AN ATOMIC BEAM TECHNIQUE FOR THE STUDY OF ACTIVE SOLID NITROGEN

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Matrix stabilized atomic N in N_2 is created in thin films with excitation introduced at the surface by atomic beam deposition. Layered film coatings of $^{14}N_2$, $^{15}N_2$, Ar and H_2 are used to elucidate the role of molecular excitons in the stimulation of emission of light. Optical intensity studies indicate that molecular vibrons are delocalized. Recombination induced desorption of H_2 from an H_2 coated surface is demonstrated.

Activated solid nitrogen (N_2–N; atomic N stabilized in an N_2 solid matrix) exhibits a remarkable optical emission spectrum at low temperatures, that was extensively investigated at the NBS in the late 1950's [1–4] and more recently has received renewed attention due to a new interpretation by Dressler and coworkers [5–8]. Previous studies of N_2–N include massive condensation from a gaseous discharge [2] and γ-ray [3] or electron bombardment [3,7,9] of bulk solid N_2. We have developed a new method to study N_2–N whereby well-defined atomic beams are used to create and excite (stimulate emission of light from) N_2–N in thin films ($< 10^5$ monolayers). We have shown that the first step of the excitation process is localized at the surface and is most likely the result of recombination of N atoms. Variation of beam intensity and film composition (using layered coatings of $^{14}N_2$, $^{15}N_2$, Ar and H_2), are used to elucidate the role of the $N_2(^3\Sigma_u^+)$-excitons and $N_2(^1\Sigma_g^+,v)$-vibrons in the generation of luminescence spectra. We have also observed H_2 desorption as a result of N- or H-atom recombination on an H_2 surface.

The excitation and spectra of N_2–N can be understood in terms of the metastable excited state of atomic N and molecular N_2 and the delocalized excitations in solid N_2, including phonons. The ground state of N is the ^{4}S state: optical transitions occur in the green (^{2}D → ^{4}S), UV (^{2}P → ^{4}S), and IR (^{2}P → ^{2}D). The ground electronic state of molecular N_2 is $^1\Sigma_g^+$ and for our dis-

cussion the most important excited electronic state is the $^3\Sigma_u^+$ ($\bar\nu \approx 5 \times 10^4$ cm^{-1}) which is delocalized as an exciton in the solid. Other important excitations in N_2–N are delocalized vibrational excitations labeled by quantum number v and phonons. Herzfeld and Broida [10] identified the spectacular green emission (the α-group) of N_2–N as the long lived decay ($\tau \approx 40$ s) of the ^{2}D metastable state of N to the ^{4}S ground state. In fact, various decay channels are observed for the ^{2}D state in the visible: (a) The α-group, consisting of the N(^{2}D → ^{4}S) transition along with phonon sidebands. (b) The α'-group corresponding to N(^{2}D → ^{4}S) plus creation of an $N_2(^1\Sigma_g^+,v=1)$ vibron also accompanied by phonon sidebands. This is shifted to a frequency lower than that of α by 2330 cm^{-1}:

$$N(^2D) + N_2(^1\Sigma_g^+, v)$$

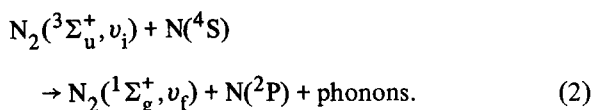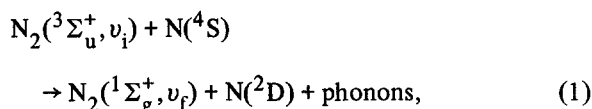$$\rightarrow N(^4S) + N_2(^1\Sigma_g^+, v+1) \quad \text{with } v = 0. \qquad (\alpha')$$
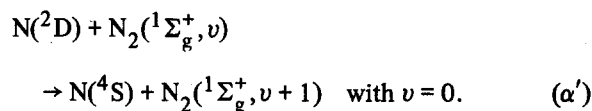
(c) The α''' group, similar to α', but with $v \neq 0$ (and much weaker than α', which involves the ground state of N_2). (d) The α'' group involving annihilation of a vibron:

$$N(^2D) + N_2(^1\Sigma_g^+, v)$$

$$\rightarrow N(^4S) + N_2(^1\Sigma_g^+, v-1). \qquad (\alpha'')$$
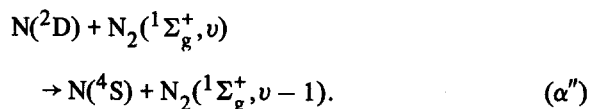
Clearly one of the most fundamental and intriguing aspects of N_2–N is the presence of both long lived excited atoms and vibrationally excited molecules and the origin of their excitation. It was shown by Peyron et al.

[3], that any satisfactory model should incorporate the in situ excitation of ground state atoms $N(^4S \to {}^2D)$. Dressler [5] has proposed a model that also accounts for the vibrationally excited molecules based upon the presence of $N_2(^3\Sigma_u^+)$ excitons resulting from the bombardment of solid N_2 by electrons [3,7,9], γ irradiation [3] or condensation from a nitrogen discharge [2]. In pure solid N_2 the $^3\Sigma_u^+$-excitons have a relatively long lifetime ($\sim$ 1 ms) and may decay radiatively giving rise to the Vegard–Kaplan bands as observed by Coletti and Bonnot [9]. In N_2–N, however, the excitons are effectively quenched by the trapped N impurities and as a result the Vegard–Kaplan bands are absent. In Dressler's model [5,11] the quenching proceeds according to:

$$N_2(^3\Sigma_u^+, v_i) + N(^4S)$$

$$\to N_2(^1\Sigma_g^+, v_f) + N(^2D) + \text{phonons},\qquad(1)$$

$$N_2(^3\Sigma_u^+, v_i) + N(^4S)$$

$$\to N_2(^1\Sigma_g^+, v_f) + N(^2P) + \text{phonons}.\qquad(2)$$

Process 2 gives rise to atoms excited into the ^2P state. Decay of this state is also observed (the δ- and μ-radiation) [7] but will be disregarded here since our study is limited to the visible part of the spectrum. In our experimental setup we use an N_2 + N beam to produce and to excite a layer of N_2–N on top of a substrate cooled to 1.8 K which sits in a UHV chamber. The beam is created by microwave discharge [12] and has an intensity of $\sim 10^{15}$ part/cm^{2}s at the substrate. The N content of the beam can be varied from a few to 80% and can be analysed during deposition with a quadrupole mass spectrometer. The intensity can be varied, without affecting the degree of dissociation, by means of a chopper or insertion of fine mesh screens in the beam path. The cold substrate is a 5 × 5 mm slab of doped silicon which also serves as a bolometer and as a thermometer. The bolometer enables a micro-calorimetric characterisation [13] of the condensation process. Several nozzles can be brought in line of sight of the substrate enabling rapid coating procedures while the discharge conditions remain unaltered. The luminescence is analysed using a low resolution spectrometer external to the UHV chamber. Optical components restricted observations to the visible (14 000–28 000 cm^{-1}). Photon counting was used; a typical thick film
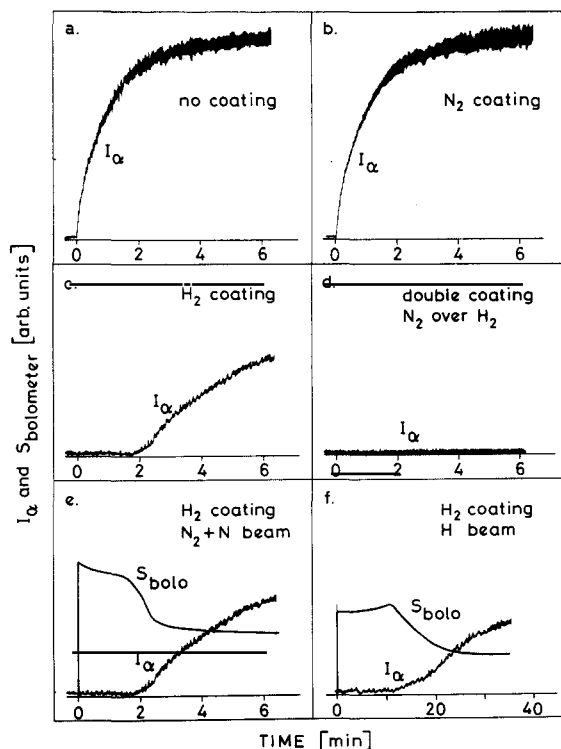

Fig. 1. The time dependence of optical and bolometric signals for N_2–N films with indicated coating. For (a)–(e), a constant flux N_2 + N beam (few percent N) is turned on at $t = 0$, for (f), a 99% pure H-beam is turned on at $t = 0$.

count rate was 10^5 Hz for the α-line. This apparatus enabled the creation of beams and films of varying thickness and composition in a controlled manner.

Films of N_2–N were most successfully created by using a beam of N_2 + N with a low degree of dissociation (few percent N). As the film was slowly built up, the intensity in the α-band grew. If the beam was blocked, the intensity would fall off with a time constant of $\tau \approx 35$–40 s due to the lifetime of the $N(^2D)$ state. Resuming with coverage, the light intensity would recover its interrupted value with about the same time constant (fig. 1a). It is believed that excitation takes place by the following process: N-atoms from the beam recombine at the film surface into an excited molecular state. A fraction of these molecules relaxes toward the lowest vibrational levels of the $^3\Sigma_u^+$-state. The $N_2(^3\Sigma_u^+)$ excitation propagates into the solid as an exciton and is trapped at an $N(^4S)$ impurity site before it can decay radiatively [9]. Here it is quenched by exciting the N

atom and creating a molecular vibron according to process 1 or 2. It is also possible that $N_2(^3\Sigma_u^+)$ excitons are introduced at the surface by adsorption of excited N_2 molecules from the beam.

This exciton model resulted from a careful analysis of the emission spectrum of bulk N_2–N [5]. We have used an independent approach to provide a test on the consistency of this model. A thick N_2–N film was covered with a few monolayers of H_2 or Ar. Neither H_2 [14] or Ar [15] have energy bands which overlap with the $^3\Sigma_u^+$ band of solid N_2 [9]. When the N_2 + N beam is again turned on, no light is observed (see fig. 1c) from the composite film: the excitons cannot propagate through the barrier. For the H_2 coated N_2–N film, the light resumes after a time delay of the order of minutes, depending on the thickness of the H_2 film. We shall interpret this delay shortly. Next an N_2–N film is created and coated by 10–20 monolayers of pure $^{14}N_2$ or $^{15}N_2$. When the N_2 + N beam is turned on, the intensity of the α-line grows with the characteristic time constant of 35–40 s providing strong evidence for the exciton model (see fig. 1b). We interpret the observed decay in emission from the H_2-coated N_2–N film as a desorption effect. In the recombination process (N + N → N_2), energy is released, which can desorb H_2 from the surface. After the H_2 is cleaned off the surface, the emission process resumes as for an N_2–N film. This is further elucidated by coating the H_2-coated N_2–N film with a few monolayers of pure N_2. In this case the emission remains quenched when the N_2 + N beam is turned on, slowly building up as in the establishment of a virgin N_2–N film (see fig. 1d). Apparently the desorption of H_2 is blocked by the N_2 layer and the H_2 layer remains locked in place.

Recombination induced desorption of H_2 has been observed before in experiments with H-beams on H_2 covered substrates [13,16–18]. The interpretation of measurements of the total power dissipated into the substrate bolometer by the atomic beam which depends somewhat sensitively on the composition of the last layer is consistent with a model of induced desorption. We have combined the optical and bolometer technique to provide evidence desorption is indeed taking place. In figs. 1e and f we show both the α-line intensity and the microcalorimetric response for the H_2 covered N_2–N film excited by the N_2 + N beam and the result of excitation by a 99% pure atomic hydrogen beam. The changes in the bolometer signal are caused by

changes in surface composition during the desorption of H_2. When desorption is completed the bolometer signal approaches the value for the uncoated N_2–N film. From the figure we note that simultaneous with the changes in bolometer signal the α-emission becomes visible indicating cleaning off of the H_2 layer. The process by which H excites the N_2–N film has not been identified. We speculate that the emission results from the stimulated recombination of trapped N-atoms in the surface layers of the N_2–N film, although more complex processes might be involved. However, this has not yet been studied in detail.

Insight into the nature of the $(^1\Sigma_g^+, v)$-vibron of solid N_2 has been obtained by studying the relative intensities of the α and α'' lines (I_α and $I_{\alpha''}$). Recalling the common origin of both the ^{2}D-atoms and the vibrons within the exciton model (see relation (1)) and the fact that only α''-emission involves vibron annihilation, one realises that any relation between I_α and $I_{\alpha''}$ must depend critically on both the relaxation and delocalisation times of the vibrons. First consider a vibron relaxation time short compared to the delocalization time. Under these conditions α'' emission results from the deexcitation of a ^{2}D atom and a vibrational excitation on a neighboring site, both excitations originating from the same quenching process. Here we are effectively dealing with localized excitations and a fixed fraction of the ^{2}D → ^{4}S transitions proceeds through the α''-channel: one concludes that $I_{\alpha''}/I_\alpha$ must be a constant, independent of the excitation rate. Now consider the case of relatively long lifetimes for the vibrons. Under these conditions the molecular vibrations delocalize into vibron bands and the vibron probability density on a site neighboring the localized $N(^2D)$ exci-
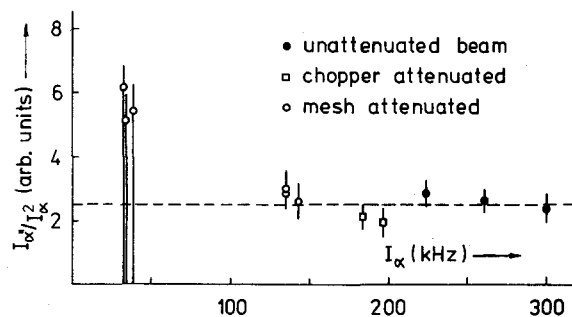

Fig. 2. Intensity of the α'' line relative to the square of the intensity of the α line versus I_α.

tations is proportional to the number of vibrons in the lattice. Since the number of vibrons is proportional to the number of excited atoms, again a consequence of the exciton model, $I_{\alpha''}$ is expected to depend quadratically on the number of excited atoms whereas I_α should depend linearly, thus we expect $I_{\alpha''}/I_\alpha^2$ to be a constant. In fig. 2 we plot this ratio against I_α. In the measurements I_α was varied over one order of magnitude by attenuation of the beam. The data clearly favor the non-local picture. The experiment was limited to this dynamic range by the minimum detectable signal for the α'' peak and the maximum obtainable beam intensity. We note that the intensity ratios can be significantly affected if vibrons are created without excitation of atoms. As an example, recombination of atoms directly into the singlet state or deposition of vibrationally excited molecules can provide such a source of vibrons. This contribution to the vibron density will depend strongly on the discharge conditions. By performing our measurements in such a way that the beam intensity is varied without affecting the beam composition we believe that possible errors of this nature are minimised. No frequency dependence was observed for attenuation with the chopper blade over the frequency range 5–180 Hz. This means that complete vibrational relaxation requires times much longer than 0.2 s, consistent with measurements by Dressler et al. [6].

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