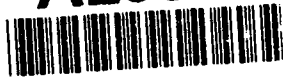AD-A258 535

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L. M. Struck and M. P. D'Evelyn

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We report the first investigation of the adsorption of deuterium and water on diamond (100) by infrared multiple-internal-reflection spectroscopy using a natural type IIa diamond internal reflection element. Infrared evidence was seen for the monohydride surface structure, with one hydrogen atom per surface carbon atom (δ_{CD} mode at 901 cm^{-1}), while the dihydride (CD_2) structure was not observed. Following exposure to water at elevated temperature, infrared absorption features were detected at 1280, 1200, 1125, 1080, and 720 cm^{-1}, and are assigned to ether (C–O–C), hydroxyl (C–OH), and carbonyl ($>$C$=$O) modes. The substantial observed reactivity of diamond with water indicates a potentially important role for surface hydroxyl and oxide species in the surface chemistry and morphological development of CVD diamond films.

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Interaction of hydrogen and water with diamond (100): Infrared spectroscopy

Lisa M. Struck and Mark P. D'Evelyn

Department of Chemistry and Rice Quantum Institute, Rice University, Houston, TX 77251-1892

Abstract

We report the first investigation of the adsorption of water on diamond (100) by infrared multiple-internal-reflection spectroscopy, using a natural type IIa diamond internal reflection element. Infrared spectroscopic results on the adsorption of atomic deuterium are also presented. Infrared evidence was seen for the monohydride surface structure, with one deuterium atom per surface carbon atom (δ_{CD} mode at 901 cm^{-1}), while the dihydride (CD_2) structure was not observed. Following exposure to water at elevated temperature, infrared absorption features were detected at 1280, 1200, 1125, 1080, and 720 cm^{-1}, and are assigned to ether (C–O–C), hydroxyl (C–OH), and carbonyl (>C=O) modes. The substantial observed reactivity of diamond with water indicates a potentially important role for surface hydroxyl and oxide species in the surface chemistry and morphological development of diamond films grown by chemical vapor deposition.

I. INTRODUCTION

The critical role played by hydrogen in diamond chemical vapor deposition (CVD) is well established. The nature of that role is thought to include the maintenance of an sp^3-bonded surface, creation of surface radical sites by abstraction of adsorbed hydrogen, and preferential etching of graphite.[1,2] Surface hydrogen also plays a crucial role in the growth of silicon by atomic layer epitaxy (ALE),[3-6] and almost certainly is critically important in diamond ALE processes currently being developed.[7] Water is produced in diamond growth reactors[8,9] upon addition of O_2[10,11] or oxygen-containing precursors[12-17] and is present at impurity levels in all reactors, yet water-diamond reactions are neglected in all existing diamond growth models and single-crystal surface studies of the interaction of H_2O with diamond have not yet been performed.

Despite its obvious importance, the surface chemistry of hydrogen on diamond is only beginning to be understood. Of the two crystal faces which are prevalent in CVD-grown diamond films, the properties of clean and hydrogenated diamond (100) are less well understood than those of the (111) face, the cleavage plane. However, the (100) face is the only low-index orientation where the actual surface of CVD films resembles the nominal orientation (i.e., the surface is smooth on the nanometer-to-micron scale),[18] and is the orientation most likely to be useful for atomic layer epitaxy. Nominally clean diamond (100) has a (2×1) unit cell,[19] suggesting, by analogy to the well-studied Si(100) and Ge(100) surfaces, the formation of dimer bonds between pairs of surface carbon atoms. Hydrogen atoms can adsorb on diamond (100) in a (2×1) structure[20-23] which suggests, again by analogy to the better-understood H/Si(100) and H/Ge(100) systems, a (2×1):H monohydride structure with one hydrogen atom per surface carbon atom. Prolonged exposure of Si(100) to atomic hydrogen results in the formation of di- and tri-hydride species with a nominally (1×1) unit cell;[24-26] whether a similar phenomenon occurs on diamond (100) is presently controversial.[20-23,27-29] H_2 desorbs from diamond (100) in the range of 1000-1300 K, as observed by temperature-programmed desorption (TPD).[20-23,29] The TPD peak was assigned by Hamza et al.[20] to hydrogen in the (1×1):2H dihydride state, leaving hydrogen in the (2×1):H monohydride state following desorption. This assignment has been questioned by D'Evelyn and co-workers[27-29] and by Thomas et al.[21-23] The former performed calculations which showed an extreme degree of steric repulsion in the (1×1):2H dihydride on diamond (100)[27] and assigned the TPD peak to hydrogen in the *monohydride* state.[29] The latter observed an apparently very low efficiency for conversion of the (2×1) diffraction pattern to a (1×1) structure by reaction with atomic hydrogen,[21] suggesting a substantial activation barrier to the formation of the dihydride.[22]

To date only a handful of studies have been performed on the surface chemistry of oxygen and water on diamond. In two infrared spectroscopic studies of the adsorption of oxygen and water on diamond powder, evidence was seen for formation of surface oxide species.[30,31] CO

desorption peaks near 820 and 1070 K and a CO_2 desorption peak near 770 K were observed by TPD following exposure of diamond powder to oxygen or water,[32] suggesting multiple surface structures. However, diamond powder is terminated by various crystal faces with unspecified relative areas, making structural and kinetic analysis very difficult.

Derry *et al.* detected 0.1-2 monolayers of oxygen on (100), (110), and (111) diamond surfaces by Rutherford backscattering following in-air polishing or detergent treatments.[33] Thomas *et al.* studied the interaction of atomic oxygen with diamond (100) by TPD and found CO, desorbing near 870 K, to be the primary desorption product.[23] Neither set of authors was able to determine the form(s) of surface oxygen present.

We have investigated the interaction of water with diamond (100) by infrared multiple-internal-reflection spectroscopy (IMIRS),[29,34] obtaining the first spectroscopic observation of hydroxyl (OH), ether (C–O–C), and carbonyl (>C=O) species on diamond (100). IMIRS results on the adsorption of atomic deuterium, reported in brief previously,[29] are included for completeness. The present results also constitute the first evidence that water can react with diamond surfaces at pressures corresponding to high vacuum (10^{-7} Torr), suggesting that surface oxide species may play a significant role in diamond CVD even when oxygen-containing species are not introduced deliberately.

II. EXPERIMENTAL

The infrared spectroscopy experiments were performed in an ultrahigh vacuum (UHV) chamber that has been described previously.[29] Briefly, the sample consists of a type IIa natural diamond internal reflection element (IRE), $15 \times 3 \times 0.22$ mm^3 in dimension, with a (100) orientation on the large-area faces and end faces polished at a 45° angle. Collimated light from a Fourier-transform infrared spectrometer is focused by an off-axis paraboloidal mirror through a differentially-pumped KBr window onto one bevelled edge of the diamond IRE. The infrared light undergoes approximately 33 internal reflections from each long face then is transmitted through the opposite end of the IRE and is collected and focused onto a HgCdTe detector by two additional off-axis paraboloidal mirrors. Diamond is effectively opaque at this long path length for frequencies between 1600 and 2800 cm^{-1}, preventing the observation of C=O stretching modes, and the transmitted intensity at frequencies above 2800 cm^{-1} is considerably less than that below 1500 cm^{-1}, so that sensitivity is greatest in the "fingerprint" region of the spectrum. The UHV apparatus, whose base pressure was 5×10^{-10} Torr for the experiments reported here, is also equipped with a mass spectrometer, LEED/Auger facilities, and tungsten filaments for generating exposures to atomic hydrogen.

Diamond cannot be sputtered and annealed without extensive graphitization,[19,35] but several groups have shown that heating a freshly polished diamond sample in UHV to $\approx$ 1300 K desorbs oxygen and generates a clean (except possibly for hydrogen) diamond surface.[2,19,20,36,37] We have followed this procedure. The diamond IRE was assumed to be well-polished as received from the vendor, and was placed in the reactor cell after degreasing with acetone and ethanol. Following a bakeout of the chamber, the sample was simply heated in ultrahigh vacuum after carefully outgassing the sample holder. In the hydrogen/deuterium experiments the IMIRS sample was heated to only $\approx$ 550 K (the temperature could not be accurately measured), and therefore the surface was probably partially contaminated by oxygen. Exposures of the diamond (100) IRE to atomic hydrogen or deuterium were made by backfilling the reactor cell with H_2 or D_2, respectively, at pressures between 1×10^{-7} and 2×10^{-6} Torr for up to two hours, with a W filament located $\approx$ 1 cm from the sample heated to 1700-1800 K. Water exposures were made by backfilling the reactor cell while the diamond sample was heated.

III. RESULTS AND SPECTRAL ASSIGNMENTS

An IMIRS spectrum of diamond (100) following an exposure to atomic deuterium at a sample temperature of $\approx$ 500 K is shown in Fig. 1. An infrared absorption feature is observed at a frequency of 901 cm^{-1} and is assigned to a C-D deformation mode. This assignment is based on the similarity of the frequency of the surface vibrational mode to CC-D bending modes of 901 and 918 cm^{-1} in adamantane-d_{16}[38] and $(CD_3)_3$C-D,[39] respectively. Several other infrared peaks have been observed, including features that may be associated with surface CH species. However, we have found that trace amounts of hydrocarbon impurities are present in the infrared detector and that miscancellation between background and sample scans can lead to spurious peaks which are difficult to distinguish from absorption features due to surface CH species.

IMIRS spectra of oxygen-containing species on diamond (100) are shown in Fig. 2. In Fig. 2(a) the diamond was heated to 1070 K for ten minutes and then cooled in a pressure of 1×10^{-7} Torr of water. Similar results were obtained in experiments where the maximum annealing temperature was $\approx$ 1400 K. The resulting infrared spectrum indicates the formation of several surface oxides, exhibiting strong peaks at 1250, 1200, 1125, and 1080 cm^{-1}. The multiple-peak features of the 1250-1200 cm^{-1} band and the 1080 cm^{-1} band were found to be quite reproducible. In some experiments a peak at 720 cm^{-1} was also observed. Since products of oxygen adsorption (CO, CO_2) desorb near 870 K,[23,32] water adsorption most likely occurred as the sample temperature dropped below the desorption threshold. The precise exposure is unknown as the rate at which the sample temperature dropped was not controlled precisely.

In a second set of experiments, the diamond sample, which had been previously oxidized, was heated to ≈1270 K while maintaining the chamber pressure below 4×10^{-9} torr. The peaks seen in Fig. 2(b) correspond to surface species that desorbed or reacted to form different species upon heating. Each of the absorption peaks shown in Fig. 2 were seen in both water adsorption experiments and oxide desorption experiments. Spectral features were generally broader in the desorption spectra than in the adsorption spectra, suggesting significantly more surface disorder and inhomogeneous broadening in the former case.

In separate experiments, the diamond sample was exposed to a 1×10^4 L (1 L ≡ 10^{-6} Torr sec) dose of molecular oxygen at room temperature. No reaction was observed by IMIRS.

The peaks observed at 1250 and 1200 cm^{-1} are assigned to an ether-type (-C-O-C-) structure. The peaks observed at 1125 and 1080 cm^{-1} are assigned to a hydroxyl (-OH) group. The peak at 720 cm^{-1} is assigned to a carbonyl (>C=O) bending mode. Mode frequencies in the fingerprint region exhibit a high sensitivity to chemical environment, which is advantageous from the standpoint of providing more information. However, functional-group modes tend to be strongly mixed with skeletal modes, greatly complicating the assignment of spectra. The assignments given above are based on comparisons with spectra of adamantanes, which are arguably the best available molecular analogues for diamond surface species.[40]

The assignment of the 1125 and 1080 cm^{-1} bands to a hydroxyl group is based on a comparison with 1-adamantanol, for which hydroxyl group modes occur at 1115 and 1087 cm^{-1}.[41] The agreement is very close, suggesting minimal steric crowding of the OH groups. The 1250 and 1200 cm^{-1} bands do not always appear or disappear concurrently with the 1125 and 1080 cm^{-1} bands, implying that the former are associated with a surface species other than OH.

We are unaware of published infrared or Raman spectra of 2-oxa-adamantane, perhaps the simplest good molecular analogue of an ether-type oxide on diamond. The assignment of the 1250 and 1200 cm^{-1} bands to bridge-bonded oxygen is based on a comparison with experimental data on other ethers and to predicted frequencies for 2-oxa-adamantane obtained from *ab initio* self-consistent-field (SCF) calculations that we performed using Gaussian 92.[42] The polycyclic ether dioxabicyclo[3.2.1]octane exhibits C-O stretching modes at 1250 and 1180 cm^{-1},[43] in quite good agreement with the surface modes. The C-O stretching mode occurs at 1271 cm^{-1} in ethylene oxide,[44] also in reasonable agreement. SCF calculations on 2-oxa-adamantane, making the usual correction for over-estimation of vibrational frequencies,[45] yields predicted infrared-active frequencies at 1266, 1200 and 1101 cm^{-1}, also in good agreement with the surface species. The latter calculated frequency, 1101 cm^{-1}, is intriguing in that it lies in the region that we have assigned to the hydroxyl group. The calculated intensities of the modes suggest that an ether-group surface

mode with a frequency near 1101 cm^{-1} may contribute to the observed 1080 cm^{-1} surface peak (Fig. 2), but the evidence summarized above indicates that the 1080 cm^{-1} feature is due primarily to surface hydroxyl groups.

Our assignment of the surface peak at 720 cm^{-1} to a carbonyl bending mode is somewhat more uncertain, as the experimental spectrum of 2-adamantone[46] shows a strong absorption at 860 cm^{-1}. The 720 cm^{-1} mode cannot be due to either an ether-type structure or an OH group, as its appearance and disappearance do not coincide with either set of infrared bands. Shifts as large as 140 cm^{-1} are not uncommon on surfaces; however, ongoing experiments will further address this assignment. In contrast, the closeness of the peak frequencies of the ether and hydroxyl assignments to those of their molecular analogues suggests that minimal strain is present in the ether and hydroxyl structures. Further experiments to test these spectral assignments are underway, including adsorption of molecular and atomic oxygen, D_2O, and $H_2^{18}O$.

IV. DISCUSSION

A. Hydrogen adsorption

Our IMIRS results show evidence for monohydride (CH) but not dihydride (CH$_2$) species, indicating that monohydride species predominate, at least under the relatively mild hydrogenating conditions achievable in high vacuum. The closeness of the peak frequency (901 cm^{-1}) to that of molecular analogues suggests that little, if any steric hindrance is present, which is consistent with the hydrogen being present in the (2×1):H structure. If dihydride were present, CD$_2$ deformation modes should have appeared at ≈ 1110 and 1071 cm^{-1}, based on the infrared spectrum of adamantane-d_{16}.[38] A population of dihydride species ≈10-20% that of the population of monohydride species cannot be excluded, however, due the limited signal-to-noise ratio in the infrared spectrum. The apparent predominance of the monohydride is consistent with the observation by Thomas et al.[21,22] that exposure of monohydride-covered diamond (100) to large exposures (by UHV standards) of atomic hydrogen does not result in formation of high coverages of dihydride species, and also with predictions that the full (1×1):2H dihydride is unstable with respect to loss of H_2.[27,47-49] In the future we hope to determine the thermal stability of the monohydride by IMIRS and to identify conditions under which CH$_2$ species can be formed.

The monohydride infrared peak has a full width at half maximum of ≈ 20 cm^{-1}, comparable to that seen for the C-H stretching mode on diamond (111)[50] and the Si-H stretching mode on Si(100).[34(c)] The linewidth for H on Si(100) was overwhelmingly due to inhomogeneous broadening,[34(c)] which is almost certainly also the source of the linewidth seen here--the diamond IRE was polished to a roughness of ≤ 40 nm. Futher insight into the structure of the adsorbed

hydrogen could be obtained from the polarization dependence of the surface infrared spectrum,[34(c)] but greater sensitivity will be necessary for such measurements. Since a nearly atomically-flat diamond (100) surface can be produced by CVD growth[18] and much wider terraces should greatly narrow the infrared peaks, as has been dramatically demonstrated for hydrogen on Si(111),[51] it should indeed be possible to greatly enhance the sensitivity of the IMIRS experiments.

B. Water adsorption

Sappok and Boehm[30] and Matsumoto et al.[32] observed a 1760-1800 cm^{-1} carbonyl stretching mode on oxidized diamond powder. Since the diamond lattice absorbs in this region, this mode is unobservable by IMIRS. Matsumoto et al.[32] also observed an ether group mode at 1280 cm^{-1} while Sappok and Boehm[30] reported two modes of an ether group formed by reaction with oxygen at 1270 and 1120 cm^{-1}. Each of the spectra reported by Sappok and Boehm also have a very broad absorption feature with local maxima near 1090 and 1120 cm^{-1} which were also assigned to an ether structure,[30] rather than to OH(a) as would be suggested by our assignments. Since the base pressure in the apparatus of Sappok and Boehm[30] was no better than 10^{-5} to 10^{-6} Torr, it seems quite possible that their samples reacted inadvertently with water upon heating, forming surface hydroxyl groups.

We postulate that the observed surface oxide species were formed by dissociative adsorption of water followed by further decomposition, by analogy to the behavior of water on Si(100)[52] and Ge(100).[53,54] Based on an analogy between dissociative adsorption and molecular addition reactions,[54] the reaction of water with diamond (100) may occur on a single dimer, as indicated in Eq. (1),

$$
\begin{array}{ccc}
\underset{\diagup}{H-O}^{\diagup H} & & \\
C=C & \rightarrow & \overset{H}{\underset{\diagup}{C}}-\overset{OH}{\underset{\diagdown}{C}} \\
\diagup \diagdown & & \diagup \diagdown
\end{array} \tag{1}
$$

forming H(a) + OH(a), as occurs on Si(100)[52] and on Ge(100).[53] We obtained the infrared spectra of oxide species (Fig. 2) using a detector that has a wider spectral range but a lower sensitivity than the detector used to observe D(a) (Fig. 1). As a consequence, the noise level in the oxide spectra (Fig. 2) is too large to observe the coadsorbed hydrogen produced by dissociative adsorption of water. Heating of adsorbed OH groups causes further dissociation to bridge-bonded oxide on both Si(100)[52(b)(d)] and Ge(100).[53(b)] It is reasonable to suppose that C-O-C ether-like species on diamond (100) are formed by decomposition of OH(a) in an analogous fashion. Formation of bridge-bonded oxygen on diamond (100) presumably disrupts the 2×1 dimer structure, but further work will be necessary in order to gain further structural information.

The well-known greater propensity of carbon relative to silicon and germanium to form double bonds is presumably the reason why carbonyl (>C=O) species are stable enough to be observed on diamond whereas the analogous silanone (>Si=O) and germanone (>Ge=O) species are *not* observed in the decomposition of water on Si(100) and Ge(100), respectively. The monoxide (CO, SiO, and GeO) is the predominant high-temperature desorption product of surface oxide on diamond (100),[23] Si(100),[55] and Ge(100),[54] suggesting that a surface species with a double bond to oxygen exists at least as a transient intermediate in each case. It is somewhat surprising that the carbonyl feature at 720 cm^{-1} did not appear in every oxidation experiment. This may be due either to the prior presence of surface carbonyl groups (so that nothing was observed in the ratioed FTIR spectrum), or to the effect of an uncontrolled variable (such as surface hydrogen coverage or the local atomic structure) on the branching ratio between formation of hydroxyl, ether, and carbonyl groups during reaction of the diamond sample with water at elevated temperature. The more ready disappearance upon annealing of the hydroxyl and carbonyl infrared features than the ether modes suggests that the bridge-bonded species is the most stable form of surface oxygen on diamond (100) just as on Si(100) and Ge(100). As with bridge-bonded oxygen, formation of surface carbonyl groups is likely to disrupt the surface structure but further work will be necessary to elucidate the details.

One of the most significant results reported here is that water reacts readily with diamond at a pressure corresponding to high vacuum (10^{-7} Torr), many orders of magnitude lower than that operant under CVD conditions. Most diamond CVD reactors are not purged or outgassed carefully; therefore, a significant partial pressure of water is likely to be present in typical growth environments. To date, the reaction of diamond surfaces with water has been completely neglected in CVD growth models. The present results suggest that reaction of water with the growing diamond surface may be important in diamond CVD, perhaps modifying the surface morphology via etching (desorption as CO) even if the growth rate is not greatly affected.

ACKNOWLEDGMENTS

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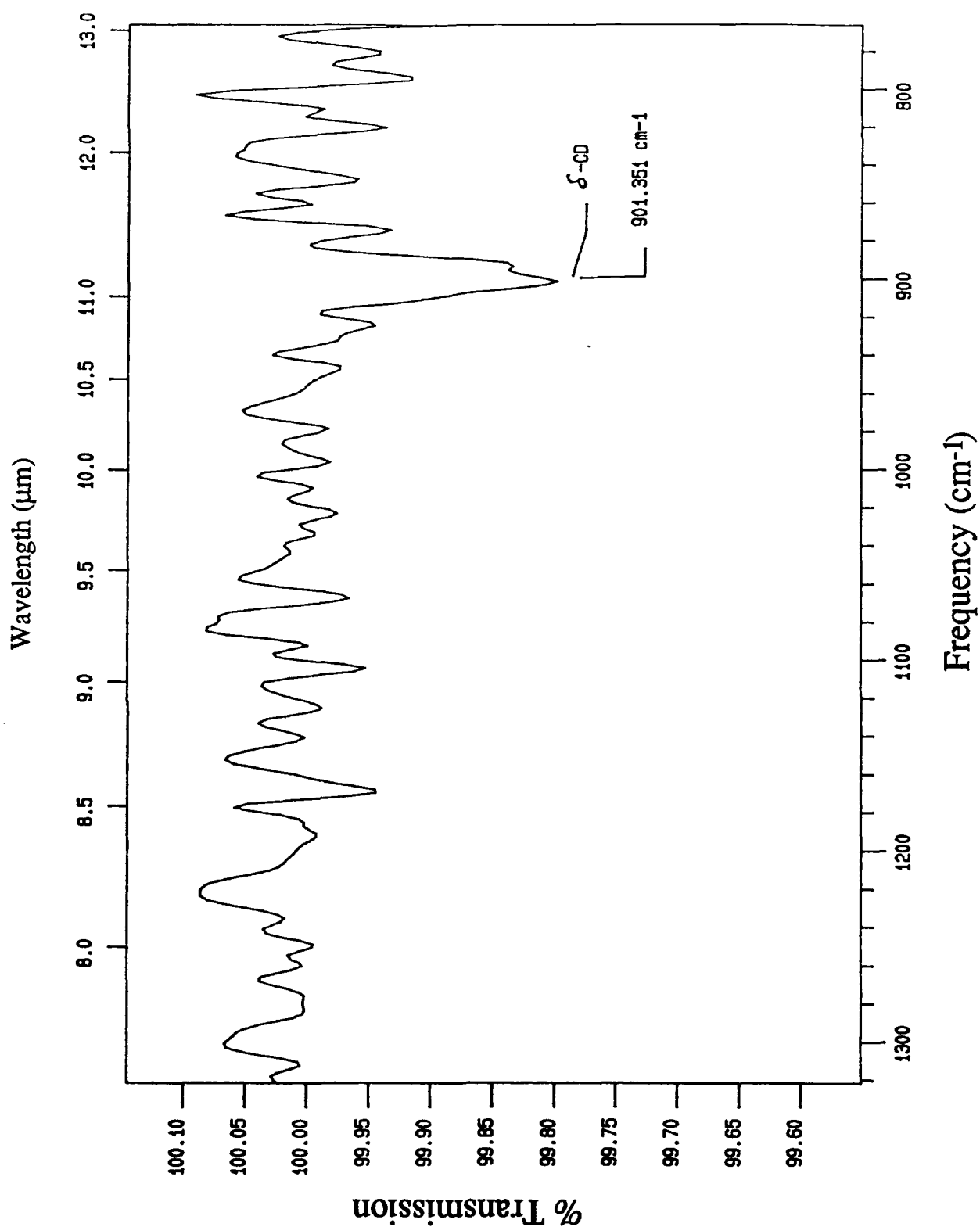55. M. P. D'Evelyn, M. M. Nelson, and T. Engel, Surf. Sci. **186**, 75 (1987).

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FIG. 1. Infrared multiple-internal reflection spectrum, taken at 4 cm⁻¹ resolution with 1024 scans, of CD species on diamond (100). Deuterated surface was prepared with a 7200 L nominal dose of a hydrogenated surface at a sample temperature of 500 K.
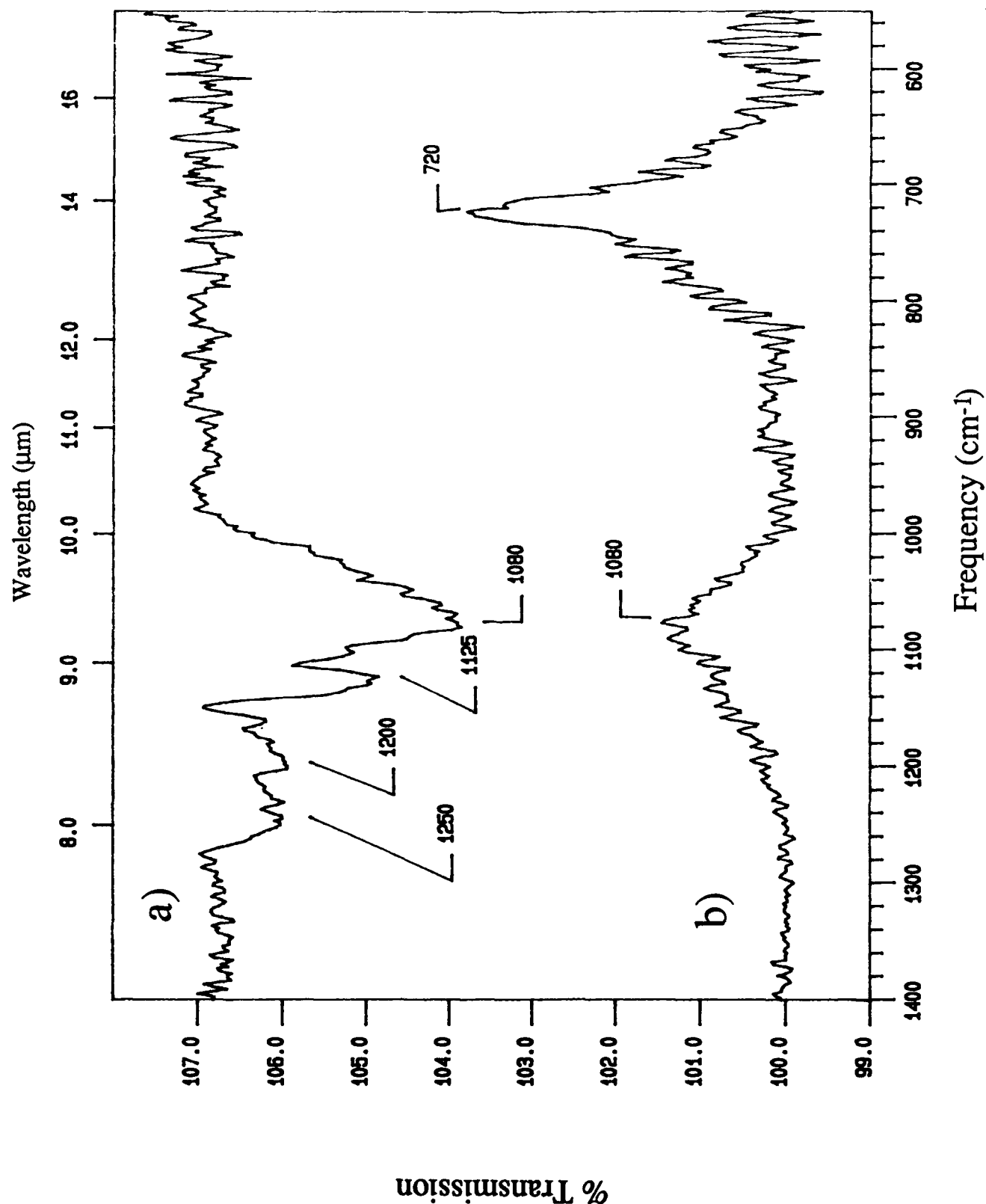
FIG. 2. IMIRS spectra, taken at 4 cm^{-1} resolution with 400 scans, of oxygen-containing species on diamond (100). Spectra were obtained by: (a) cooling the sample from ≈1070 K in 1 × 10^{-7} Torr of H_2O; (b) heating an oxidized surface to ≈1270 K in UHV.