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Use of Solid N₂ Surfaces in Metastable Particle Detection.

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Abstract:

A novel detector is described in which solid nitrogen at 17 K is used as the most significant element. Metastable particles impinge on this element and immediately transfer their internal energy to the solid nitrogen producing photons, via excimer formation or otherwise, whose wavelength depends on the metastable being detected and the energy transfer process. The performance of the instrument for detection of atomic oxygen and molecular nitrogen metastables is discussed.

Introduction:

Metastable atoms and molecules are important species in a wide variety of applications ranging from low temperature electrical discharges to planetary atmospheres and astrophysical sources. Their metastability can result from being in a state which is forbidden to radiate to a lower level by optical selection rules involving angular momentum, spin or parity. Because of the varying degree of rigor of these selection rules, lifetimes of metastable states can range from tens or hundreds of microseconds to seconds to hours or even longer. Detection of these metastable species has been achieved in an equally wide range of techniques ranging from direct detection following release of electrons from low work function surfaces [1] to use of multiphoton ionization using high intensity lasers or synchrotrons [2]. In our laboratory we have pioneered [3] the use of solid rare gas matrices at low temperatures to allow detection of metastable atomic species with an np^4 electron configuration, such as O (¹S) or (¹D), both prominent species in Earth's upper atmosphere. The surfaces were shown to be sensitive also to other metastable species such as S (¹S) [4] and CO (*a* ³Π) [5]. In this technique the metastable particle impinges on the solid surface and forms an excimer which immediately radiates. The wavelength of the resultant photon (visible or near infrared) is readily detectable. The effect of the excimer formation results in a lifetime reduction of the metastable species sometimes as much as a factor of 10⁷. Thus the O (¹S) state with a lifetime of ~1s radiates via the Xe surface in ~100ns [3]. In the

present work we investigate the behavior of a solid N_2 surface as a metastable detector, compare its performance to that of the rare gas matrices and use it to investigate the excitation of metastable species in N_2 .

Experimental Details:

The apparatus used in this work has been described fully in earlier communications (see references 3-5 and references in these) and so only a brief summary will be given together with any details which are particularly relevant to the present work. For convenience the set-up is shown schematically in Figure 1.

Figure 1. Block diagram of the metastable particle detector system. A, amplifier; D, discriminator; P, pulser; F, filter; TP, turbopump; EG, electron gun; FC, Faraday cup; FG, feed gas; BG, Baratron gauge; NV, needle valve; CG, convectron gauge; CF, cold finger; He, helium cryostat; RG, rare gas or N_2 ; De, deflector plates; MCS, SR430 multichannel scaler; PMT, photomultiplier tube ([Hamamatsu R943](#), spectral range 190 – 930 nm).

The target gas beam intersects the pulsed electron beam at right angles. Photons produced in coincidence with the electron pulses are reflected off the solid detector surface into the photomultiplier. From there the signal is routed to a SR430 multichannel scaler. A short time later the slower metastables reach the cold finger, interact with the surface and release photons which are detected in turn by the photomultiplier. The type of interaction which occurs, excimer formation or an

energy transfer process for example, is discussed in more detail later. Repeated electron pulses lead to the build-up of a time-of-flight (TOF) spectrum. An example of this is shown in Figure 2. Suitable gating allows the prompt photon and metastable signals to be processed separately when required. Dissociative excitation of metastable particles normally is accompanied by the release of significant amounts of kinetic energy and so, in this case, the gas beam is directed orthogonal to the detector direction. Where metastables are produced with just thermal energies, the gas beam direction is changed to point towards the detector. Otherwise the initial thermal motion would prevent the metastables from reaching the detector. In the present work where N_2 metastables are produced and detected, the straight-on configuration is used. Currently a plexiglass lightpipe is used to guide photons from the cold finger to the photomultiplier. In earlier work [5] quartz optics were used to allow access to wavelengths shorter than 350 nm. Filters can be interposed in the photon flight path to limit the wavelength range detected. We note that the metastables pass through a pair of quenching plates separated by 1 cm en route to the cold surface. These are unchanged from earlier work [3-5] as is the flight path and geometry. The quenching plates are positioned so as not to cause any reduction in metastable flux at the cold surface and enable checks to be made for the possible presence of Rydberg species. Charged particles such as ions or scattered electrons are prevented from leaving the gun region and reaching the detector by the 200 gauss magnetic field which is used to confine and direct the electron beam. Prior to operation, a surface layer must be deposited on the surface of the cold finger. During operation this must be refreshed continually by leaking the appropriate gas into the detector chamber. The cold finger was normally maintained at a temperature of 17K, the lowest temperature attainable using our He compressor. Calibration of the electron beam energy was achieved by examining the threshold for prompt photon production. For example a 430 nm filter, 10 nm bandpass, was used to isolate the (0,1) vibrational N_2^+ (B-X) First Negative emission at 427.8 nm with a threshold of 18.8 eV. The uncertainty in the energy scales was estimated to be ± 1 eV. Initial experiments were carried out as discussed later to ensure that target gas pressures were in a range where collisional transfer or destruction effects were not occurring. Base pressure in the system was 10^{-7} torr but this rose to 10^{-5} torr when the target gas beam was operational.

System Performance:

(a) Detection of $O(^1S)$ atoms:

The relative sensitivity for detection of O(¹S) by the various rare gases has been given in Reference 3. The N₂ surface was found to have a sensitivity very similar to that of Xe though a number of important differences should be noted. First, the excimer emission occurred in the green near 560 nm rather than in the near IR at 725 nm [3]. This is consistent with the results of Schoen and Broida [7] who examined the fluorescence from solid nitrogen with a small oxygen impurity upon bombardment with high energy (keV) electrons. Second, the photon emission from the cold surface was found to be delayed with respect to the Xe case. This is similar to what was observed [3] when rare gases other than Xe were used on the cold finger. Delays in excimer emission of 0.2, 23.4 and 4.2 μs were observed for Ne, Ar and Kr respectively. The present situation is illustrated in Figure 2 which shows TOF spectra of O(¹S) from CO₂ targets using 100 eV electron impact with Xe and N₂ cold surfaces as detectors. A clear shift to longer flight times is seen in the N₂ case. The situation may be modelled readily by introducing an exponential factor, exp[-t/τ], where τ represents the difference in excimer lifetimes between Xe and N₂. (This was found to be 14±2 μs in this instance as discussed below). The modeling is based on the following equation:

$$f(t) = \int_0^t f_{Xe}(t') \cdot \exp(-(t-t')/\tau) \cdot dt' \quad (1)$$

Where f(t) defines the time evolution of the detected signal when a matrix other than Xe is used, and $f_{Xe}(t')$ is the time evolution of the detected signal from the XeO* excimer. The XeO* excimer lifetime is known to be approximately 0.2 μs [6] and thus is negligible on the timescale of Figure 2. For purposes of illustration we show on Figure 2 how the excimer emission from the surface develops when different effective lifetimes are assumed. Thus, when a lifetime of 7 μs is assumed, the emission from the surface is delayed and some of the structure below 100 μs is smoothed out. As successively longer lifetimes are assumed the emission is observed to occur at larger and larger delays and eventually the structure on the curve disappears. Mathematically, a non-linear parameter estimation procedure similar to that used by Wraith and Or [8] was employed to obtain the lifetime of 14±2 μs which gave the best fit to the N₂ curve. This was done following subtraction of a constant background from the data sets.

Figure 2. O (1S) from CO₂ targets produced using 100 eV electron impact. The TOF data are taken under identical conditions but using Xe or N₂ surfaces on the cold finger. Red and green filters were used with Xe and N₂ surfaces respectively. The prompt photon peaks at short times have been truncated to highlight the metastable signals. Note the delay in the (N₂)O* surface fluorescence. This can be modelled (see text) assuming a delay in excimer emission in N₂ of 14 ± 2 μs . Sample theoretical curves made using delays of 7, 11 and 19 μs are shown for comparison. See text for further details.

We note that the structure observed originally by LeClair and McConkey [5] is largely absent from the data of Figure 2. For reasons of low signal strength when detecting metastable molecules, the electron pulse width used in the present work (25 μs) is an order of magnitude longer than was used earlier. Hence most of the detail in the metastable peak (Figure 2) has been smoothed out.

The sensitivity of the solid N₂ surface was found to increase rapidly as the temperature of the cold finger was reduced below 35K. This is illustrated in Figure 3. Above this temperature the N₂ vapor pressure is probably too high to allow efficient transport of the metastable particles to the cold surface.

Figure 3. Variation of O(1S) detection sensitivity as a function of the temperature of the N₂ surface. 100 eV electron impact on CO₂ targets provided the source of O(1S). Metastable TOFs from 50 to 200 μ s were included in the measured signals. A green filter (500-600 nm) was used in the optical channel. The data have been normalized to take account of any differences in data acquisition time (20-60 minutes) or electron beam current. A constant background was subtracted from the data prior to normalization. The error bars represent statistical errors only. Details of rare gas surface sensitivities as a function of temperature have been given elsewhere [3].

(b) Detection of N₂ metastables.

The response of the N₂ surface to metastable nitrogen particles was very different to what was observed using rare gas matrices for atomic metastable detection. Signals were at least an order of magnitude weaker and flight times for the metastables being detected were much longer than when using rare gas matrices. In fact they were entirely consistent with the detection of metastable nitrogen molecules rather than atoms. This is illustrated in Figure 4 which shows TOF data taken under different experimental conditions – source gas pressures and detected wavelengths. The solid curve through the “green” data, Figure 4B, is a calculated curve assuming N₂ metastable species and an N₂ target beam temperature of 292 K. The fact that such good agreement exists between the observed and calculated curves suggests that any momentum transfer effects between the colliding electron and the molecule were negligible. This is expected given the fact that the gas target beam is not well collimated. It also indicates that the energy transfer at, and

subsequent emission from, the surface both take place on a time scale that is short compared to the time scale on Figure 4.

To check whether Rydberg atoms or molecules were contributing to the signal we applied a 5 kV/cm field between the quenching plates (see Figure 1). This is sufficient to quench the high lying Rydbergs (see Tarr et al [9]). No indication of Rydbergs was observed. Rydberg atom production in e-N₂ collisions has been extensively studied by e.g. Schiavone et al [10]. Electric field quenching of high-Rydberg states has been studied by Schiavone et al [11].

Figure 4. Metastable N₂ TOF curves taken under different conditions. (A) shows the effect of using different source driving pressures, 7 and 14 Torr respectively, and the same green filter. The higher pressure curve is shifted slightly to shorter flight times. (B) shows the distinctly different data sets obtained using green (500-600 nm) and red (600-900 nm) filters. The solid curve through the “green” data is a calculated curve assuming thermal N₂ metastables and a gas beam temperature of 292 K. The solid curve through the “red” data is what the 292 K data would look like if the N₂ metastable lifetime was 75 μs. In all cases the energy of the pulsed e-beam was 100 eV and the pulse repetition rate was 700 Hz. See text for further details.

Note the distinct differences in the data obtained with broadband red and green filters and at low and high source pressures. These illustrate the loss of metastables en route to the detector due [most probably](#) either to in-flight decay (B) or collisional loss (A). The data sets were obtained at an e-beam energy of 100 eV. If the effective lifetime of the “red” [metastable](#) component [is significantly less than the travel time to the detector surface](#) then many will be lost en route to the

detector and because the slower metastables will be lost preferentially, the peak in the observed metastable signal will move to lower TOFs. Using an analysis similar to that discussed earlier one can calculate what the metastable TOF curve will look like assuming different effective lifetimes for the metastables. An example of this is shown in Figure 4B where a lifetime of 75 μs is assumed. We note the good agreement with the observed data. The $a\ ^1\Pi_g$ state of N_2 has a reported lifetime in this region (see [12] for fuller details) so it might well be the metastable responsible for the red emission from the detector surface. The shortness of the lifetime explains the low observed signal strength since a number of lifetimes have elapsed before the surviving metastable molecules reach the detector surface. We note that there is a hint of some structure in the “red” curve in the tail of the prompt photon signal at a TOF near 100 μs that might suggest the presence of an atomic metastable feature. However additional data runs failed to confirm this structure.

Our measured lifetime must be considered as somewhat uncertain as there is the possibility of some loss via collisions en route to the detector. The possibility of some delay in emission at the detector surface should also be noted as well as the possibility of in-flight population from other long-lived states via cascade. States such as $a'\ ^1\Sigma_u^-$, $w\ ^1\Delta_u$ or $E\ ^3\Sigma_g^+$ have significantly long lifetimes [12] but possess excitation functions much more sharply peaked (see Refs 13, 14 and 15) than obtained in the present work. This rapid fall off in excitation probability for states like $w\ ^1\Delta_u$ which could give in-flight cascade population to $a\ ^1\Pi_g$ means that such an effect would be negligible in 100 eV data such as in Figure 4. Delay in emission of photons from the matrix surface, such as was observed when detecting O (1S_0) using the N_2 matrix, would also result in an effective lengthening of the observed TOF.

We note that if any of the long-lived states, such as $a'\ ^1\Sigma_u^-$ or $w\ ^1\Delta_u$, reached the solid N_2 surface they could in principle rapidly populate the $a\ ^1\Pi_g$ state via a collision induced energy transfer (CIET) process on the surface. Such a process is known to occur in gas phase collisions [16]. However if this was occurring in our case we would expect the resultant radiation to appear as a perturbation or broadening on the longer time region of the “red” curve, Figure 4B, coincident in time with the peak of the “green” curve in the figure. (As mentioned earlier the “green” curve is representative of thermal molecules arriving at the detector surface from the target region). Clearly, from Figure 4B, such a CIET process is not significant.

Additional insight into what processes are contributing is obtained from a study of the excitation probability curves. Figures 5 and 6 show data obtained without any filters and give the overall excitation curves as a function of energy for prompt photons and metastables respectively. The prompt photon emission was predominantly red with a small green component. This is entirely consistent with the work of Mangina et al [17] who have studied in detail the emissions from N_2 following electron impact in the spectral region 330-1100nm. The sharp initial rise to a peak is due to radiation from the First Positive ($B^3\Pi_g - A^3\Sigma_u$) system which is very extensive over the wavelength range 570-900nm. The broad peak extending to higher energies is due mainly to the First Negative ($B^2\Sigma_u^+ - X^2\Sigma_g^+$) and Meinel ($A^2\Pi_u - X^2\Sigma_g^+$) systems of N_2^+ together with some contributions from excited N and N^+ resulting from dissociation of N_2 in the initial collision. The inset shows the threshold region in more detail. The low-energy peak shown in Figure 5, and particularly in the inset, is quite broad because it is the summation of many different First Positive bands all with peaks at slightly different energies. Cascade contributions from the Second Positive ($C^3\Pi_u - B^3\Pi_g$) bands also serve to broaden this structure. Because of the wide range of wavelengths included, the overall shape of the excitation curve does not allow any conclusions to be drawn regarding any possible secondary electron component in the electron beam. This possibility was suggested using data [18] taken with a red filter in the detection channel.

Figure 5. Prompt photon excitation as a function of exciting electron energy for the impact energy range 0 – 300 eV. The inset shows additional data taken in the near

threshold region. No filters are included in the detection channel. See text for further details. A TOF window covering the 0-25 μs region was used for data collection.

Figure 6, which shows the variation of metastable excitation probability with exciting electron energy, is very informative also. These data were taken simultaneously with the prompt photon data of Figure 5 and so the energy scales are identical. Large background signals have been subtracted from the data of Figures 5 and 6. This was due to stray light from the filament of the electron gun and did not vary with electron energy. Most of the light resulting from metastable interaction with the detector surface was in the green spectral region with a smaller red component. Comparing the threshold regions of Figures 5 and 6 we see that the metastable signal threshold is delayed with respect to that of the prompt photons. This is seen with higher resolution in the inserts of Figures 5 and 6. Here an initial small rise in the metastable signal is seen to occur very close to the prompt photon threshold followed by a major rise some 3-4 eV later. The initial rise is due to the small red component in the signal and the major threshold is due to the green emission which predominates.

Figure 6. Metastable signal as a function of impact electron energy. The data were taken simultaneously with the prompt photon data of Figure 5. A large constant background signal has been subtracted from the data as discussed in the text. The inset shows additional data taken in the near-threshold region. No filters were used in the detection channel. TOF signals in the 200-800 μs region were included in the data presented.

We note that this excitation probability curve is quite different to that observed by for example Borst and Zipf [19] using a more conventional Auger emission detector. They observed the A ($^3\Sigma_u^+$), E ($^3\Sigma_g^+$) and a ($^1\Pi_g$) states with a combined excitation function which peaked close to 15 eV and fell off rapidly towards higher energies. Our solid N₂ based detector appears to be insensitive to the triplet metastable states.

A full discussion of data taken with different filters in the detection channel leading to identification of the two observed metastable states as a $^1\Pi_g$ and $^1\Gamma_g^+$ has been given separately [18]. The latter state had not been observed previously though it had been predicted by Michels [20, 21]. The most likely sequences which occur when the metastable molecules are excited and reach the solid N₂ surface are the following energy transfer and emission processes:

We note that these energy transfer processes are quite different to the excimer formation processes which characterize the detection of atomic metastables.

Figure 7. Simplified energy level diagram for the N_2/N_2^+ system. Note that only the lowest ro-vibrational levels are shown in each case.

Figure 7 shows a simplified energy level diagram for the N_2/N_2^+ system indicating the relative positions of the states mentioned in this study particularly those indicated in Equations 2 and 3. We note that a potential energy diagram with more detail in the 10-14 eV region at large inter-nuclear distances is given in [18].

Conclusions.

A novel detector for metastable atoms and molecules is described. Its operation depends on the interaction of the metastable particle with a solid nitrogen surface at a temperature of 17K with the subsequent emission of a photon of characteristic wavelength. The performance of the instrument in detecting $O(^1S)$ atoms and metastable N_2 molecules is discussed. In any particular experimental set-up the sensitivity of the detector will be greatest for metastables whose lifetimes are longer than the flight times to the detector surface. For others, like $a\ ^1\Pi_g$ in this case, where the lifetime is much shorter, the sensitivity is significantly reduced. The highly selective nature of the detector for both metastable atoms and molecules allows considerable simplification of one's understanding of the processes involved.

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