermediate lifetime. The results with respect to CH_4 adsorption will be reported in a separate paper.[19] Figures 2 and 3 show the temperature dependence of τ_2 and I_2.

The values of τ_2 (~ 0.31 ns) correspond to the positron lifetime on the surface of graphite. Detailed arguments on the assignment of this component have been made in our preceding paper.[21] A direct correlation between I_2 and surface area was found in the graphite system. In Grafoils where various imperfections exist, we expect a large fraction of I_2. The τ_2 and I_2 obtained are slightly lower than previous reported values. This can be due to a slight difference in the Grafoil samples. The Grafoil in the preceding study contained a higher surface area (22–28 m^2/g) than that employed in this study (17 m^2/g). The observed I_2 are also consistent with those reported in a different type of graphite.[26] We, therefore, discuss the surface structure and phase transition from the variations of τ_2 and I_2 results shown in Figs. 2 and 3.

In bare Grafoil ($n = 0.0$), τ_2 increases with temperature (Fig. 2) with a slope of 1.12×10^{-4} K^{-1} which may be due to the thermal effect of lattice expansions. The positron mobility in graphite has been known[27] to be independent of temperature in this temperature region. This is consistent with our finding that I_2 stays nearly constant (Fig. 3). The most interesting results are the variations of τ_2 with respect to temperature at $n = 0.50$ and 0.81 CH_4 monolayer adsorptions.

As shown in Fig. 2, τ_2 starts to increase at 26 and 30 K for $n = 0.50$ and 8.1, respectively. Then τ_2 increases monotonically to maximum values at 56 and 78 K for $n = 50$ and 0.81, respectively. Beyond these temperatures, τ_2 begins to decrease and reach the τ_2 value of bare graphite at 90 and 96 K for $n = 0.50$ and 0.81, respectively. These temperatures are related to the known phase transition temperatures of 2D methane on graphite surfaces.

At very low temperature, only rotational order-disorder phase transitions have been reported[13] at 17–23 K. Our positron results do not show any change at these temperatures. Either positrons are not sensitive to a rotational order-disorder transition or this transition does not exist in 2D CH_4 surfaces. At this moment, we can not address this difference from our current positron technique. In the regions where τ_2 is monotonically increasing, there exists a well-known commensurate-to-incommensurate solid phase transition (CIT) at 47.6 and 54.4 K for $n = 0.50$ and 0.81 adsorptions.[13] Only a decreasing trend of I_2 is detected at these CIT transition temperatures (see Fig. 3). τ_2 does not show a jump at these CIT temperatures (see Fig. 2). This finding is consistent with our previous results[18] for Ar and N_2 monolayer adsorptions on Grafoils.

The maximum values of τ_2 coincide with the known 2D melting temperatures, i.e., 68.8 and 72 K for $n = 0.50$ and 8.1, respectively. From the results for Ar and N_2 of our preceding study and the current CH_4 results, we conclude that positron lifetime undergoes the biggest change at 2D melting points. A detectable change of I_2 corresponding to 2D melting points is also shown in Fig. 3. The increase of τ_2 below the melting point indicates that the electronic density, where positron annihilation occurs, decreases with respect to temperature. In PAS, an increase of τ_2 can occur due to phase transition and defect formation. The possible candidates for surface defects are vacancy, void, and dislocation. Since we do not observe an abrupt change of τ_2 at CIT transitions, we seek the explanation for τ_2 variation due to defect formation at 2D surfaces. The exact type of defect cannot be

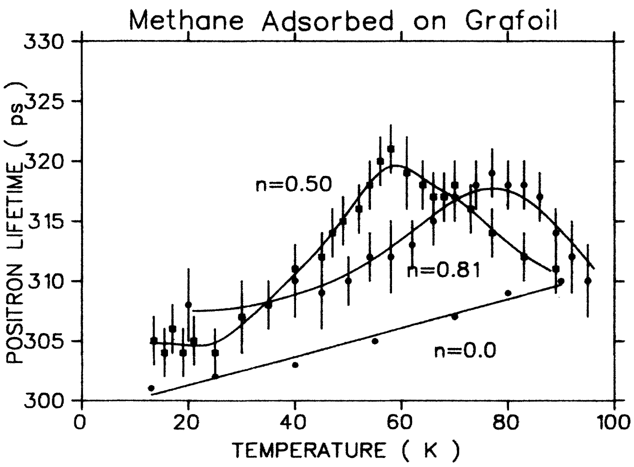

FIG. 2. Surface positron lifetime (τ_2) vs temperature for submonolayer methane adsorbed on Grafoil. n is the fraction of complete monolayer adsorption. The results of τ_1 and τ_3 are 180±20 ps and 2.5±0.5 ns. Errors are statistical. Lines are drawn as a guide to the eye.

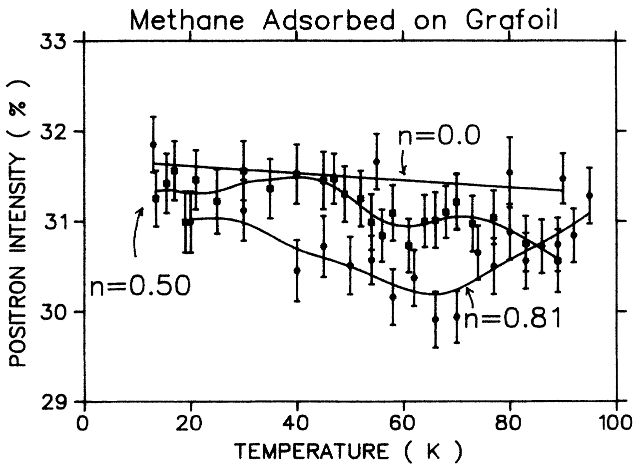

FIG. 3. Surface positron lifetime (I_2) vs temperature for submonolayer methane adsorbed on Grafoil. n is the fraction of complete monolayer adsorption. The results of I_1 and I_3 are 69±1% and 0.4±0.1%, respectively. Errors are statistical. Lines are drawn as a guide to the eye.

specified by the current PAS results. From the magnitude of the τ_2 increase, which is only about 5% (see Fig. 2), a surface vacancy is the most likely candidate responsible for this τ_2 variation although we can not rule out the possibility of dislocation. An increase of τ_2 indicates an increase of defect concentration and defect size. When the defect size increases, the electronic density decreases so that the positron lifetime increases. At the same time an increase of defect concentration can result an increase of τ_2. The latter consideration follows the well-known two-state positron trapping model which has been developed by positron solid-state theory.[17] A change of defect concentration may also change the observed I_2 values. Since the results of I_2 show a slight decrease, a quantitative interpretation from lifetime results becomes difficult and may not lead to useful information. On the other hand the Doppler-broadening results give a composite effect of surface defect formation.

We have obtained an S parameter which is taken as the ratio of total counts in the central region (± 0.90 keV) of the 511 keV annihilation peak to the total count of spectra, where the background was subtracted. This S parameter is a sensitive method to detect defect formation due to the change of electronic structure in the momentum space of electrons.[17] The resulting S parameters as a function of temperature for $n = 0$, 0.50, and 0.81 are shown in Fig. 4.

In bare graphite ($n = 0.0$), the S parameter increases as a function of temperature with a slope $= 3.92 \times 10^{-5}$ K^{-1}. Since lifetime increases intensity slightly decreases (Figs. 2 and 3), we expect the slope of the S parameter to be smaller than that of τ_2. Similar to the τ_2 results, the variation of S parameters for $n = 0.50$ and 0.81 has the same slope as $n = 0$ at temperatures below 30 K, then increase monotonically between 30 and 58 K and between 30 and 72 K for $n = 0.50$ and 0.81, respectively. Between 58 and 70 K and between 72 and 81 K, S stays constant for $n = 0.50$ and 0.81, respectively. Beyond 72 and 81 K, S decreases and finally returns to the value for $n = 0.0$.

As expected, we do not observe a drastic change of S at the rotational order-disorder (17–23 K) transition temperature nor at the CIT temperature (46.7 and 54.4 K for $n = 0.50$ and 0.81). The sigmoidal behavior of S with the temperature shown in Fig. 4 indicates a thermally activated process for defect formation on the 2D surface. We assume that the S parameter probes thermally generated defects on the surface and obeys an Arrhenius equation

$$S = S_0 e^{-E_a/RT}, \qquad (1)$$

where R is the ideal gas constant and E_a is the activation energy for defect formation. S_0 is related to the entropy and thermal expansion coefficients of solids. Here we use the slope of S as 3.92×10^{-5} K^{-1}, which are the slopes for $n = 0.0$ and for $n = 0.50$ and 0.81 at very low temperatures (< 30 K). S values at high temperatures above 58 and 70 K for $n = 0.50$ and 0.81 (Fig. 4) are nearly constant. Therefore, a simplified Arrhenius plot of $\ln[(S_2 - S)/(S - S_1)]$ versus $1/T$ is obtained by fitting the data of Fig. 4 between 30 and 52 K for $n = 0.50$ and between 35 and 68 K for $n = 0.81$ coverages. The obtained slopes are shown in Fig. 5. E_a are found to be 193.5 K (0.017 ± 0.002 eV) and 82.8 K (0.007 ± 0.002 eV) for $n = 0.50$ and 0.81 coverages, respectively.

The dynamics of methane monolayers adsorbed on graphite is an interesting research subject. The positron results presented in this study offer some useful information about the activation mechanism of 2D melting, i.e., from commensurate, extended solids to the liquid phase. Several possible 2D mechanisms have been discussed in the literature. Among these are domain-wall unpinning,[28] dislocation dynamics,[29] and grain-boundary generation.[30] Recent nuclear-magnetic-resonance (NMR) results[7,8] give an activation energy for moving a $\mathrm{CH_4}$ molecule on a surface of 0.056 eV (650 K) for $n = 0.5$ and of 0.069 eV (800 K) for $n = 0.81$ monolayer coverage ac-

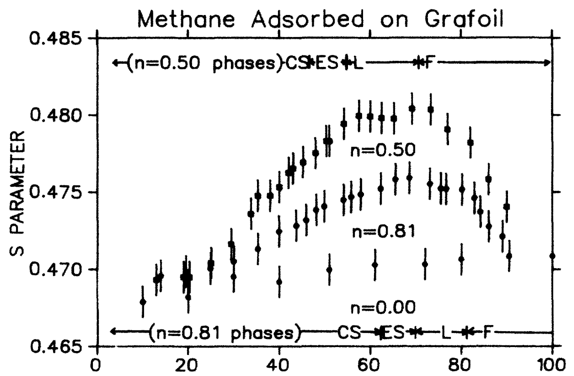

FIG. 4. S parameter of Doppler broadening vs temperature for submonolayer adsorption. n is the fraction of complete monolayer adsorption. The S is the ratio of the sum of the counts in central region ($\Delta E \pm 0.9$ keV) to the total accounts of 511 keV peak. Errors are statistical. The 2D phases, CS (commensurate solid), ES (expanded solid), L (liquid), and F (hypercritical fluid) were taken from Ref. 13.

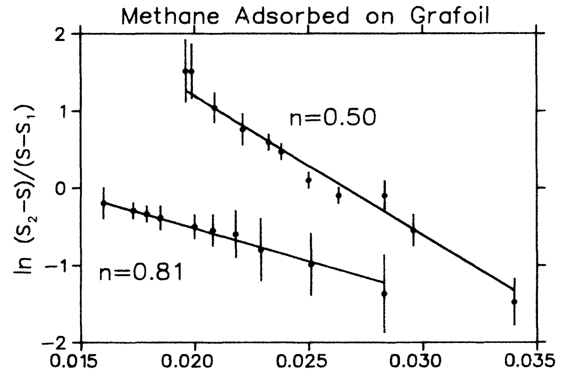

FIG. 5. The Arrhenius plot of S parameter vs temperature for methane adsorbed on Grafoil. S is the observed S parameter at temperature (T). S_1 is taken as $0.4686 + 3.92 \times 10^{-5} T$ and $0.4691 + 3.92 \times 10^{-5}$ T from the results of Fig. 4 for $n = 0.50$ and 0.81 coverage, respectively. S_2 is taken as 0.4800 and 0.4760 from the results of Fig. 4 for $n = 0.50$ and 0.81 coverage, respectively. The obtained activation energies were found to be 193.5 and 82.8 K for $n = 0.50$ and 0.81 from the best linear fit.

cording to the dislocation model. Our E_a results are much lower than those from these results. In fact, we obtain a larger value of E_a in $n = 0.50$ than in $n = 0.81$ coverage which is opposite to the trend of NMR results. The actual dynamic mode that changes 2D phases cannot be specified clearly from our PAS data alone. Judging from the large discrepancy on the obtained activation energies from PAS and NMR results, we suspect that the dislocation model is an incorrect mechanism. On the other hand, we could not attribute the 2D phase-transition mechanism to the other two models since there is no data from them to be compared with ours directly.

In PAS method, the interpretation of results should include positron dynamics. The positron diffusion constant (D_+) and its mobility on graphite surface have not been reported. From the reported D_+ on metals[31] and semiconductors,[32] we estimate D_+ for graphite 1 cm^2/s. The methane diffusion constant has been known to be 3.8×10^{-5} cm^2/s.[33] The diffusion length of the positron is ~ 1700 Å $[(D_+\tau_2)^{1/2}]$ on graphite surface while that of the methane is only ~ 10 Å at the mean lifetime of surface positrons. Therefore, PAS probes the equilibrium states of adsorbates at a certain temperature. This is very different from the NMR method in which spin relaxation time (T_1) is on the order of 0.1 s. According to the defect model for the 2D melting mechanism as suggested by our PAS study, the obtained energy E_a should be close to the barrier activation energy for molecular motion to create a vacancy in order to trap the positron on the surface. This energy is similar to the vacancy formation enthalpy in 3D systems. The magnitude of the energy should be much smaller than that for three dimensions due to the absence of long-range interactions. The obtained vacancy formation enthalpy for 3D methane by means of PAS (Ref. 34) was found to be 0.10 ± 0.01 eV which is about 6 to 14 times larger than that of 2D systems. Therefore vacancy formation energies of 0.017 and 0.007 eV for 2D systems are reasonable values. On the other hand, the energy from NMR, i.e., 0.056 eV (650 K) and 0.069 eV (800 K), are certainly too large for 2D vacancy formation energy. One possible explanation for this discrepancy is that PAS probes the energy of moving a CH_4 molecule away on the surface in order to form a vacancy while NMR probes the total energy of moving a CH_4 molecule which includes the energy of desorption. By comparing with various reported energies we found that our activation energy is close to the Lennard-Jones potential energy parameter $\varepsilon = 148.9$ K in methane-graphite system.[33] This energy parameter decreases to 125 K at high coverage.[8] Therefore, the activation energy obtained by a PAS study is more likely to represent the intermolecular energy barrier for forming a methane vacancy on graphite surfaces.

The constant S-parameter results above 2D melting points (Fig. 4) are consistent with the known positron annihilation characteristics in liquids.[17] Beyond the liquid$\rightarrow$hypercritical fluid transition temperatures, i.e., $T = 68.8$ and 81 K for $n = 0.50$ and 0.81, respectively, S parameters converge to the S value of the $n = 0.0$ surface. This can be explained by the desorption of CH_4 above these temperatures. The hypercritical fluid methane does not have a noticeable chemical quenching with Ps because ortho-Ps lifetimes do not change with respect to temperatures. If we assume the desorption of two dimensions from liquid to hypercritical fluid is a thermally activated process, and we use an equation similar to Eq. (1) to fit the S data of Fig. 4 (5 data points in the high-temperature regions) in a similar way as described above, we estimate the energies of desorption to be 0.06 ± 0.03 eV and 0.09 ± 0.03 eV for $n = 0.50$ and 0.81 monolayer coverages, respectively. These energies are comparable to the desorption energies (~ 0.03 eV) estimated from NMR results.[8]

IV. CONCLUSION

Positron lifetime and Doppler-broadening methods have been demonstrated to be a highly sensitive tool to study 2D phases and phase transitions. In submonolayer regions where the weight (%) of CH_4 adsorption is only 0.1%, the positron lifetime and S parameters of Doppler broadening show significant temperature variations. Both lifetime and S parameter can be used to detect defect formation in 2D surfaces, 2D melting, and 2D desorption. The formation enthalpy, tentatively assigned as vacancy formation, was obtained to be 193.5 K (0.017 ± 0.002 eV) and 82.8 K (0.007 ± 0.002 eV) for $n = 0.50$ and 0.81 monolayer coverages. The energies of desorption were also estimated for $n = 0.50$ and 0.81, respectively. In the methane monolayer adsorbed on graphite systems, the current PAS method is not able to detect the known rotational order-disorder and CIT solid phase transitions. Angular correlation measurement on annihilation radiation (ACAR) with better momentum resolution and using a monoenergetic positron beam are needed in order to obtain more surface information on 2D systems by means of positron methods.

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