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Phase transitions in physisorbed ethane investigated by positron-annihilation spectroscopy

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Data are presented for the lifetime and Doppler broadening parameters for positrons annihilating in ethane physisorbed on grafoil. The coverage dependence of these parameters has been investigated up to about 2.5 monolayers at 108 K. Both the positron lifetimes and Doppler broadening parameters reflect significant variations in the surface electron density as a function of adsorbate coverage, with clear evidence for minimum electron density occurring at coverages of ~0.8 and 2. The temperature dependencies of the lifetime and Doppler broadening data, studied for coverages of 0.4, 0.9, and 1.5 monolayers, show structural phase transitions in the adsorbate. We propose a mechanism for this structural phase transition at 39 K.
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I. INTRODUCTION

Two-dimensional (2D) physisorbed gases on highly uniform substrates have been the subject of considerable interest.[1–5] These systems exhibit phases and phase transitions which have no analog in bulk matter and therefore assume special significance. Simple molecules adsorbed on graphite exhibit a variety of structures. In general, these structures are dependent on surface coverage, temperature, and relative strength of the intermolecular and molecule-surface potentials. The studies of such systems have, therefore, provided a wealth of information about phase transitions, molecular dynamics, and molecule-substrate and molecule-molecule interactions. Methods employed for such investigations include heat capacity measurements,[6] volumetry,[7] neutron scattering,[8–10] molecular dynamics,[11] low-energy electron diffraction (LEED),[12,13] high-resolution electron-energy loss spectroscopy (HREELs),[8] and nuclear resonance photon scattering (NRPS).[14] Positron-annihilation spectroscopy (PAS), which is a sensitive technique for investigating the electronic properties of condensed matter,[15,16] has also been employed to study certain features of physisorbed gases.[17–24]

The ethane-graphite system has been examined by several experimental methods. At low temperatures, it exhibits a very rich phase diagram. The suggested phase diagram[12] at these temperatures features three solid phases S_1, S_2, and S_3, two intermediate phases I_1 and I_2, and fluid phases L and F. At coverages below 0.75, ethane forms the S_1 phase: a registered $4\times\sqrt{3}$ commensurate solid in which the C-C axis of the molecule forms a herringbone pattern.[25] On heating, the S_1 solid transforms to a lattice fluid I_1 at 65 K. For coverages near 0.82, the S_2 phase is formed. For coverages in the ranges 0.77–0.86 and 0.9–<1.0, two-phase regions (S_1+S_2) and (S_2+S_3) are observed. The range of stability of the S_2 phase is very narrow, so it is difficult to produce a pure S_2 phase experimentally. The structure of the S_2 phase has not been resolved. However, the LEED experiments[13] suggest that it is an incommensurate herringbone with a 5.24×7.39 Å unit cell, rotated by 5.7° with respect to the lattice vectors which describe the graphite basal plane. For coverages between 0.8 and 1.0, the $S_2\rightarrow I_2$ transition occurs at 57 K.[12] At one monolayer, the ethane molecules stand on methyl tripods with their C-C axis perpendicular to the graphite plane and form a $\sqrt{3}\times\sqrt{3}$ solid labeled as the S_3 phase.

In spite of considerable work on the structure of various phases and phase transitions, information on molecular dynamics in 2D ethane adsorbate is still meager. In only few 2D systems has the rotational dynamics been studied.[25,26] This has been largely due to a low sensitivity of most experimental techniques to the degree of rotational mobility in the film. NMR has been employed to study rotational transitions in methane and ethylene.[27] In both of these systems substantial rotational mobility is observed below the freezing transition. Some or all of this mobility is lost in rotational transition for ethylene at about 35 K and for methane at about 17 K. Due to an asymmetric shape, the ethane molecule can exhibit several types of mobilities. In the solid phase, it can execute an isotropic rotation either about its center of mass or a twist rotation. It can also experience rotation of methyl groups about the C-C axis. It is reported that in the solid phase, the ethane molecule exhibits a rotational transition at 53.5 K, where it begins to undergo a jump rotation about the C-C axis.[10] In the intermediate state, rodlike ethane molecules can lose their positional and orientational order with increasing temperature and form a strongly correlated lattice liquid. In the liquid state translational and brownian mobility is added to these motions.

The sensitivity of PAS to structural transformations[28] and to segmental motion of certain molecules[29] has been demonstrated in bulk systems, however, its efficacy in 2D systems still needs to be established. We have, therefore, utilized PAS to further investigate 2D ethane adsorbate on grafoil. Preliminary results from this work, in which only the Doppler broadening measurements were made at a single coverage of 0.9 monolayer, have appeared in the literature.[24] In this early work, it had been observed that the Doppler broadening spectra undergo significant changes around 39 K. Here we present results on the positron lifetime spectra that substantiate our earlier observation of a structural phase transition at 39 K and 0.9 monolayer. We have extended measurements of the Doppler broadening spectra to other coverages and temperatures and these results are also presented. Based on the combination of the positron lifetime and Doppler broadening data, we propose a mechanism, involving inelastic e^+-C_2H_6 collisions, for the effect occurring at 39 K. Some important features of this work are (i) coverage dependence up to about 2.5 monolayers that clearly shows repetitive nature of the surface electron density, (ii) observation of phase transformations at different temperatures, (iii) elucidation of the nature of the S_2 phase, and (iv) proposal for a new mechanism to explain the nature of the 39 K transition.

II. EXPERIMENTAL DETAILS

Research grade ethane gas, used in the present work, was obtained from Matheson Gas Co. and had a purity of 99.987%. A standard procedure was adopted for the preparation and characterization of adsorbates. Details of the volumetry equipment used are given elsewhere.[23] The system consisted of a gas manifold system, two beratron absolute pressure gauges with overlapping ranges, a high vacuum system, and a closed-cycle helium Displex Cryostat equipped with a temperature controller with an accuracy of ±0.1 K. Standard baking and flushing techniques were used in order to clean the entire system prior to measurements. A stack of 31.154 g grafoil discs was baked at 1073 K under 10^{-4} Torr for 38 h and subsequently transferred to the sample cell under dry helium atmosphere. A 80 μCi ^{22}Na positron source evaporated onto 0.81 mg/cm^2 Al foil was sandwiched between grafoil discs at the center of the stack. The sample cell was evacuated under 10^{-5} Torr for about 15 h prior to isotherm measurements. In order to determine the total area available for adsorption and to calculate ethane volume for monolayer coverage, adsorption isotherms were measured at different temperatures. A typical result of such measurements provided a volume of 125 cm^3 at STP corresponding to one monolayer coverage at 108 K. The adsorbate coverages were calculated, with an uncertainty of about 10%, by accounting for the dead volume of the sample cell. For temperature-dependent experiments, a given coverage was maintained constant by adjusting the number of the molecules in the ‘‘dead-volume’’ of the cell.[23] For example, additional molecules were added to compensate for desorption, especially at $T > 77$ K.[24] Since the number of molecules in the dead volume was negligibly smaller than needed for a monolayer, only a small correction was needed.[24]

The positron lifetime and Doppler broadening measurements were performed simultaneously as a function of coverage (θ) at 108 K and as a function of temperature at fixed coverages of 0.4, 0.9, and 1.5 monolayers. The positron lifetime measurements were made using a standard timing spectrometer. The ^{60}Co resolution spectrum was represented by a sum of two Gaussians with full-width at half maximum of 0.357 and 0.522 ns with an intensity of 65.5% of the narrower Gaussian. The positron lifetime spectra could, in general, be resolved by the POSITRONFIT (Ref. 30) program into two components only. In some cases the lifetime spectra consisted of two short components, each characterized with a lifetime <0.4 ns and in others the spectra contained a short as well as a long component of lifetime in the range 1–3 ns. The short lifetimes probably represent contributions from annihilations of free positrons in the bulk, on the surface, and in the interfacial regions. Due to limited statistics, the lifetime spectra could not be resolved to separately examine each one of these contributions. However, the exfoliated graphite (grafoil) is characterized with a layered structure with average thickness of each layer on the order of 400 Å. Each submillimeter of this material, therefore, consists of a large number of internal surfaces to adsorb the ethane molecules. On entering such a layered structure, an energetic positron undergoes a large number of events involving diffusion within the layer, re-emission from the internal surfaces, etc. The annihilation characteristics of the positrons are influenced by the modifications in the electronic structure of the internal surfaces because of the adsorption of ethane molecules. Based on these considerations, whenever the lifetime spectra could be resolved into two short components only, the effect of the adsorbate was examined by calculating a mean lifetime τ. The long-lived component represents pick-off annihilations of the ortho-positronium atom (o-Ps). The Doppler broadening spectra of the annihilation radiation were measured using a high purity Ge solid-state detector spectrometer equipped with a digital stabilizer. The energy resolution of the Ge detector was 1.2 at 511 keV. These spectra were analyzed for the S and Y parameters. The S parameter is defined as the ratio of the sum of the counts in the central region (±0.90 keV) of the 511 keV annihilation peak to the total counts under the spectrum after subtracting the background. This parameter is a measure of the momentum distribution of the electrons and can, therefore, be used to study changes in the electronic structure of the adsorbate. The Y parameter is defined as the ratio of the sum of the counts within a certain energy window below the Compton edge to the total counts in the central region of the 511 keV peak. This parameter is sensitive to Ps formation and can, therefore, be used to study changes in surface topography via Ps formation and its zero-point energy.

III. RESULTS AND DISCUSSION

A. Coverage dependence of the positron annihilation parameters at 108 K

The S and Y parameters of the Doppler broadening spectra as well as the positron lifetimes, τ_1 and τ_2, are plotted in Figs. 1 and 2 as functions of coverage at 108 K. Although, the data on the S parameter at 108 K have already been published,[24] they are shown here so that their features can be compared with new data presented in this paper. It is observed that the S parameter remains at a high value of 0.4245 for $\theta \leqslant 0.7$ and then drops to a lower value of 0.423 near $\theta = 0.8$. Following this drop, it rises slowly with increasing coverage. This coverage dependence of the S parameter is qualitatively similar to what has been seen in cases of nitrogen and argon[17,22,23] where it shows a maximum at $\theta \sim 0.5$. This parameter is sensitive to changes in the (1) valence vs core electrons contributing to the annihilation probability, (2) Ps formation, and (3) zero-point energy of the Ps atom. The changes in the valence vs core electron contributions to the annihilation process could occur due to either modifications in the electronic charge distributions as a result of the intermolecular interactions or due to positron-trapping in defects. The Ps formation lowers the S parameter due to increased $3\gamma/2\gamma$ ratio which enhances contributions under the valley region at the expense of the central region of the Doppler

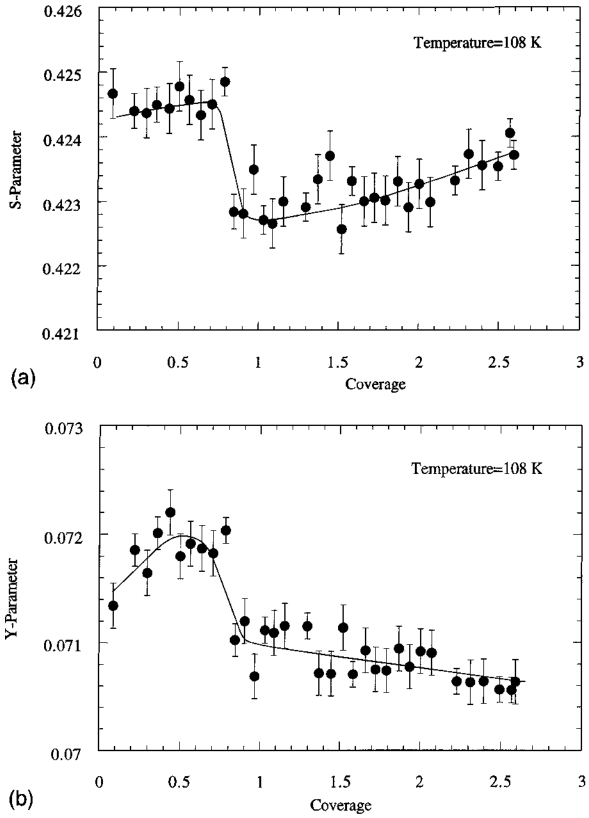

FIG. 1. (a) The *S* parameter, (b) the *Y* parameter vs coverage of ethane on grafoil at 108 K.

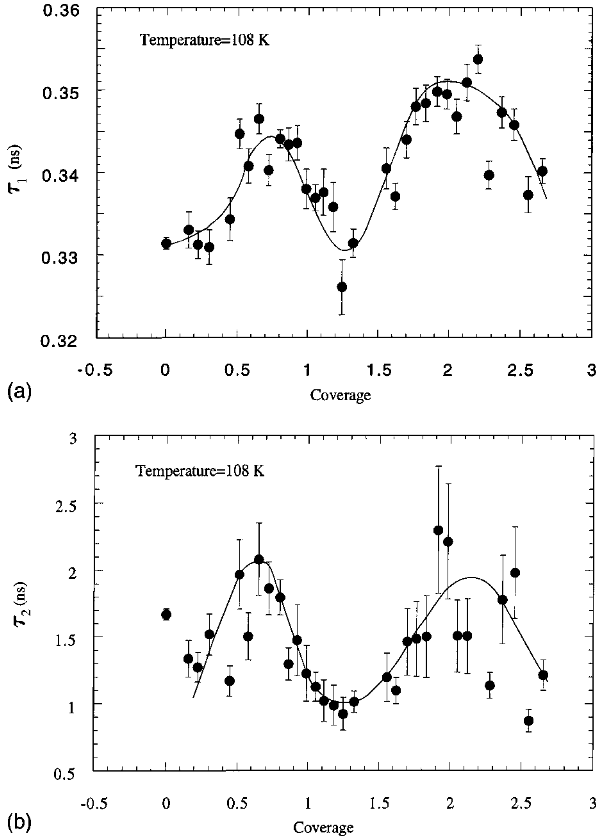

FIG. 2. (a) Lifetime of the short-lived component, (b) lifetime of the longer-lived component vs ethane coverage on grafoil at 108 K.

spectrum. The zero-point energy considerations affect the *S* parameter when a significant fraction of the positrons forms Ps that annihilates, particularly from regions between adsorbate-islands on the surface. New *Y* parameter and positron lifetime data help us better understand relative contributions from these different processes. Similar to the *S* parameter, the *Y* parameter also drops to a lower value near $\theta = 0.8$. Being proportional to Ps formation, this drop in the *Y* parameter signals a decline in Ps formation near $\theta = 0.8$. As discussed below, the intensity of the Ps component in the lifetime spectrum is relatively small, only about 2% at all coverages investigated. Nonetheless, a decline in the Ps formation, consistent with the decline seen in the *Y* parameter (even with as low as 2% Ps intensity) should have resulted in a rise in the value of the *S* parameter. On the contrary, the *S* parameter drops significantly around $\theta = 0.8$. Only by considering the behavior of both the *S* and *Y* parameters, it becomes apparent that around $\theta = 0.8$, it is a change in the electronic structure of the adsorbate, rather than a decline in the Ps formation, that supports these observations. The relative contribution of the valence vs core electrons to the total annihilation probability changes so as to compensates for an expected rise in the *S* parameter and produces an overall decline in its value. As stated earlier, such a change in the electronic structure of the adsorbate could arise as a result of (a) rearrangement of the electronic charge distributions and/or (b) rearrangement of the adsorbate leading to surface defects. For $\theta > 0.9$, the *Y* parameter decreases and the *S* parameter increases, which is consistent with decreasing Ps formation with increasing coverage beyond a monolayer. Whether the positrons/Ps annihilate from intrasland vs inter-island regions may also explain differences in the data below and above full coverage of the surface.

The lifetime spectra could be resolved into two components only; a short-lived component of lifetime $\tau_1 \sim 0.34$ ns and a longer Ps-component of lifetime τ_2 in the range of 1–2 ns. The intensity of the Ps component, being relatively small $\sim$2%, has large statistical uncertainty. No specific coverage dependence in this intensity can, therefore, be ascertained. Unlike the *S* and *Y* parameters, τ_1 and τ_2 exhibit two maxima, one at $\theta \sim 0.8$ and another at $\theta \sim 2$. We further discuss these lifetime results in the following paragraph under models. To our knowledge, these lifetime data present clear evidence for what appears to be a repetitive variation in the surface electron density with minimum electron density occurring at $\theta \sim 0.8$ and 2. Wang *et al.*[31] have investigated multilayered methane physisorbed on graphite. They also observe weak features of maxima in the positron surface lifetime at $\theta \sim 0.5$ and 1.5. The drop in the *S* parameter around 0.8 monolayer ethane in our data is in good agreement with the observation by Wang *et al.* of a similar drop between 0.5 and 0.8 monolayers of methane.

Two models have been proposed to explain the coverage dependence of the positron annihilation parameters.[17,22,23] In one of these models, adsorption is viewed as creating defects on the surface that trap positrons and Ps. Since even a small coverage, on the order of 0.1 monolayer, significantly changes the annihilation parameters, adsorption should be affecting the surface state. It is possible that adsorption leads to the formation of islands on the surface.[32] With increasing coverage, the size and surface density of the islands are expected to increase. Assuming that the positrons/Ps are trapped in intraisland and/or interisland regions, the surface density of the trapping sites will increase with increasing coverage. Under these conditions, the positron surface lifetime reflects average electron density in and the Ps lifetime measures the size of the trapping site. In the second model, adsorption is assumed to modify the surface electronic structure and these modifications are probed by the annihilation parameters.[22,23] Adsorbate-surface interactions are known to modify the surface electronic structure; for example, the surface work function of metals changes due to Cs coverage.[33,34] Similarly, hydrogenated surface of diamond acquires negative electron affinity.[35,36] The positron annihilation parameters presented here clearly show that the surface electronic structure undergoes changes with coverage. They do not, however, show whether the change in the surface electronic structure is brought about by possible rearrangement of the electronic charge density due to intermolecular interactions or by the creation of surface defects. Nonetheless, the data support the well-known fact that physisorption modifies the surface electronic structure.

B. Temperature-induced phase transformations

In order to study phase transformations, the positron lifetime and Doppler broadening parameters were measured as a function of temperature for bare grafoil and grafoil having 0.4, 0.9, and 1.5 monolayers of ethane adsorbate. In agreement with previously reported results,[17,22] the positron lifetime, and the *S* parameter vary linearly with temperature for bare grafoil. In the presence of the adsorbate, these parameters behave very differently. Additionally, the differences are specific for the adsorbate. Detailed results obtained for three different coverages of 0.4, 0.9, and 1.5 monolayers are presented below.

1. Ethane coverage, $\theta = 0.4$

The temperature dependencies of the positron mean lifetime (τ) and the *S* parameter for ethane coverage of 0.4 monolayer are shown in Fig. 3. The positron lifetime spectra could be resolved into two short components only and a mean lifetime τ was calculated from these components. Due to relatively low intensity ($<1\%$), the *o*-Ps component could not be resolved with acceptable statistics. In the plot for τ, there are signatures of phase transitions at about 39, 50, and 65 K. The temperature dependence of the *S* parameter also shows deviations from a linear temperature dependence observed for bare grafoil. Steps are seen in the data around 39 and 45 K. Beyond 45 K the *S* parameter increases linearly with temperature. Both, the positron lifetime and *S* parameter show signatures, albeit weak, of phase transitions in the adsorbate.

It is known from the phase diagram that at 0.4 monolayer coverage, the 2D ethane surface exhibits S_1 phase. It is a registered $4\times\sqrt{3}$ commensurate 2D solid and transforms to a lattice fluid, I_1, at 65 K. Much below the melting transition, the S_1 phase of the system exhibits a transition at 53.5 K to another 2D solid structure in which the molecules are rotationally disordered.[10] At this temperature, the methyl groups are known to perform 120° jumps between indistinguishable orientations. In this kind of rotation the inclination of the *C*-*C* axis with respect to the basal plane flips between $+10$ and $-10°$. Therefore, we ascribe changes in the positron mean lifetime and *S* parameter near 50 and 65 K to rotational disordering of molecules and a solid-to-fluid transformation, respectively.

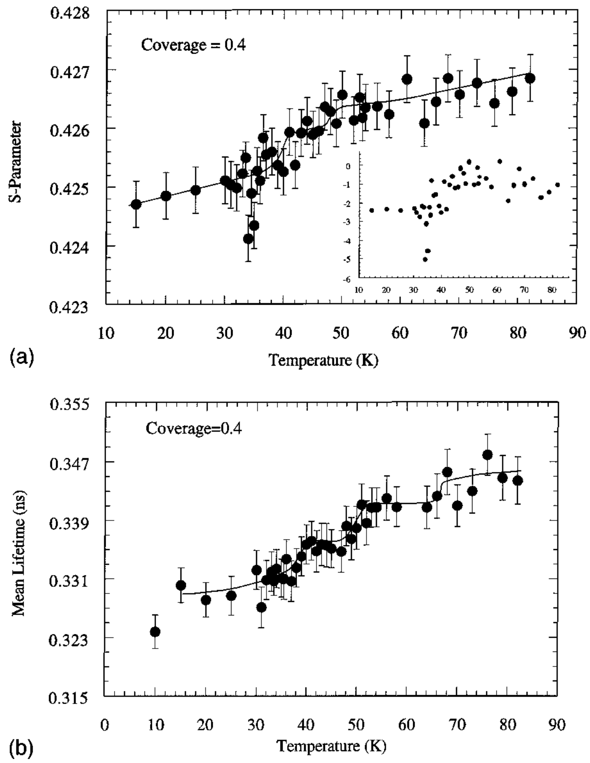

FIG. 3. (a) The *S* parameter. (b) Mean lifetime vs temperature for a constant ethane coverage of 0.4 monolayer on grafoil. The inset shows the difference, in units of the statistical uncertainty in the measurement, between the data obtained with and without coverage.

2. Ethane coverage, $\theta = 0.9$

The temperature dependencies of the positron lifetime as well as the *S* and *Y* parameters for ethane coverage of 0.9 monolayer are shown in Fig. 4. The major feature, which is present in all four parameters measured by techniques probing two different electronic characteristics, is a signature of structural phase transition at 39 K. The temperature dependence of the *S* parameter shows a sharp and pronounced dip at about 39 K and a step around 50 K. Following this step, the *S* parameter increases more or less monotonically with increasing temperature. The major effect, in the *Y* parameter, is a pronounced dip around 39 K which reflects a significant decrease in Ps formation ~39 K. The positron lifetime spectra obtained at various temperatures for this coverage could be decomposed into two components; a short component τ_1 having an average value ~0.37 ns and a long component τ_2 that remains more or less around 2 ns. The long-lived component represents pick-off annihilation of the *o*-Ps atom. The relative contributions from positron annihilations in the bulk and surface are lumped together in the shorter component. However, it is expected to reflect effects of the adsorbate. The intensity of the long component I_2 varied between 0.5–2%. The temperature dependence of I_2 also shows a sharp

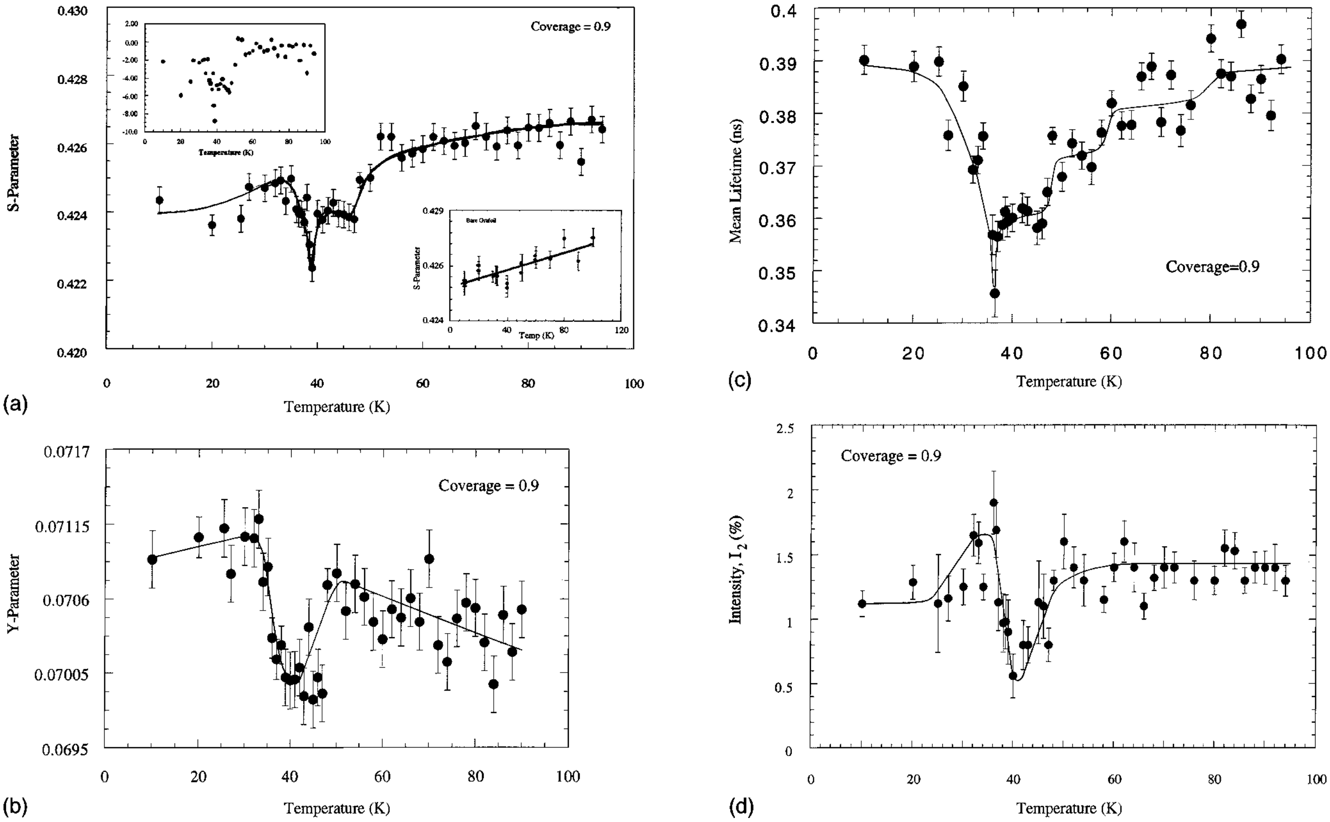

FIG. 4. (a) The *S* parameter. (b) *Y* parameter. (c) Mean lifetime. (d) I_2 vs temperature for a constant ethane coverage of 0.9 monolayer on grafoil. The top inset in (a) shows the difference, in units of the statistical uncertainty in the measurement, between the data obtained with and without coverage. The bottom inset shows data for bare grafoil.

decrease in Ps formation around 39 K. Both the *Y* parameter and I_2, that have been measured by two different techniques, exhibit by dips around 39 K, a process by which the Ps formation is suppressed around 39 K. In the following paragraphs, we propose and discuss possible mechanism for this effect that has not been seen, to our knowledge, by any other technique.

The data presented in Fig. 4 for $\theta = 0.9$ indicate occurrence of phase transitions around 39, 50, and 60 K. It is observed that near 0.9 monolayer at low temperatures, 2D ethane exists in either a purely S_2 phase or in a mixture of the S_2 and S_3 solid phases.[12] It is, therefore, expected that the changes in the positron annihilation parameters should be characteristic of these phases. The structure of the S_2 phase has not been resolved. However, LEED experiments[13] suggest that it is an incommensurate herring bone with a 5.24×7.39 Å unit cell, rotated by 5.7° with respect to the lattice vectors which describe the graphite basal plane. Similar to the S_1 phase, the *C*-*C* bonds are aligned nearly parallel to the surface. Therefore, the jump rotational motion observed in the S_1 phase, may also be possible in the S_2 phase. Leaving aside the effect at 39 K (which is discussed below in a separate paragraph), we first comment on the steps seen around 50 and 60 K. The step seen around 50 K is consistent with the setting-in of molecular jump rotational motion. It has also been reported that the S_2 phase transforms into an intermediate phase I_2 at ~ 57 K (Ref. 12) and on further increase in temperature, I_2 transforms continuously into S_3. The features seen in our data around 60 K are consistent with the transformation of the S_2 solid to an ordered 2D liquid phase. Our results, however, indicate that for $\theta \sim 0.9$ coverage, the 2D solid is dominated by the S_2 phase.

3. Ethane coverage, $\theta = 1.5$

The temperature dependencies of the mean positron lifetime, τ and the *S* parameter for a coverage of 1.5 monolayer are shown in Fig. 5. Similar to the measurements for $\theta = 0.4$, the positron lifetime spectra could be resolved into two short components. Both sets of data show phase transitions around 39 and 80–90 K. It is known from the phase diagram[12] that for $\theta \geqslant 1$, the adsorbate is in the S_3 phase. In this phase the ethane molecules stand on methyl tripods with their *C*-*C* axis perpendicular to the graphite plane and form a $\sqrt{3} \times \sqrt{3}$ solid. The molecules, therefore, cannot execute jump rotation. Absence of a signature of phase transition around 50 K in the mean lifetime and *S* parameter data is consistent with this view. It has been reported that the melting of the S_3 phase is different from that of S_1 or S_2 phase.[25] It melts between 82 and 87 K without transforming to an intermediate phase. The data of Fig. 5 support this picture.

4. Possible mechanism for the transition at 39 K

One of the most important features of these data is the signature of a transition around 39 K, which is observed for all three coverages. The measurements of several different positron annihilation parameters, obtained by two different techniques, verify the occurrence of this transition. An examination of the temperature dependence of any of the measured quantities around 35–40 K shows features of an order-

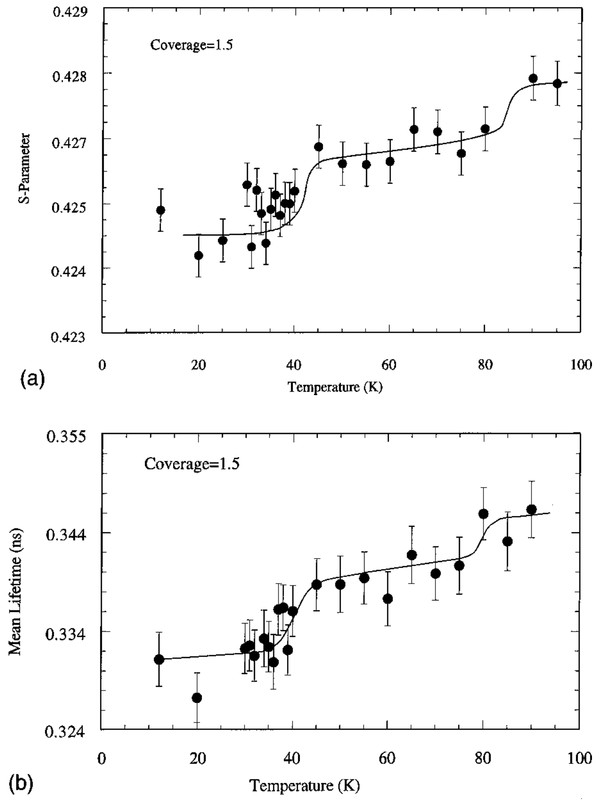

FIG. 5. (a) The S parameter, (b) mean lifetime vs temperature for a constant ethane coverage of 1.5 monolayer on grafoil.

disorder transition. To our knowledge, such a transition has not been detected by any other technique. The availability of new data, especially on Ps, allows us to suggest a mechanism for the transition at 39 K. In the following, we discuss this mechanism.

It is well known that two types of temperature-induced structural phase transformations can occur in the adsorbate: (i) translational disorder and (ii) orientational disorder. It is known from the phase diagram that at 39 K the adsorbate exists either in S_1 phase, or as a mixture of S_2 and S_3 phases, or in the S_3 phase. Since, all these are solid phases, translational disorder is ruled out as being the cause for the transition at 39 K. The onset of an orientational disorder at 39 K is, however, possible. Such an effect has been observed by NMR in the cases of CH_4 and C_2H_2 at 17 and 35 K, respectively, where these molecules execute isotropic rotation.[27] Since the transition around 39 K is seen at all coverages investigated in this work, the molecular motion, responsible for this effect, should be possible in all three solid phases. In this connection, it is important to realize that the ethane molecule can undergo several types of rotational motion. Among these are (i) jump rotation, (ii) isotropic twist rotation, and (iii) isotropic rotation about the center of mass. Out of these, the jump rotation is ruled out as it is known to set in at 53.5 K and is also not possible in the S_3 phase. Having ruled out the jump rotation, a transition between the gauche and trans stearic conformations of the ethane molecule should be considered. Such a transformation takes place by a 60° twist rotation of one methyl group with respect to the other. Besides this type of a quantum jump, a continuous twist rotation is also possible. In fact, it is energetically favored over isotropic rotation about the center of mass. We suggest that the effect seen in our data on ethane around 39 K is due to the setting in of a continuous rotation of this type. Near 39 K, the ethane molecules in the adsorbate appears to be susceptible to rotation. A rotational transition could be excited in the molecule by either thermal energy (kT) or by energy gained by the molecule in a e^+-C_2H_6 collision. It is the latter that we envision as the process that brings about the transition at 39 K. In agreement with the data presented here, this mechanism will have to account for (i) a decline in Ps formation, (ii) a shorter lifetime of the surface component, and (iii) a modification in the electron momentum distribution so as to account for changes seen in the Doppler broadening spectra. As far as item (i) is concerned, an inelastic e^+-C_2H_6 collision, which competes with Ps formation, will result in a decline in Ps formation. According to the Ore model,[37] which is known to explain Ps formation in low-density ethane gas,[38] Ps is formed in e^+-C_2H_6 collisions while energetic positrons undergo thermalization. The Ps is formed by only those positrons whose energies fall in the range I to $(I-6.8)$ eV. Here I is the ionization energy of the molecule and 6.8 eV is the binding energy of the Ps atom. In a collision between C_2H_6 and a positron with energy just above the lower limit of the Ore gap $(I-6.8)$ eV, the positron either forms Ps or excites rotational transition and is consequently removed from the Ore gap. The latter results in a decrease in the Ps formation. The branching between these two competing processes will, of course, depend on the relative magnitudes of the cross sections for Ps formation and rotational excitation at the specific value of the positron energy. The rotational motion of the molecule can also conceivably modify the ''local'' surface electronic structure so as to account for items (ii) and (iii). Recent theoretical work on the vibrational and rotational excitation of CO by low-energy positrons provides some interesting results in this connection.[39] In this work, the vibrational and rotational excitation processes have been studied for CO molecules in collisions with positrons of energy just below the threshold for Ps formation. It is of particular interest that in such e^+-CO collisions, where the positron energy is below the threshold for Ps formation, the interaction between the low-energy positron and the molecular charge distribution induces sizable deformations in the total electron density. The low-energy positron usually alters the valence electron density and does not significantly affect electron density in the inner core region due to the Coulomb repulsion from the core of the molecule. Such changes in the electron density distributions are expected to alter both the total positron decay rate as well as the shape of the Doppler broadening spectrum. The calculations on the e^+-CO system show that the rotovibrational coupling increases for faster rotating target and the vibrational motion is dynamically more coupled to the impinging positron's motion when the target molecule is also rotationally excited. Under such conditions, it is reasonable to expect significant changes in the ''local'' surface electron density and the momentum distribution of the electrons. However, to our knowledge, no calculations have been performed to study the precise nature of the changes in the electron density and momentum distributions brought about by collisions between the ethane molecule and positrons of energy just above the threshold for Ps formation. Additional much work is needed for a better understanding of whether the proposed mechanism, involving e^+-C_2H_6 collisions, can explain the transition seen at 39 K.

IV. CONCLUSIONS

We have presented detailed results for the positron lifetime and Doppler broadening parameters as functions of coverage and temperature for ethane physisorbed on grafoil. The coverage dependent measurements have been made up to 2.5 monolayers at 108 K. We observe significant changes in the positron lifetime and Doppler broadening parameters near coverages of 0.8 and 2 monolayers. We have also conducted positron lifetime and Doppler broadening experiments as functions of temperature in the range 10–100 K for constant ethane coverages of 0.4, 0.9, and 1.5 monolayers. For all three coverages, the temperature dependence of the data confirms the occurrence of a feature near 39 K. We propose that this feature is due to isotropic twist rotation of the ethane molecule that is excited because of energy gained by the molecule in e^+-C_2H_6 collisions. Additional features of the data are consistent with reported phase transitions in the adsorbate. Results of this study demonstrate the usefulness of PAS for investigating phase transitions in 2D adsorbates.

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