

Orientational Ordering of N₂O Molecules Adsorbed on Graphite (0001): A Novel Commensurate Pinwheel Structure

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The structure and orientational ordering of N₂O molecules physisorbed on graphite (0001) is investigated applying x-ray, neutron, and low-energy electron diffraction techniques. Combining the results of the three techniques, we find that N₂O forms a highly ordered, hexagonal, commensurate ($\sqrt{21} \times \sqrt{21}$)R10.89° phase. The unit cell contains seven molecules which are arranged in a seven-sublattice pinwheel structure, unexpected for linear molecules on a hexagonal lattice. Potential energy calculations corroborate these results.

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Orientational order, in bulk as well as in two-dimensional (2D) molecular crystals, is a topic of abiding interest in condensed matter physics. It provides a basis for the understanding of thermodynamic and dynamic properties of matter in a large class of systems ranging from orientable molecules to dielectric and magnetic systems. In surface science, simple linear molecules physisorbed on graphite often serve as test systems for potential models and resulting ordering phenomena [1]. Under the constraints of reduced dimensions and frustrated interactions, these systems give rise to a rich variety of distinct types of orientationally ordered structures.

In a simplified model, small linear molecules may be treated as point quadrupoles. From mean-field studies of point quadrupoles on an ideal and rigid, hexagonal lattice [2,3], a generic phase diagram has been deduced in which strictly four distinct orientationally ordered phases can exist. Depending on the temperature, the relative strength of the holding potential, and the quadrupole coupling constant, this theory predicts the formation of (i) a two-sublattice, “two-in” herringbone phase, where the molecules lie flat on the surface, (ii) a two-sublattice, “two-out” herringbone phase, where the molecular axes are tilted with respect to the surface plane, (iii) a four-sublattice “pinwheel” phase, where one upright standing “pin” molecule is surrounded by six molecules forming a “wheel,” and (iv) a ferrorotational phase with a single tilted molecule per unit cell (see Refs. [2] and [4] for illustrations). Realizations of the phases (i)–(iii) have been found, for instance, in the simple, linear molecular systems N₂ and CO physisorbed on graphite and have been revealed by a large number of experiments (see, e.g., Ref. [4], and references therein).

The triatomic linear molecules CS₂, CO₂, and N₂O possess larger aspect ratios and quadrupole moments compared with N₂ or CO. The question arises whether the novel types of orientationally ordered structures, beyond the phases (i)–(iv), can be found in submonolayer films

of these prolate, linear molecules. In CS₂ and CO₂ films on graphite only one single solid phase occurs. X-ray diffraction studies [5,6] have shown that this phase can be assigned to an incommensurate herringbone structure similar to the two-in phase (i). The system N₂O on graphite has been examined by means of adsorption isotherm [7], nuclear resonance photon scattering [8], and calorimetric measurements [9] in the temperature range between 4 and 130 K and in the coverage range between $\rho = 0.05$ and $\rho = 1.2$. ($\rho = 1$ is defined as the coverage equivalent of a complete ($\sqrt{3} \times \sqrt{3}$)R30° monolayer.) In Refs. [7] and [9] the occurrence of one single solid phase in submonolayer films of N₂O on graphite has been observed which, also according to our results, extends from the lowest temperatures up to $T = 101.2$ K at coverages $0.11 \leq \rho \leq 0.82$ and up to $T \approx 117$ K at coverages $0.82 \leq \rho \leq 1.2$. The surface area per molecule in the solid phase was found to be $15.1 \pm 0.7 \text{ \AA}^2$ [7], which is close to the value of 15.7 \AA^2 for the ($\sqrt{3} \times \sqrt{3}$)R30° superstructure. The small dipole moment of N₂O has a negligible effect on the properties of the monolayer [9]. Since N₂O molecules exhibit properties similar to CO₂, N₂O adsorbed on graphite was expected to adopt a herringbone structure [1]. The results of Refs. [7] and [8] lead to the conjecture of the formation of a ($\sqrt{3} \times \sqrt{3}$)R30° two-in phase (i), whereas the observation of an extremely small gap in the phonon density of states in Ref. [9] questions the existence of a commensurate phase.

In this Letter, we report on the first direct determination of the structure of N₂O monolayers physisorbed on graphite (0001) and come to exciting new conclusions. We find that the N₂O molecules are arranged in a commensurate, hexagonal, seven-sublattice pinwheel structure hitherto not known to exist in physisorbed systems on graphite. Three different experimental techniques were used in the investigations: x-ray diffraction (XRD), neutron diffraction (ND), and low-energy electron diffraction (LEED). In

addition, potential calculations were performed to check the stability of the structure.

The XRD measurements were carried out on a rotating anode x-ray generator using Cu radiation (wavelength $\lambda = 1.54 \text{ \AA}$). ND spectra were recorded on the 2-axis-diffractometer E6 of the Hahn-Meitner-Institut in Berlin, Germany, employing thermal neutrons with wavelength $\lambda = 2.4 \text{ \AA}$. In XRD and ND measurements sheets of Papyex were employed, a powdery substrate with preferred orientation and coherence length $\sim 250 \text{ \AA}$ [10]. The substrate was contained in sealed, cylindrical sample cells made of beryllium and aluminum, respectively. The commensurate monolayer capacity of the substrates was determined from the substep in a N_2 vapor-pressure isotherm at 77 K as in Ref. [11]. Before introducing the N_2O gas into the sample cell, background spectra were measured. The N_2O gas used possesses a nominal purity of 99.999% and was dosed into the cell at 70 K. It was carefully annealed at 150 K for several hours before recording the spectra. The LEED measurements were carried out applying a LEED system with four grids and a single-stage multichannel plate as detector. In the ultrahigh vacuum chamber the base pressure was $5 \times 10^{-9} \text{ Pa}$. We used natural graphite single crystals with a typical size of $3 \text{ mm} \times 3 \text{ mm}$. The N_2O was dosed directly onto the crystal surface at 70 K with a chamber pressure at layer growth of $2 \times 10^{-8} \text{ Pa}$. We determined the monolayer completion from the change of the slope in the LEED spot intensities as a function of gas exposure time as in Ref. [12].

XRD spectra were measured at several coverages between $\rho = 0.5$ and $\rho = 1.3$ and temperatures between 10 and 150 K. Figure 1(a) shows a typical XRD difference spectrum taken in the solid phase. Two peaks appear, which were fitted by 2D, powder-averaged Lorentzian-squared line shapes [13]. The moduli Q of the respective scattering vectors are 1.706 and 2.324 \AA^{-1} . A typical ND difference spectrum is plotted in Fig. 1(b). ND

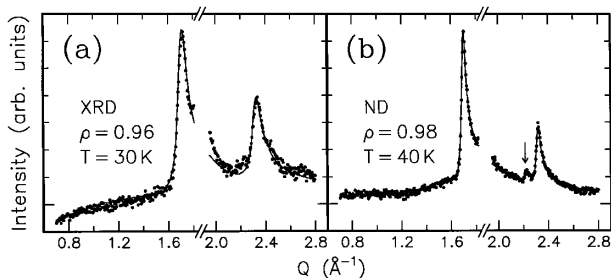


FIG. 1. (a) XRD spectrum of N_2O on graphite recorded at $\rho = 0.96$ and $T = 30 \text{ K}$. (b) ND spectrum of N_2O on graphite taken at $\rho = 0.98$ and $T = 40 \text{ K}$. The additional peak at 2.233 \AA^{-1} is indicated by an arrow. In both spectra the background due to the empty sample cell is subtracted from the data, while the region around the graphite (002) reflection is left out because of incomplete background subtraction. The solid lines show powder-averaged Lorentzian-squared line shape fits [13] with coherence length $\lambda_c = 250 \text{ \AA}$ to the data.

spectra were measured at coverages $\rho = 0.60$, $\rho = 0.95$, and $\rho = 0.98$, and at temperatures between 1.9 and 120 K. In the ND spectra we observed a third peak at $Q = 2.233 \text{ \AA}^{-1}$ in addition to those found in XRD. LEED measurements were carried out in the temperature range between 20 and 78 K and in the coverage range between $\rho \approx 0.3$ and $\rho \approx 1.2$ using LEED energies from 40 to 200 eV. Figure 2(a) presents the LEED pattern at an energy of 143 eV. Spots originating from the N_2O superstructure were observed at $Q = 1.71$ and 2.32 \AA^{-1} and from multiscattering at $Q = 1.26 \text{ \AA}^{-1}$ in addition to the spots of the graphite surface structure. The existence of a sixfold axis and several mirror lines in the pattern is evident. In each of the diffraction methods applied, the peak positions relative to the graphite substrate are independent of coverage and temperature throughout the entire region of the solid phase up to melting, a fact which provides evidence that N_2O on graphite forms a commensurate solid phase.

From the analysis of the LEED measurements the unit cell of the superstructure and the rotation angle φ of the N_2O unit cell with respect to that of the graphite surface was inferred. It turns out that the superstructure actually is commensurate [see Fig. 2(b)] with lattice constants $a = \sqrt{21} \times a_{\text{gr}}$ and $\gamma = 120^\circ$ ($a_{\text{gr}} = 2.456 \text{ \AA}$ is the lattice constant of the graphite basal plane). The rotation angle turned out to be $\varphi = \tan^{-1}(\sqrt{3}/9) \approx 10.89^\circ$. Thus, N_2O on graphite forms a $(\sqrt{21} \times \sqrt{21})R10.89^\circ$ superstructure. The positions of all Bragg peaks observed in XRD and ND measurements match to this unit cell. Considering the symmetry of the graphite lattice, the unit cell of the superstructure can be constructed in two mirror-symmetric ways [indicated by solid and dashed lines in Fig. 2(b)], which represent two equivalent domains of the superstructure. The observed spots result from a superposition of the scattering from these domains. The observation of a

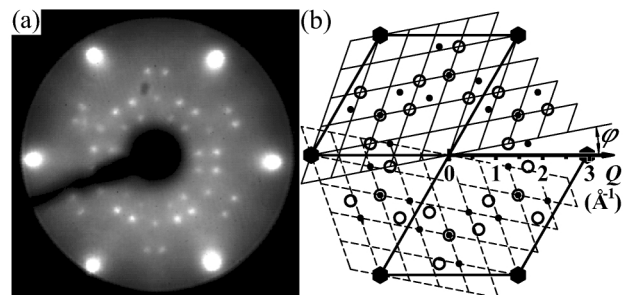


FIG. 2. (a) LEED pattern of N_2O on graphite taken at $T = 70 \text{ K}$, $\rho = 0.8$, and LEED energy $E = 143 \text{ eV}$. (b) The sketch of the LEED pattern shows the positions of the graphite spots (solid hexagons) and of the N_2O superstructure spots (circles). The thick and thin lines indicate the reciprocal lattice of the graphite surface and of the $(\sqrt{21} \times \sqrt{21})R10.89^\circ$ superstructure, respectively. Open and filled circles (solid and dashed thin lines) are used to distinguish the contributions from two equivalent domains.

hexagonal LEED pattern reveals, that the superstructure in real space possesses at least a threefold symmetry axis.

The number of N_2O molecules in the unit cell is seven or eight, since the surface area per molecule in the solid phase is $15.1 \pm 0.7 \text{ \AA}^2$ [7], compared to 109.70 \AA^2 for the area of the N_2O unit cell. With the additional constraint of a threefold symmetry axis this number reduces to seven. One pin molecule stands upright, whereby the molecular axis is chosen as the symmetry axis of the unit cell, while two further molecules can, in principle, be arbitrarily placed within the unit cell. The positions and orientations of the remaining four molecules are determined by the application of the threefold symmetry operation. The fitted, relative peak intensities inferred from the XRD and ND spectra (see Table I) imply information about the orientation of the molecules. These intensities were compared with calculations for the 2D structure factor. We assumed that all molecules, except the pin molecule, lie flat on the surface. A χ^2 minimization procedure was employed in order to find a set of parameters that minimizes the sum of the quadratic differences between the relative intensities obtained from the XRD and ND measurements and the calculated relative intensities, respectively. We took into account that several reflections are absent in the measured spectra. As a representation of a completely dipolar disordered phase, an “unpolar” configuration, where each N_2O

molecule was modeled by an average of two molecules rotated by $\Delta\omega_1 = 180^\circ$, was also used in these calculations. We found that the unpolar arrangement shown in Fig. 3(a) agrees best with both XRD and ND data. The parameters and the calculated intensities are presented in Table I. It is evident from these parameters and from Fig. 3(a), that the molecular arrangement has hexagonal symmetry, which is supported by I - V curves obtained from our LEED measurements (not shown in this Letter). This type of structure can be denoted as a hexagonal seven-sublattice pinwheel structure. Calculations assuming nonzero tilt angles for the wheel molecules were performed. The best agreement with the experimental results was found for the wheel molecules lying flat on the surface. We should point out that the results of the calculations are in accord with the observed LEED patterns.

The novel structure presented in this Letter differs from the pinwheel structure (iii) predicted in Refs. [2] and [3] and observed in CO films on graphite (0001) (see, e.g., Ref. [15]) and from the commensurate structure of submonolayer films of N_2 on Cu (110) [16,17]. CO forms an incommensurate, four-sublattice pinwheel structure with a unit cell containing four molecules and with each wheel molecule belonging to two neighboring pinwheels. In contrast, the structure of N_2O on graphite is commensurate and its unit cell hosts seven molecules, of which all six wheel molecules belong to a single pinwheel. The Cu (110) surface structure is rectangular, in contrast to the hexagonal structure of the graphite (0001) surface. The N_2 superstructure on Cu (110) possesses an oblique, quasihexagonal unit cell ($a/b = 0.973$, $\gamma = 57.3^\circ$), which does not exhibit a threefold or sixfold symmetry axis. Note that the

TABLE I. Measured and calculated relative peak intensities for the configuration shown in Fig. 3(a). The measured intensities were obtained from fits to the spectra recorded at temperature 40 K and coverage $\rho = 0.98$. The intensities are normalized with respect to the peak at $Q = 1.706 \text{ \AA}^{-1}$. χ^2 is a measure for the degree of agreement between measured and calculated intensities. The parameters of the structure, as defined in Fig. 3(b), are given below the reflection list. The parameters are chosen in such a way that the best agreement with the XRD and ND data was obtained. The indices (a), (b), and (p) refer to the three labeled molecules in Fig. 3(a). z is the height of the molecules above the substrate surface, which was adapted in such a way that the total energy U is minimum. A model potential was used to check the stability of this structure. U_{es} and U_{od} were adapted from Ref. [20], while U_{as} was adapted from Ref. [18]. The average energies per molecule calculated according to the model potential are also added to the table.

Q (\AA^{-1})	Obs. rel. int.		Calc. rel. int.	
	XRD	ND	XRD	ND
0.645	0.01	0.00
1.117	0.01	0.00
1.706	1.00	1.00	1.00	1.00
2.233	(<0.03)	0.09	0.03	0.05
2.324	0.47	0.32	0.32	0.33
2.810	0.01	0.01
χ^2	0.116	0.084

Parameters: $r^{(a,b)} = 4.17 \text{ \AA}$, $\phi^{(a)} = -32.6^\circ$, $\phi^{(b)} = 27.4^\circ$,
 $\omega_1^{(a)} = 94.2^\circ$, $\omega_1^{(b)} = 154.2^\circ$, $z^{(p)} = 4.3 \text{ \AA}$, $z^{(a,b)} = 3.3 \text{ \AA}$.

Potential energies: $U = -208 \text{ meV}$

($U_{es} = -15 \text{ meV}$, $U_{od} = -39 \text{ meV}$, $U_{as} = -154 \text{ meV}$).

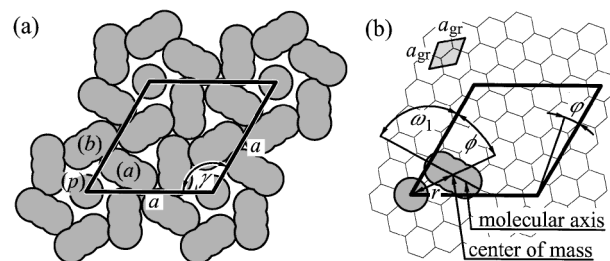


FIG. 3. (a) Structure model of the hexagonal, seven-sublattice pinwheel structure of N_2O on graphite. The sketch exhibits the structure of the unpolar configuration. The commensurate unit cell (thick lines), with $a = \sqrt{21} \times a_{gr}$ and $\gamma = 120^\circ$, hosts seven molecules, one “pin” molecule, and six “wheel” molecules. The shape of the molecules is represented by the van der Waals radii of the atoms [14]. Taking the existence of a threefold symmetry axis into account, the three molecules denoted by (a), (b), and (p) determine the positions and orientations of all molecules within the unit cell. (b) The position of the N_2O unit cell (thick lines) with respect to the graphite surface structure (thin hexagons). Some of the parameters mentioned in the text are indicated. According to potential energy calculations the pin molecule is located above the center of a graphite hexagon.

corrugation of the substrate plays an important role in the formation of the structure and the orientational ordering of this system [17].

Potential energy calculations were performed in order to check the stability of the novel pinwheel structure. The adsorbate-substrate potential we employed is closely related to that introduced originally by Steele (see, e.g., Ref. [18]). The Lennard-Jones parameters were taken from Ref. [19]. The N_2O intermolecular potentials were adapted from the model presented in Ref. [20]. The total potential U is given by the sum of three contributions, $U = U_{es} + U_{od} + U_{as}$: the electrostatic energy U_{es} between the N_2O molecules, the overlap-dispersion interaction potential U_{od} between a pair of N_2O molecules, and the adsorbate-substrate energy U_{as} . In the calculation the height of the molecules above the surface was adjusted, in order to minimize the total potential energy U (see Table I). Calculating the potential energies, the structure shown in Fig. 3(a) turned out to be stable using the parameters listed in Table I. The average energy per molecule was found to be $U \approx -208$ meV (for details, see Table I). The corrugation of the surface potential is rather small (~ 1 meV per molecule) and favors the pin molecule to be located above the center of a graphite hexagon [hollow site; see Fig. 3(b)]. This small corrugation energy might explain the small phonon gap observed in Ref. [9]. A dipolar ordered configuration of the same type is energetically favored over the unpolar configuration ($\Delta U \approx -10$ meV per molecule). However, it fails to reproduce the observed intensity of the peak at $Q = 2.233 \text{ \AA}^{-1}$ by $\sim 50\%$. We also tested the commensurate and incommensurate herringbone structure using the same potential, and found that the seven-sublattice pinwheel structure is energetically strongly favored against these previously supposed structures (see Refs. [1,7-9]). The overlap-dispersion potential, which is related to the steric hindrance of the molecules, becomes antibinding ($U_{od} > 0$) and, thus, counteracts the formation of the alternative structures.

In conclusion, we have shown that the application of three independent diffraction methods (XRD, ND, and LEED), which complement each other, leads to a comprehensive and unambiguous elucidation of the structure, symmetry, and orientational order of the solid phase of submonolayer films of N_2O physisorbed on graphite (0001). The N_2O molecules are arranged in a $(\sqrt{21} \times \sqrt{21})R10.89^\circ$ superstructure. The unit cell contains seven molecules forming a hexagonal, seven-sublattice pinwheel structure where one molecule standing upright is surrounded by six flat lying molecules forming a "wheel." This type of structure has, to the best of our knowledge, not been predicted or observed

for molecules adsorbed on a hexagonal substrate lattice before. The results of potential energy calculations prove the stability of the structure and demonstrate that the competing interplay between the intermolecular and the adsorbate-substrate forces leads to the formation of this novel pinwheel structure.

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