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# Orientation of $N_2O$ molecules adsorbed on Grafoil

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The nuclear resonance scattering of 6324-keV photons from $^{15}N$ was used to study the tilt angles of $N_2O$ molecules adsorbed on graphite. It is shown that for a coverage $n = 0.8$ and 1.3 commensurate $\sqrt{3}\times\sqrt{3}$ monolayers, at $T = 12$ K, the $N_2O$ tilt angles are $\phi = 4° \pm 4°$ and $\phi = 16° \pm 2°$, respectively, with respect to the graphite planes. The orientation angle remains nearly the same between 12 K and $\sim 150$ K, while the $N_2O$ film passes from a solid to a liquid and then to a gaseous phase.

## I. INTRODUCTION

We used the nuclear resonance photon scattering technique to measure the tilt angle of the linear $N_2O$ molecule adsorbed on graphite for two different coverages. The same method was used earlier for studying the tilt angle of $N_2$ and NO molecules with respect to the graphite planes[1,2] as a function of temperature.

This method was described in detail in an earlier publication.[3] Briefly, the resonance scattering process monitors the Doppler broadening of the nuclear level caused by the zero-point energy of the vibrational motion of the molecule. Since $N_2O$ is a linear molecule, the main contribution to the vibrational motion is along the line joining the three atoms and hence the Doppler broadening is maximum along this direction and minimum perpendicular to it. This method relies on the fact that the 6324-keV nuclear level of $^{15}N$ is photoexcited by a chance overlap with one of the $\gamma$ lines of the $Cr(n,\gamma)$ reaction. It turns out that in this nuclear resonance process, the scattering cross section $\sigma_s$ is proportional to the Doppler broadening and hence can be viewed as a measure of the tilt angle of the $N_2O$ molecule with respect to the adsorbing graphite plane as is explained in more detail below.

A preliminary report[4] on this work contained an error; the value of the coverages were reported to be $n = 0.49$ and $n = 0.85$ instead of the correct value $n = 0.77$ and $n = 1.33$ ML, respectively.

## II. EXPERIMENTAL METHOD

The experimental arrangement (Fig. 1) consisted of a photon beam, scattering chamber, a target contained in a cryostat, and two Ge(Li) detectors. The photon beam is generated by the $(n,\gamma)$ reaction on three chromium disks placed along a tangential beam tube and near the core of the IRR-2 reactor. Each disk was about 8 cm in diameter and about 1 cm thick. The intensity of the 6324-keV $\gamma$ line is about $10^4$ photons/cm$^2$ sec at the target position. It is about 2 orders of magnitude weaker than some of the intense $\gamma$ lines of the $Cr(n,\gamma)$ reaction. Each $\gamma$ line emitted by the $(n,\gamma)$ source is highly monochromatic with a width determined primarily by the Doppler broadening $\Delta_s$ of the thermal motion of the emitting nucleus. For the 6324-keV $\gamma$ line emitted by the $^{53}Cr(n,\gamma)$ reaction, the Doppler width amounts to 10.6 eV. The photon beam was neutron filtered by passing it through a 40 cm length of borated paraffin and then allowed to strike the adsorption target. More details concerning the photon beam and the scattering chamber are given elsewhere.[5] The target consisted of isotopically enriched $N_2O$ gas (99% $^{15}N$) enclosed in a thin-walled (0.4 mm) stainless-steel cylindrical cell (5 cm diam, 4.5 cm high) containing 83.5 g of Grafoil in the form of 120 parallel sheets. The amount of the $N_2O$ gas was determined by weighing the adsorption cell before and after filling it with gas.

Isotopic $N_2O$ was used where only one of the nitrogen atoms in the molecule was labeled $^{15}N$, namely ($^{15}N$-$^{14}N$-O, 99% $^{15}N$). The geometry of the adsorption cell and the Grafoil sheet are illustrated in Fig. 1(b). The target was prepared by keeping the Grafoil cell at liquid-nitrogen temperature and inserting the $N_2O$ gas (through a valve fitted on the top of the cell) while measuring the vapor pressure. With this arrangement, the atomic attenuation of the photons were the same for the two geometries of the target with respect to the photon beam. In one geometry, the Grafoil planes were set parallel, and in the second perpendicular to the photon beam. The

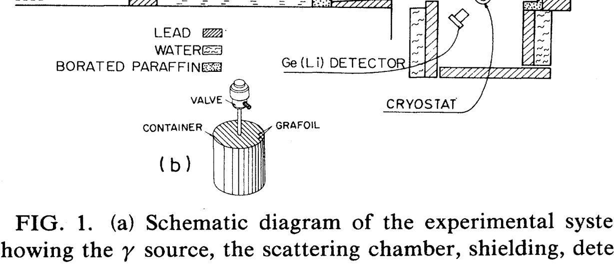

FIG. 1. (a) Schematic diagram of the experimental system showing the $\gamma$ source, the scattering chamber, shielding, detectors, and adsorption target. (b) Schematic view of the geometry of the Grafoil sheets inside the stainless-steel container.

measurements were performed using two coverages: $n=0.77\pm0.05$ and $n=1.33\pm0.09$ ML, the corresponding amounts of $N_2O$ were 573 and 984 mg, respectively. The monolayer coverage was determined by measuring the vapor pressure of the gas at liquid-nitrogen temperature and by relying on the results of Terlain and Larher.[6] The pressure buildup of $N_2O$ inside the adsorption cell at a coverage of 1.33 ML and at $T=297$ K was 180 psi. The cell was placed inside a Displex cryostat which varied the temperature of the sample between 12 and 300 K. At each temperature the cryostat was rotated around an axis (coinciding with that of the cylindrical cell) from one geometry to a perpendicular one and vice versa.

The scattered radiation from the target was detected using two 120-$\text{cm}^3$ Ge(Li) detectors, placed symmetrically at 15 cm and an angle 130° on both sides of the target. The background spectrum was measured using an identical cell containing the same amount of graphite and with no gas in it. Figure 2 shows the result of subtracting the background from the scattered radiation spectrum.

## III. RESULTS

As mentioned in Sec. I, the ratio of the scattered intensities in the two geometries of the target with respect to the beam is a very sensitive monitor of the tilt angle of the $N_2O$ molecule with respect to the graphite surface. These ratios were measured against $T$ for two coverages and are displayed in Fig. 3(c). It is clear that the data points corresponding to the low coverage are much larger than those corresponding to the higher coverage. Both ratios converge to the value $R=\sigma_a/\sigma_a=1.00$ at $T=297$ K.

A qualitative understanding of the data is straightforward because a higher vlaue of $R$ implies a smaller tilt angle of the linear $N_2O$ molecule with respect to the graphite surface. The tendency of the molecules to lie flat on the graphite surface is disturbed with increasing temperature which increases the amplitude of the librational motion of the adsorbed molecules. Thus at $T=300$ K, it seems that the instantaneous angle of the $N_2O$ symmetry axis with respect to the graphite planes becomes isotropic, and hence the ratio $R$ approaches unity.

In order to determine the tilt angles, it was necessary first to get a quantitative measure of the zero-point energies (ZPE) of the potentials governing the $N_2O$-Grafoil system. This was done, as in Ref. 1, by measuring the photon scattering cross section from a pure $N_2O$ target and also from $N_2O$ adsorbed on a nonoriented Grafoil target both in the temperature range 15–297 K (Fig. 3). From these data the ZPE were deducted and were used to obtain the tilt angle of the $N_2O$ molecule as a function of $T$.

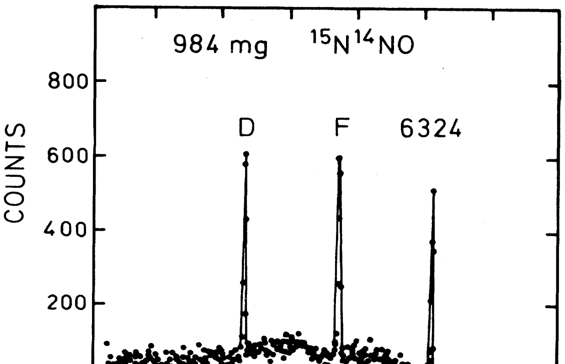

FIG. 2. Typical scattered radiation spectrum from a $^{15}N^{14}NO$-Grafoil and a stainless-steel container as measured using a 120-$\text{cm}^3$ detector. $F$ and $D$ indicate single- and double-escape peaks while the other line is the photopeak of the 6324-keV $\gamma$ line. The background spectrum using the same target with no $N_2O$ was subtracted.

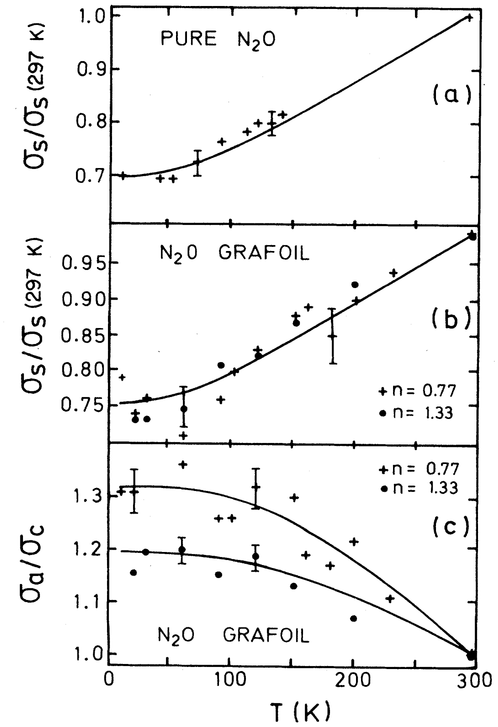

FIG. 3. Ratios of measured scattered intensities (relative to 297 K) from (a) pure $^{15}N^{14}NO$ contained in a 2-cm-diam spherical stainless-steel container. The solid curve is obtained using Eq. (3) with $h\nu_t/k=190$ K and $h\nu_r/k=150$ K after converting the values of $T_e$ to scattering cross sections using the results of Ref. 7. Typical experimental errors are indicated. (b) $^{15}N^{14}NO$ adsorbed on nonoriented graphite for two coverages: $n=0.77$ ML (triangles) and $n=1.33$ ML (circles). The solid curve represents the calculated results obtained using Eq. (7) (with the values of $h\nu_j$ given in the text) and converting the results to effective cross sections. (c) Measured ratios $\sigma_a/\sigma_c$ of scattered intensities vs $T$ (relative to 297 K) from the $N_2O$-Grafoil target for two geometries in which the incident photons are parallel ($\sigma_a$) and perpendicular ($\sigma_c$) to the graphite planes. The results are given for coverages $n=0.77$ and 1.33 ML. Lines are drawn through the points to guide the eye.

Another measurement which assisted in understanding the data was the amount of adsorbed $N_2O$ on Grafoil as a function of temperature for the two coverages: $n=0.77$ and 1.33 ML. We found that approximately 23% of $N_2O$ in the cell was adsorbed at room temperature (297 K) increasing to about 80% at $T=220$ K and practically 100% at $T\approx 180$ K. These amounts are much larger and are indicative of much stronger binding forces than the corresponding case of the $N_2$-graphite system.[1]

## IV. THEORETICAL REMARKS

In the present work, we measure scattering cross sections which can be easily converted to effective temperatures using Fig. 2 of Ref. 7. We first write the expression of the effective temperature of the $^{15}N$ atom in the various situations occurring in this work.

(1) *Pure* $N_2O$ *gas.* As mentioned above, we are dealing with an isotopic gas of the form $^{15}N$-$^{14}N$-O. The effective temperature of the $^{15}N$ atom may be obtained by considering the nine kinetic degrees of freedom of the entire molecule: Three are translational $(3kT/2)$, only two are rotational $(kT)$ because of the linear character of $N_2O$, and four are vibrational. In each mode, the energy fraction $S_j$ carried by the $^{15}N$ atom is taken into account. Since the total number of the *kinetic* degrees of freedom carried out by $^{15}N$ is three, hence

$$3kT_e/2=S_t(3kT/2)+S_r(kT)+0.5\Sigma_1^4 S_j k a_j \ . \tag{1}$$

$S_t=\frac{15}{45}$ and $S_r=0.498$ are the energy fractions shared by the $^{15}N$ atom in the translational and rotational motions, respectively, where

$$k a_j = h f_j \{[\exp(h f_j/kT)-1]^{-1}+\tfrac{1}{2}\} \ . \tag{2}$$

The factor 0.5 multiplying the third term on the right-hand side of Eq. (1) signifies the fact that the kinetic energy of vibration is equal to one-half the total vibrational energy assuming that no anharmonic terms contribute.

Out of the four internal vibrational modes of the $N_2O$ molecule there are two degenerate bending modes, $f_1=f_2$ in two directions perpendicular to the molecular symmetry axis, and two stretching modes, $f_3$ is between the $N^+$ and $O^-$ atoms, and $f_4$ is between the $^{15}N$ and $^{14}N^+$ atoms. The experimental values of $f_j$ for $N_2O$ reported in Ref. 8 are in the infrared region and are listed in Table I together with the values of $S_j$ which we calculated using methods of molecular spectroscopy.[9]

Substituting the values of $S_t$, $S_r$, and $S_j$ in Eq. (1), we may obtain an approximate value for $T_e$, valid at low values of $T$ where $h f_j \gg kT$ and hence $a_j \approx h f_j/2k$. For such cases we obtain

$$T_e \approx 0.665T+288 \tag{3}$$

which implies that the zero-point energy (at $T=0$ K) of the $^{15}N$ atom in $N_2O$ is $T_e=288$ K. At temperatures $T<180$ K, gaseous $N_2O$ turns to a solid; the translational and rotational motions turn into vibrations and librations of the entire $N_2O$ molecule with frequencies $\nu_t$ and $\nu_r$ and average energies $k\alpha_t$ and $k\alpha_r$. For an Einstein model of solid $N_2O$, we have

$$T_e=S_t\alpha_t+2S_r\alpha_r/3+\tfrac{1}{3}\Sigma_1^4 S_j a_j \ , \tag{4}$$

where $\alpha_t$ and $\alpha_r$ are defined in a similar manner to that of $a_j$ in Eq. (2).

(2) $N_2O$ *adsorbed on fully oriented graphite.* Here, we define two effective temperatures of the $^{15}N$ atom: $T_a$ and $T_c$ in directions parallel and perpendicular to the graphite planes. To calculate $T_a$ and $T_c$, we use a simple model in which we assume a decoupling between the in-plane and out-of-plane degrees of freedom of motion of the $N_2O$ molecule with respect to the graphite surface. We also assume (a) that the internal vibrational frequencies of the $N_2O$ molecule are not influenced by the adsorption process, and (b) that the relative motion of the $N_2O$-graphite system can be represented by five Einstein oscillators: (i) an out-of-plane vibration $\nu_1$ of the entire $N_2O$ molecule with respect to the graphite plane; (ii) an out-of-plane libration $\nu_2$; (iii) in-plane libration $\nu_3$; and (iv) two in-plane degenerate vibrations $\nu_4$ of the entire $N_2O$ molecule.

We now consider a single $N_2O$ molecule and assume that as a result of all interactions with other $N_2O$ molecules and the graphite surface, the molecular $N_2O$ axis is tilted an angle $\phi$ with respect to the graphite plane with one external atom sticking to the surface. The same tilt angle is assumed irrespective of whether the N end or the O end of the $N_2O$ molecule sticks to the surface.

The motion of this adsorbed $N_2O$ molecule can thus be projected along and perpendicular to the graphite planes to get the corresponding effective temperatures $T_a$ and $T_c$ of the $^{15}N$ atom:

$$T_a=(0.5\Sigma_2^4 S_j a_j)\cos^2\phi+0.5S_1 a_1 \sin^2\phi +0.333\alpha_4+0.249(a_3+a_2\sin^2\phi) \ , \tag{5}$$

$$T_c=(\Sigma_2^4 S_j a_j)\sin^2\phi+S_1 a_1\cos^2\phi+0.498\alpha_2\cos^2\phi+0.333\alpha_1 \cdot \tag{6}$$

TABLE I. Normal frequencies $f_j$ (in units of $cm^{-1}$) of the normal $N_2O$ and the labeled $^{15}N$-$^{14}N$-O molecule (taken from Ref. 8) together with the calculated fractions $S_j$ of the kinetic energy of the left N atoms.

| | | $^{14}N_2O$ | | $^{15}N^{14}NO$ | |
|---|---|---|---|---|---|
| | Normal modes | $f_j$ | $S_j$ | $f_j$ | $S_j$ |
| $f_1=f_2$ | bending | 588.8 | 0.1682 | 585.3 | 0.1690 |
| $f_3$ | $N^+$—$O^-$ stretching | 1284.9 | 0.4954 | 1269.9 | 0.4954 |
| $f_4$ | $N\equiv N$ stretching | 2223.8 | 0.1712 | 2201.6 | 0.171 |

where $\alpha_j$ $(j=1,\dots,4)$ are defined in a similar manner as that of Eq. (2) but with $\nu_j$ replacing $f_j$. It may be noted that for low values of $T$ where $kT \ll hf_j$ we have $S_1a_1 \approx 71$ K and $\Sigma S_j a_j \approx 397$ K $(j=2,\dots,4)$. Equations (4) and (5) may be used for deducing the effective temperature $T_g$ of the N atom for the case of $N_2O$ adsorbed on *nonoriented* graphite by using the relation:

$$\begin{aligned} T_g &= (2T_a+T_c)/3 \\ &= [3\Sigma_1^4 S_j a_j + \alpha_1 + 1.494(\alpha_2+\alpha_3) + 2\alpha_4]/9 \ . \end{aligned} \tag{7}$$

The scattering cross sections $\sigma_a$, $\sigma_c$, and $\sigma_g$ corresponding to the effective temperatures $T_a$, $T_c$, and $T_g$ may be deduced by using the calculated curve given in Ref. 7.

(3) *$N_2O$ adsorbed on Grafoil.* The above values of $T_a$ and $T_c$ which were calculated for fully oriented graphite should be corrected to account for the actual structure of Grafoil. The latter is known to contain a randomly oriented fraction $(f=0.44)$ of crystalline surfaces having a mosaic spread with a half width at half maximum angle $\theta_0=15°$. The corrected values $T_c^*$ and $T_a^*$ can thus we written as

$$T_c^* = fT_g + (T_c\langle\cos^2\theta\rangle + T_a\langle\sin^2\theta\rangle)(1-f) \ , \tag{8}$$

$$T_a^* = (3T_g - T_c^*)/2 \ , \tag{9}$$

where

$$\langle\sin^2\theta\rangle = \int_0^{\pi/2} \sin^3\theta \exp\{-[(\theta/\theta_0)^2 \ln 2]\} d\theta \bigg/ \int_0^{\pi/2} \sin\theta \exp\{-[(\theta/\theta_0)^2 \ln 2]\} d\theta \tag{10}$$

from which the corrected cross sections $\sigma_a^*$, $\sigma_c^*$, and hence the corrected ratios $R_c=(\sigma_a/\sigma_c)^*$ can be deduced. In order to obtain the tilt angle of the $N_2O$ molecules with respect to the graphite surface the following procedure was followed: First, the empirical values of $\nu_r$ and $\nu_t$ were deduced by trying to best fit the measured data of pure $N_2O$ [Fig. 3(a)] using Eq. (4). The values of $\nu_r$ and $\nu_t$ thus obtained were assumed to be the same as those of adsorbed $N_2O$ on graphite, namely $\nu_3=\nu_r$ and $\nu_4=\nu_t$. Next, we used $\nu_3$ and $\nu_4$ as input data on Eqs. (8) and (9) to deduce the values of $\nu_1$ and $\nu_2$ from Fig. 3(b). The results obtained are

$$h\nu_1/k = 690\pm80 \text{ K}, \quad h\nu_2/k = 260\pm40 \text{ K} \ ,$$

$$h\nu_3/k = 150\pm20 \text{ K}, \quad h\nu_4/k = 190\pm30 \text{ K} \ .$$

It is very important to note that $h\nu_3$ and $h\nu_4$ are not independent, neither are $h\nu_1$ and $h\nu_2$. This means that if we decrease $\nu_3$, the value of $\nu_4$ will increase and vice versa. The same reasoning applies to the values of $\nu_1$ and $\nu_2$. In selecting the value of $\nu_3$ we were guided by the fact that the in-plane librational energy in $N_2O$ is expected to be lower than the vibrational $N_2O$-$N_2O$ motion. Further, in selecting the value of $\nu_2$ we used the fact that the deviation of $\sigma_a$ from $\sigma_c$ (which gives a measure of the out-of-plane librational energy) starts at $\approx 260$ K.

Using the above empirical values of $h\nu_j$, we calculated $R_c$ as a function of $\phi$ at $T=12$ K. The results are plotted in Fig. 4 from which the values of $\phi$ were deduced at the two coverages of $N_2O$ employed in the present work: $\phi=4\pm4°$ (for $n=0.77$ ML) and $\phi=16\pm2°$ (for $n=1.33$ ML). It should be emphasized, however, that essentially the same type of agreement with the experimental data of Fig. 3 can be obtained if one assumes $\nu_1=\nu_2$ and $\nu_3=\nu_4$. In that case, a best fit can be obtained using

$$h\nu_1/k = h\nu_2/k = 460 \text{ K}, \quad h\nu_3/k = h\nu_4/k = 170 \text{ K} \ .$$

## V. DISCUSSION

### A. Tilt angle

As mentioned in a previous work,[1] the present technique is very sensitive to the out-of-plane tilt angle of the molecule with respect to the graphite plane; it is entirely independent on the type of in-plane ordering or on whether the $N_2$ film is commensurate or incommensurate with the graphite hexagons. In deducing the tilt angle, we have assumed that for low coverages, $n \approx 1$, the graphite-$N_2O$ potentials and hence the values of $h\nu_j$ are independent on the coverage. Figure 4 shows that at the lower coverage the $N_2O$ molecule tends to lie flat on the surface while at higher coverages the *average* tilt angle increases. This behavior is similar to that of the $N_2$-graphite system;[1] it is entirely different from that of the NO-graphite system[2] where no coverage was observed in which the NO molecules lie flat on the graphite planes. The present value of the tilt angle for $n<1$ is in essential agreement with that based on adsorption isotherm measurements of Ref. 6 who also suggested that the $N_2O$ molecules should form a $\sqrt{3}\times\sqrt{3}$ structure.

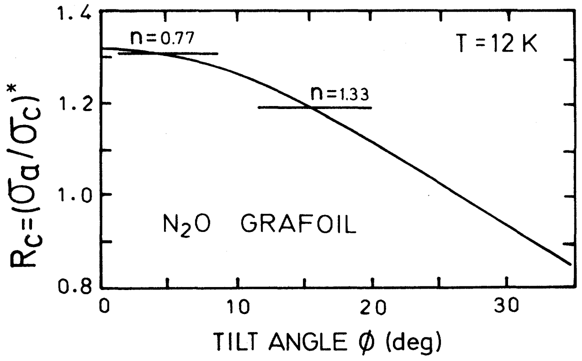

FIG. 4. Calculated values at $T=12$ K of $R_c=(\sigma_a/\sigma_c)^*$ vs $\phi$ (the average tilt angle) of the $N_2O$ molecular axis with respect to the graphite planes. The measured ratios for $n=0.77$ and 1.33 ML are indicated.

This behavior, which is similar to the $N_2$-graphite system, is also expected from the large quadrupole moment of the $N_2O$ molecule ($Q=-3.5$ esu cm$^2$ compared to $-1.5$ esu cm$^2$ for $N_2$).

For the higher coverage, $n=1.3$, the average tilt angle obtained in the present work $\phi=16°$ is much higher than that obtained for $n<1$. The rapid increase in the tilt angle for a relatively small increase in coverage could be indicative of an orientational phase transition occurring after the completion of the first monolayer. This point is considered in more detail below when we compare the present results with theoretical expectations.

According to Terlain and Larher,[6] the $N_2O$ film (for a coverage of 1 ML) is in a solid phase up to 107 K. A solid-liquid transition occurs between 107 and 115 K, while a liquid-gas transition occurs in the range 112–117 K. The fact that the data points of Fig. 3(c) for a coverage $n=0.8$ ML remain flat from 12 K up to 150 K means that the average tilt angle of the $N_2O$ molecular axes remains essentially the same ($\phi=4\pm4°$) when the $N_2O$ adsorbed film passes from solid to liquid and to the gaseous phase. The most significant result in this respect is that while in the vapor phase, at $120\text{ K}<T<150\text{ K}$, where the $N_2O$ molecules move freely on the graphite surface, the molecular axes tilt at an angle essentially parallel to the graphite surface. In fact, a significant tendency to lie parallel to the surface remains up to about 250 K as may be seen by comparing the results of Fig. 3(c) with Fig. 4. Such a situation occurs only when the out-of-plane forces are far larger than the in-plane forces acting on the $N_2O$ molecules. This finding is in accord with the deduced values of the ZPE of the potentials governing the $N_2O$-graphite system; here, the out-of-plane forces expressed by the energies ($h\nu_1/k=690$ K and $h\nu_2/k=260$ K) are far larger than the in-plane forces expressed by ($h\nu_3/k=150$ K and $h\nu_4/k=190$ K).

### B. Zero-point energies (ZPE) of the potentials

The values of the ZPE obtained by the above procedure seem to be too high and may be viewed as an estimate only. The high values could probably be caused by the assumptions of the simple model used to deduce them. It should be emphasized, however, that the accuracy in the tilt angles deduced by this procedure should be far better than that of the ZPE. This is because the internal vibrational energies of the $N_2O$ molecule are much higher than the energies $h\nu_j$ of the $N_2O$-graphite system. In fact, a similar situation ocurred in the case of the $N_2$-graphite system where the same model was used[1] and the tilt angles obtained were in good agreement with those of other measurements and with predictions of molecular-dynamics simulations.[10]

The measured ratio of $\sigma_a/\sigma_c$ [Fig. 3(c)] should be contrasted with that of $N_2$-Grafoil and also of NO-Grafoil. The first drops sharply with temperature from a value of 1.60 at $T=20$ K to 1.1 at $T=70$ K while the second yielded values between 1.08 and 0.95 at $T\approx20$ K depending on the coverage and varied between these two limits with increasing $T$. It is also of interest to note that while a relatively large difference occurs between the behavior of $\sigma_a/\sigma_c$ against $T$ for the two coverages, the normalized data of $\sigma_s$ versus $T$ for nonoriented graphite seem to be independent on coverage as may be seen from Fig. 3(b). This is again due to the fact that the out-of-plane forces are much larger than the in-plane forces governing the $N_2O$-graphite system as was found above.

### C. Comparison with theoretical expectations

Theoretically, the $N_2O$-graphite system was not studied yet because the $N_2O$-$N_2O$ and the $N_2O$-graphite potentials are not known. Qualitatively, some insight into this system may be obtained by considering the predicted phases of the $N_2$-graphite system which was studied in detail by Steele[10] and by Harris and Berlinsky.[11] It may be noted that $N_2O$ has a quadrupole moment 2.3 times larger than $N_2$; it has a molecular area of 15.7 $\text{Å}^2$ and can be compactly packed into a $\sqrt{3}$ ML commensurate structure similar to that of $N_2$ on graphite. Hence, some resemblance in the behavior of the $N_2$-graphite and the $N_2O$-graphite systems as a function of $T$ and $n$ is expected.

Such systems may be described by a mean-field theory, developed in Ref. 11; it treated the adsorbed molecules as point quadrupoles forming a triangular lattice on an axially symmetric crystal field perpendicular to the graphite substrate. Several phases were predicted and were identified experimentally for the $N_2$-graphite and for the CO-graphite systems using the low-energy electron-diffraction technique.[13,14] Thus, the "two-in" phase may be identified with the $\sqrt{3}\times\sqrt{3}$ commensurate structure observed here at $n<1$ and low $T$ in which the adsorbed molecules lie flat on the graphite surface. A similar phase was identified, in the $N_2$-graphite system, using the present technique.[1] In Ref. 11, other phases were predicted: a "two-out" and "pinwheel" structures which correspond to different intensities of the crystal field of the graphite. In the two-out phase the molecules are allowed to tilt out of the graphite surface at a certain angle and correspond to a coverage higher than 1 ML. In the pinwheel structure, it is assumed that on the average for each four adsorbed $N_2O$ molecules, three lie flat on the graphite surface while the fourth molecule stands up on the surface.

The possible occurrence of a pinwheel structure[11–14] at a coverage $n<1$ may be ruled out because the corresponding calculated value of $(\sigma_a/\sigma_c)^*$ is 0.91 to be compared with a measured value of 1.31. A similar result is true for the higher coverage $n=1.3$. However, it may be possible to identify the structure observed in the present work for $n=1.3$ ML as a two-out phase if one assumes that such a high areal density is permissible for this phase. This is because the deduced tilt angle $\phi=16°\pm2°$ is within the expected range of values obtained for such a structure in the $N_2$-graphite system.[14]

In the following we consider a possible composite structure in which the first monolayer in the $n=1.33$ coverage is a commensurate $\sqrt{3}$ ML (with the $N_2O$ molecules lying flat on the graphite surface) while the remaining partially filled second layer, $n=0.33$, lie above the first and forms a "pinwheel" structure. Such a composite phase cannot be ruled out by the present results because the corresponding calculated value is $(\sigma_a/\sigma_c)^* = 1.22$ to be compared with our measured value of $1.19 \pm 0.02$ [Fig. 3(c)]. Such a structure, mentioned in Ref. 12 for the $N_2$-graphite system may explain the present result at $n = 1.33$. Thus, the present value of $\sigma_a/\sigma_c$ may indicate the presence of one of the above two structures. More measurements as a function of coverage are needed before being able to distinguish between them. Due to some technical problems, it was not possible to carry out further measurements on this system.

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