ADSORPTION OF N_2 ON GRAFOIL IN THE FLUID AND VAPOR PHASES

Y. Finkelstein[+], R. Moreh[+] and O. Shahal[*]
[+]Physics Department, Ben-Gurion University, Beer-Sheva 84105, Israel
[*]Physics Department, Nuclear Research Center - Negev, Beer-Sheva, Israel

Introduction

The nuclear resonance photon scattering (NRPS) technique, based on the (n,γ) reaction, was used to monitor the tilt angle of adsorbed N_2 molecules, in the fluid and *vapor* phases, (i.e. at T > 75 K) relative to the basal graphite planes at a coverage of ~ 0.6 monolayer (ML). This is a continuation of a previous work [1] in which the tilt angle of the N_2 molecules was measured as a function of T between 20 K and 80 K and a coverage of 1.05 ML, where the N_2 was in a solid or a fluid phase. It may be noted that this is the only technique which can monitor the tilt angle of the N_2 molecules in the vapor phase. The tilt angle is governed by the quadrupole interaction between the N_2 molecules and the surface and by the librational and vibrational energies of the molecules.

The adsorption of N_2 molecules on Grafoil, at T < 85 K, i.e. in the liquid or solid phases, was studied using several techniques such as n-diffraction, LEED, NMR and specific heat measurements [2-5] where the various phases of the system were reported. Theoretical studies using molecular dynamic simulations (MDS) and group theoretical methods were also carried out [6,7]. The basic idea of the NRPS technique relies on monitoring the Doppler broadening of a nuclear level in ^{15}N caused by the internal zero-point vibrational motion of the N_2 molecules. It so happens that one of the γ-lines of the Cr(n,γ) reaction overlaps by chance the 6324 keV nuclear level of ^{15}N. The overlapping process is such that the resonance scattering cross section is proportional to the Doppler broadening $\Delta_r = E_r(2kT_r/Mc^2)^{1/2}$ of the nuclear level [8], where E_r is the energy of the resonance level, T_r, M are the effective temperature and nuclear mass of the scatterer, and k the Boltzmann constant. It may be noted that T_r expresses the *total kinetic* energy of the scattering atom including that of its zero-point motion. In a N_2 molecule, the total kinetic energy of the N-atom is maximum along the N_2 molecular axis and minimum in the perpendicular direction. Hence the Doppler broadening of the nuclear level should have a maximum $\Delta_\parallel$ along the symmetry axis of the molecule and a minimum, $\Delta_\perp$ along the perpendicular direction; the corresponding scattering cross sections $\sigma_\parallel$, $\sigma_\perp$ fulfills the relation $\sigma_\parallel >> \sigma_\perp$. The directional dependence of the scattering cross section σ_r on the orientation of N_2 with respect to the photon beam is being used here for monitoring the tilt angle of the N_2 molecules with respect to the photon beam direction and hence with respect to the graphite planes.

Experimental

The photon beam is generated by the Cr(n,γ) reaction using the IRR2 nuclear reactor. The scattered radiation from the (Grafoil + N_2) samples was detected using two Ge detectors placed at 15 cm and at an angle of 130° relative to the γ-beam. Isotopically enriched N_2 (99% ^{15}N) was used. The present work had several improvements compared to previous work. (i) The stainless steel container of the Grafoil, having a high initial N_2 gas pressure (110 psi) at 300 K and 1.05 monolayer, was replaced by a thin-walled pure aluminum made of two cylindrical compartments (see the inset to Figure 1). The small one, containing the Grafoil, is positioned in the path of the photon beam, while the large one, serving as a gas reservoir, was outside the beam region. With this design the scattered background is reduced enormously; the scattered signal arises primarily from the adsorbed N_2, while the contribution of the free non-adsorbed gas is very small. (ii) The Grafoil (purchased from Deutsch Carbon) had a good quality in the sense that the product fϕ (where f = 0.31 is the randomly oriented fraction of the crystallite surfaces and ϕ = 30° the FWHM angle of the mosaic spread) is now smaller by about 30% compared to that of ref. [1].

The aluminum Grafoil cell (40 mm internal diameter, 40 mm high) contained 40.5 g Grafoil consisting of 86 rectangular parallel sheets whose planes are parallel to the axis of cylindrical cell. This cell was mounted inside a variable temperature cryostat (10 K to 300 K) which could be rotated around an axis coinciding with that of the Grafoil cylindrical cell from one position where the photon beam was parallel to the graphite planes of the sample to a perpendicular position.

Results and Discussion

In the vapor phase, the N_2 occurring in the Grafoil region consists of an adsorbed part and a free non

adsorbed part. Above 90 K, the adsorbed part was determined by measuring the scattered intensities from the Grafoil compartment as a function of T. The data were then corrected to account for the fact that the scattered intensity from a constant amount of N_2 normally decreases with decreasing T (see ref. [1]). We thus found that the adsorbed fraction of gas in the Grafoil at 140 K is ~ 85%; the remaining amount occurs as a free non-oriented gas. The measured fractions were used to deduce the out-of-plane tilt angle from the measured ratios of R as a function of T at a coverage n ~ 0.6 ML and using the same procedure and parameters given in ref. [1]. Figure 1 shows the scattered radiation spectrum from the (Grafoil + N_2) sample, at 20 K, containing 184 mg $^{15}N_2$ (corresponding to a coverage n ~ 0.6 ML) and using a 150 cm^3 Ge detector for the two geometries in which the photon beam is parallel and perpendicular to the graphite planes of the Grafoil.

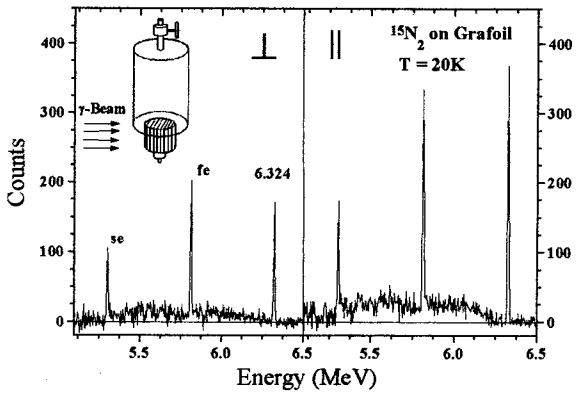

Figure 1. Scattered radiation spectra from the two orientations of the γ-beam with respect to the Grafoil planes at a coverage of ~ 0.6 ML and T = 20 K. The ratio of the scattered intensities is $R = \sigma_{\parallel}/\sigma_{\perp} = 1.97$. The inset shows the Grafoil + N_2 cell in which the path of the γ-beam is indicated. The gas reservoir is not hit by the γ-beam.

Note the large ratio of the scattered intensities revealing strong anisotropy R ~ 2.0; which is caused by adsorbed N_2 molecules lying nearly parallel to the graphite planes at 20 K. The measured ratio decreases with increasing T reaching R = 1.34 at 80 K and 1.20 at 140 K. This trend continues down to R = 1.0 at T ≥ 170 K, where the librational amplitude of the N_2 becomes very large. From the measured R, the tilt angles θ of the N_2 molecular axis with respect to the graphite planes may be obtained using the vibrational and librational energy parameters deduced in ref. [1]. Our deduced results (at n ~ 0.6 ML) are: θ = 5.0° ± 3.0°, 22.5° ± 1.3°, 28.5° ± 1.0° at T = 20 K, 80 K and 140 K respectively. The measured average tilt angles at 20 K and 80 K agree nicely with θ = 8.0°, 21.2° ± 1.0° predicted in refs. [9-11] at n = 1.0 ML, T = 16.2 K and n = 0.64, T = 75.9 K respectively, which are close to the coverages and temperatures used in the present work.

Two very significant conclusions emerge from the present data. (1) A pronounced forward tilt θ = 28.5° of N_2 molecules on the graphite surface is detected at 140 K where the gas is in the *vapor* phase and the N_2 is believed to stick loosely to the graphite surface. It will be very interesting to carry out MDS of the N_2-graphite system in the vapor phase to see to what extent the above properties measured at T = 140 K, could be reproduced. (2) At the same temperature, T = 80 K, the tilt θ was found to increase with increasing coverage from 22.5° at n ~ 0.6 ML to 28.0° at n = 1.05 ML (see ref. [1]). The same effect was reproduced nicely in ref. [11] using MDS at nearly the same values of n and T whereby θ changed from 21.2° at n = 0.64 ML, T = 72.3 K to 28.5 ° at n = 1.0 ML and 75.9 K. The present work shows that the NRPS technique is a powerful tool for measuring the properties of adsorbed molecules on graphite.

Acknowledgments

This research was supported by the German-Israeli Foundation for scientific Research and Development (GIF).

References

1. R. Moreh and O. Shahal, Surf. Sci. **177**, L963 (1986).
2. J. K. Kjems, L. Passell, H. Taub, J. G. Dash and A. D. Novaco, Phys. Rev. B13 1446 (1976).
3. R.D. Diehl and S.C. Fain Jr., Surf. Sci. 125 (1983) 116.
4. A. D. Migone, H. K. Kim, M. H. W. Chan, J. Talbot, D. J. T. Tildesley and W. A. Steele, Phys. Rev. Lett. 51, 192 (1983).
5. N. S. Sullivan and J. M. Vaissiere, Phys. Rev. Lett. 51, 658 (1983).
6. W. A. Steele, J. Phys., Paris, C4, 61 (1979).
7. A. B. Harris and A. J. Berlinsky, Can. J. Phys. 57, 1852 (1979).
8. R. Moreh, O. Shahal and V. Volterra, Nucl. Phys. A262, 221 (1976).
9. J. Talbot, D. J. Tildesley and W. A. Steele, Faraday Discuss. Chem. Soc. 80, 1 (1985).
10. K. D. Miner, M. H. W. Chan, and A. D. Migone, J. Talbot, D.J. Tildesley, W.A. Steele, Phys. Rev. Lett. 51, 192 (1983).
11. J. Talbot, D. J. Tildesley and W. A. Steele, Surf. Sci. 169 (1986) 71.