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PHYSISORPTION OF DEUTERIUM ON DEUTERATED NICKEL CLUSTERS*

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The physisorption of deuterium molecules on small nickel clusters already saturated with chemisorbed deuterium atoms is identified. The principal evidence for physisorption is the appearance at reaction temperatures below 200 K of product species having more deuterium bound to them than the chemisorption maximum, and a lowering of cluster ionization potentials (IPs) for these species. It is argued that the IP lowering is a consequence of molecular physisorption, and that identification of the number of physisorption sites on cluster surfaces can be used to infer structural information.

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I. Introduction

The physisorption of molecules on metal surfaces has been studied both theoretically [1-3] and experimentally [4-6]. Molecular physisorption is often invoked as a precursor step to eventual chemisorption, and as such may play an important role in the gas phase reactions of metal clusters. Since physisorption is the consequence of a weakly attractive van der Waals interaction, physisorption binding energies are very small [4], ranging from 3.5 to 15 kJ/mol for H_2 (D_2), depending on the system. As a result, surface investigations have to be carried out at very low temperatures. Physisorption of H_2 has been reported on edge sites of a stepped Ni(100) surface by means of electronic energy loss spectroscopy (EELS) at a temperature of about 100 K [5]. A broad, weak vibrational band (ν_{H-H}) was found after saturation of chemisorption sites with hydrogen atoms. Recently, Russel et. al.[6] have identified a molecular D_2 species on Ni(111) at an adsorption temperature of 87 K and H_2 (D_2) coverages greater than $\Theta = 0.5$.

In this paper, we present the experimental observation of D_2 physisorption on deuterated nickel clusters at temperatures below 193 K. In addition, the uptake of physisorbed D_2 vs D_2 pressure is measured and clearly demonstrates saturation of the first monolayer of physisorbed molecules. It is argued that physisorbed D_2 thus provides a new probe of cluster structure applicable to hydrogenated or deuterated metal clusters or to systems that do not chemisorb H_2 (D_2).

II. Experimental

The experimental apparatus has been described in detail elsewhere[7,8]. Briefly, clusters are generated in a laser vaporization source coupled to a flow-tube reactor (FTR). The pulsed output from a Q-switched Nd:YAG laser (Continuum, NY 60B-50) at 532 nm vaporizes metal from an isotopically pure ^{58}Ni target into a continuous flow of helium carrier gas. Metal atoms thus produced are entrained and cooled by the carrier gas, resulting in rapid cluster growth. The pressure of the carrier gas is kept low (9-20 Torr) to insure a rapid diffusive loss of metal atoms to the wall of the flow-tube so that termination of cluster growth is achieved before the clusters enter the FTR. At the end of the FTR, the clusters and their reaction products expand through a 1 mm diam nozzle into vacuum. This expansion stops further reaction and to some extent cools the internal energy of the clusters.

The central portion of the cluster expansion passes through a conical skimmer and several collimators to form a molecular beam. After two stages of differential pumping, the molecular beam arrives at the ionization region of a time-of-flight (TOF) mass spectrometer. The clusters are photoionized by a pulsed excimer laser (Questek, 2620) which is delayed from the vaporizing laser pulse. In the present study, both ArF (193 nm, hν = 6.42 eV) and F_2 (157 nm, hν = 7.98 eV) lasers are used for photoionization. The ions produced are analyzed in the TOF mass spectrometer (1 m drift tube, mass resolution ~600). Ion signals are acquired, digitized, and averaged in a LeCroy oscilloscope and sent to a computer for analysis.

The physisorption of D_2 has been examined at five temperatures, 118 K, 133 K, 153 K, 173 K, and 193 K. Low reaction temperatures are obtained by flowing liquid nitrogen through a cooling block attached to the bottom of the cluster source and FTR. The temperatures of the cluster source and the FTR are kept the same in the present experiments. The reaction temperature is monitored using a thermocouple located at the end of the FTR.

Deuterium is added to the FTR either as a pure gas or as a mixture in He. The mixtures are passed through filters (Oxysorb, MG Scientific Gases) before use. Carrier and reagent gas flow rates are measured with mass-flow meters (Hastings). The total pressure in the FTR is continually monitored with a capacitance manometer (MKS).

III. RESULTS AND DISCUSSION

The saturated chemisorption of D_2 on nickel clusters (Ni_n) has been examined at room temperature previously[9], and the ionization potentials for fully deuterated clusters smaller than n ~ 40 are found to be higher than the energy of ArF laser photons. The experimental evidence for the physisorption of molecularly adsorbed D_2 on nickel clusters comes from measurements of the nickel cluster mass spectra as a function of D_2 pressure at temperatures below 193 K. Shown in Fig. 1 are product mass spectra at 133 K using ArF laser photoionization. At very low D_2 pressures, deuterium dissociatively chemisorbs on nickel clusters and products of the general form Ni_nD_{2m} are seen. As deuterium pressure increases, two groups of peaks are observed: one group has m_{max} smaller than the corresponding chemisorption saturation m_{sat}, while the other exhibits m_{min} greater than that for chemisorption saturation. (Values of m_{sat} can be determined with F_2 laser ionization.) Since 193 nm ArF photons cannot ionize small nickel clusters saturated with deuterium atoms, the observation of Ni_nD_{2m} products with m_{min} larger than the known chemisorption saturation suggests the existence of molecularly physisorbed D_2 on nickel clusters that are already saturated with chemisorbed deuterium atoms, and also indicates that physisorption of D_2 molecules reduces the clusters' ionization potentials. The observation of the group of peaks with $m_{min} > m_{sat}$ *only at* $T \leq 193$ *K* further indicates that molecular physisorption contributes to this group of peaks. As the D_2 pressure is increased further, the group of peaks with $m < m_{sat}$ disappears. At very high D_2 pressures, some of the nickel clusters achieve physisorption saturation. Shown in Fig. 2 are the product mass spectra in this high D_2 pressure region, for both F_2 and ArF excimer laser photoionization. Since the F_2 laser photon energy is ~1.5 eV above the ionization potential of the $Ni_{15}D_{2m}$ cluster, loss of physisorbed D_2 in the ionization process is certainly possible, and the lower spectrum in Fig. 2 shows that it is occurring. The spectra also show, however, that m_{max} is the same for both lasers, demonstrating that loss of physisorbed D_2 is not occurring with ArF laser photoionization for those clusters that show a single peak (e.g. $Ni_{15}D_{40}$) and is not likely occurring for other clusters as well.

Shown in Fig. 3 is an uptake plot obtained with ArF laser ionization which illustrates the dependence of the average value of m for $Ni_{15}D_{2m}$ species as a function of D_2 pressure at 133 K. There is some distortion at low physisorption coverages since the fully chemisorbed clusters cannot be ionized without some physisorption. The uptake plot, which covers almost three orders of magnitude in D_2 pressure, shows two plateaus, which indicate the presence of at least two types of physisorption sites. In order to separate the contribution of molecular physisorption from that of dissociative chemisorption, it is necessary to determine m_{sat}, the chemisorption saturation level. This can, in principle, be done by ionizing with an F_2 laser at temperatures somewhat above 193 K. If the chemisorption saturation does not have a strong temperature dependence, then we can assume it will be unchanged at lower temperatures. Experiments show that some clusters have temperature-independent chemisorption saturations and others do not. Ni_{15}, in particular, shows a clear chemisorption saturation at $Ni_{15}D_{20}$ for the temperature range $193 K < T < 293 K$. From the results in Fig. 3 we see that the $Ni_{15}D_{20}$ cluster achieves physisorption saturation with the adsorption of ten D_2 molecules. The plateau structure in Fig. 3 shows that there are three sites of one type and seven other sites (which may or may not be of the same type.)

The present study clearly demonstrates the existence of molecular physisorption on gas phase nickel clusters. An interesting feature is that D_2 physisorption is observed only after the dissociative chemisorption reaction is complete. This is not unreasonable, since the dissociative chemisorption of D_2 on nickel clusters is a non-activated process[10]. As a result, all the D_2 molecules that initially react with the cluster dissociatively chemisorb. Once the chemisorbed sites are occupied (or a barrier to further dissociation is created), molecularly physisorbed D_2 becomes possible.

Saturated physisorption of D_2 on metal clusters provides information about the number of physisorption sites on these clusters. Since the number of physisorption sites is a unique property for a cluster with a given geometrical structure, physisorption of adsorbates can be helpful in determining the structure of these clusters. In combination with the structural information obtained from chemical probes, a clearer picture of the geometrical structure of metal clusters can be expected.

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Figure Captions

Fig.1 Portions of the 133 K deuterated nickel cluster TOF mass spectra in the 13- to 16-atom size range for three D_2 pressures in the FTR. For some of the mass peaks the number of nickel atoms n and the number of deuterium molecules m that are chemisorbed and/or physisorbed are indicated. The dotted lines mark the products with the same n and m values.

Fig. 2 Portions of the 133 K nickel cluster time-of-flight mass spectra with 610 mTorr of D_2 added to the reagent port. (Upper panel): ArF laser photoionization. (Lower panel): F_2 laser photoionization.

Fig.3 Deuterium uptake plot for Ni_{15} at 133 K; ArF laser ionization.

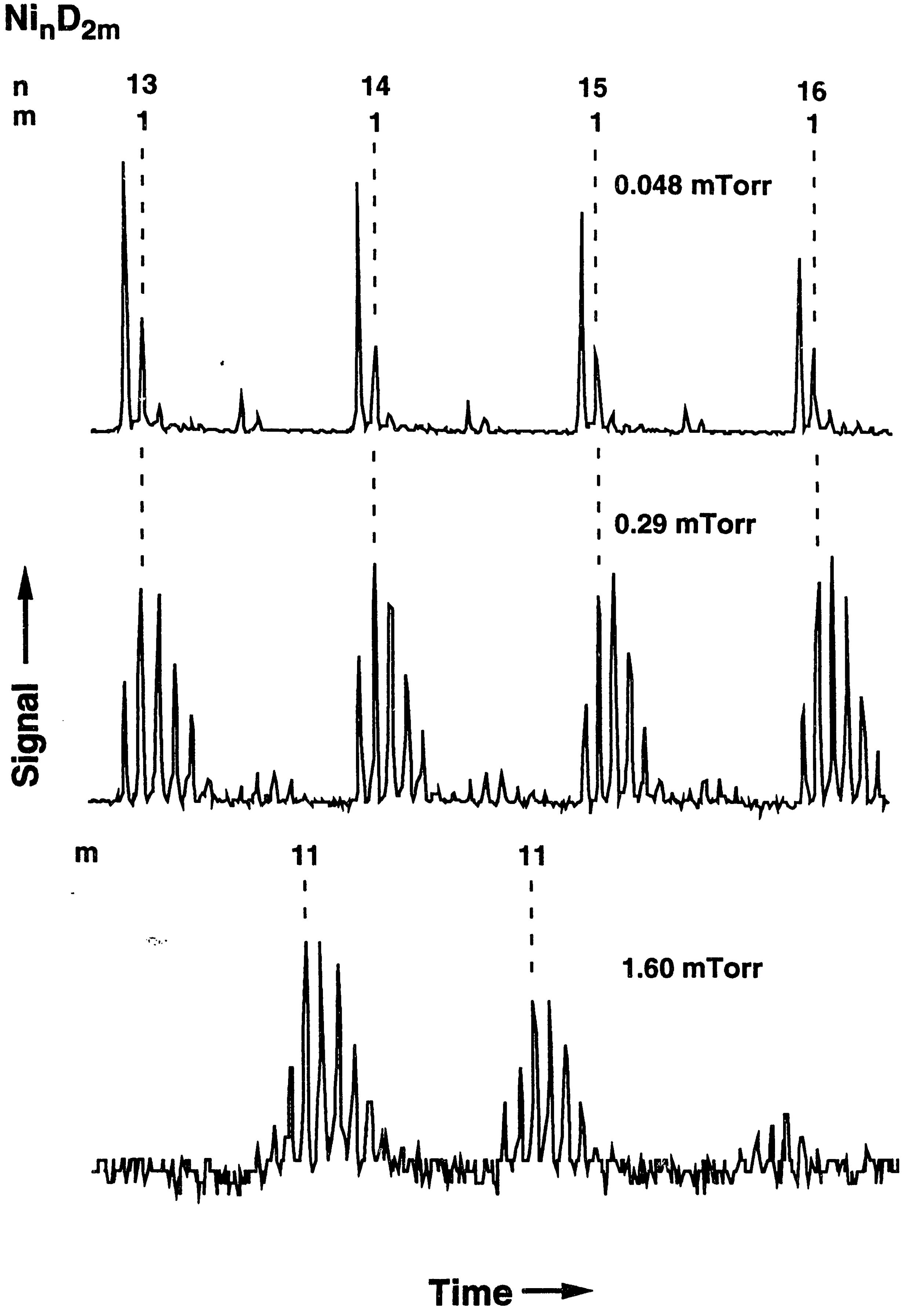
Ni_nD_{2m}
n
m
13
1
14
1
15
1
16
1
0.048 mTorr
0.29 mTorr
Signal
m
11
11
1.60 mTorr
Time

Figure 1

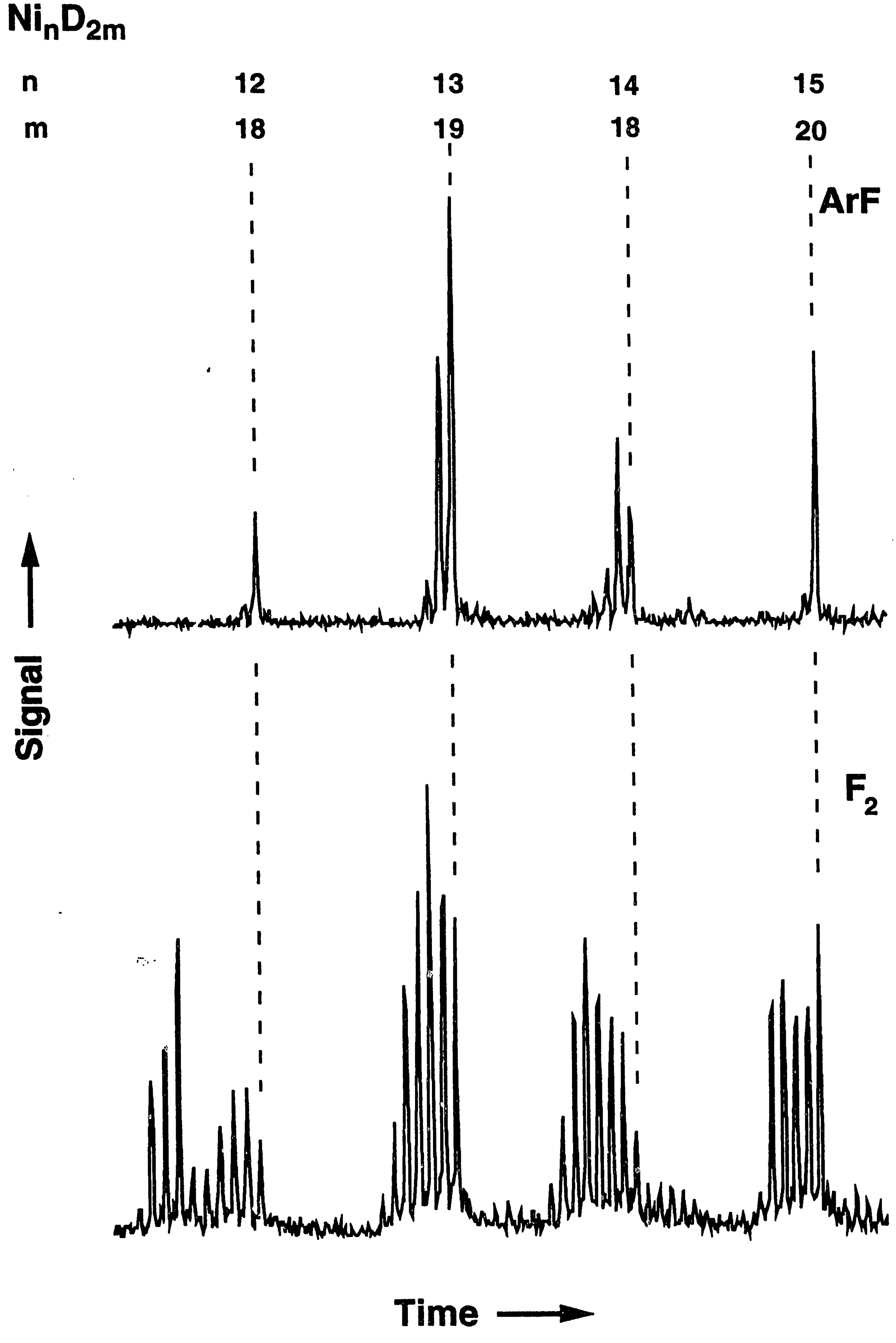

Figure 2

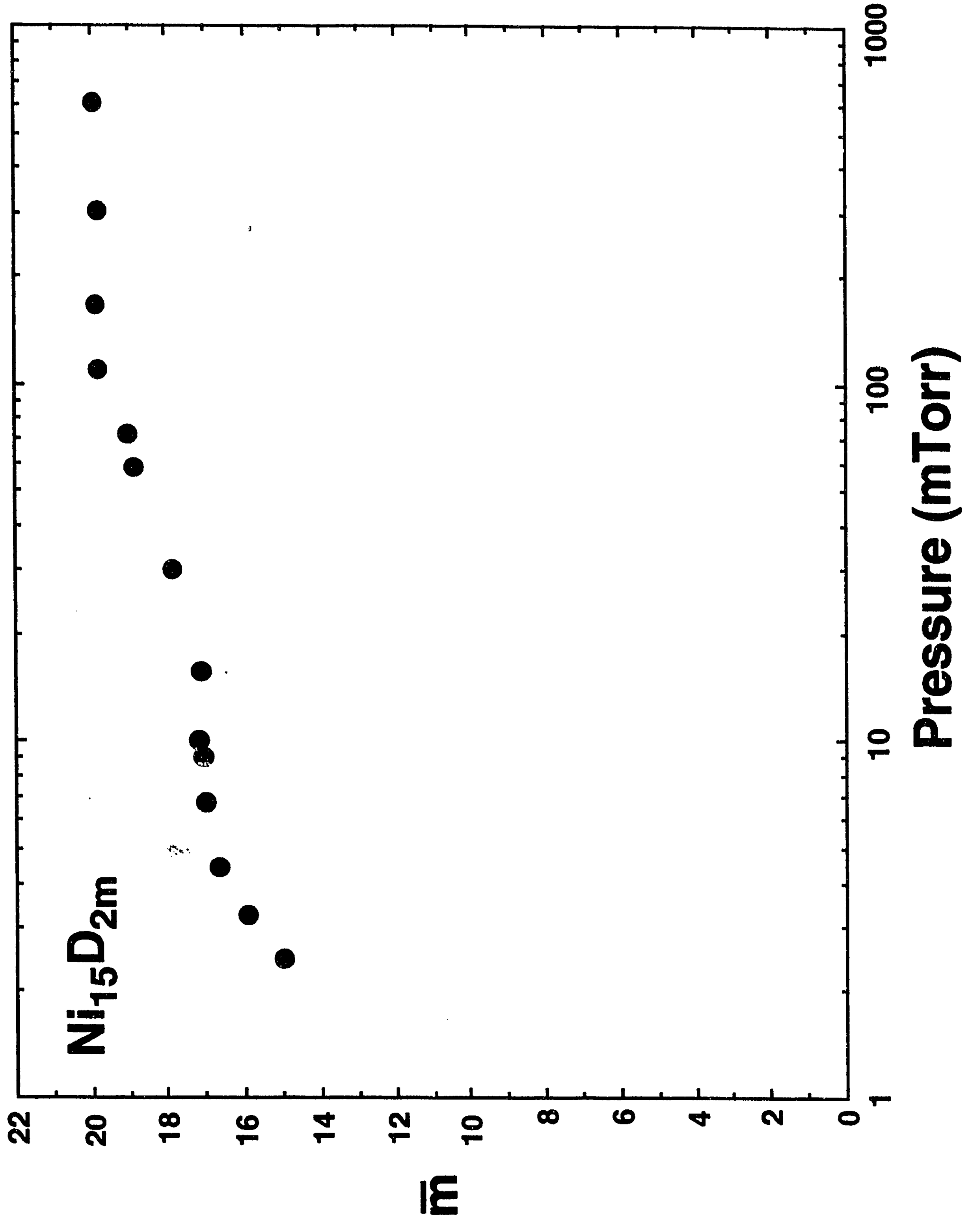
$Ni_{15}D_{2m}$
$\bar{m}$
22
20
18
16
14
12
10
8
6
4
2
0
1
10
100
1000
Pressure (mTorr)

Figure 3

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