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The N_4 project.
Activity report for the first half of the year 2001.

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Progress report

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Introduction

During the first half of 2001, the main efforts within the N_4 project have been concentrated to electric discharge excitation, ion-bombarding and microwave excitation experiments on cryogenic nitrogen-containing matrices. Several synthesis attempts have been made using long integration times in order to suppress random noise. Attempts to excite liquid nitrogen with a 193 nm ArF laser have been performed. Initial temperature-controlled experiments have been performed on products from microwave discharge condensed on a sapphire window in a small cryostat.

Synthesis experiments in cryogenic matrices

After the initial experiments with ion gun (VG Microtech AG5000 ION/8) for the production of N_2^+, N^+ or positive rare gas ions for direct bombardment of cryogenic nitrogen-containing matrices, two additional means of matrix excitation have been tested. A microwave cavity of commercial design (SAIREM GMP 03 KE/D) and a laboratory-built small hollow cathode device. All three devices are mounted simultaneously to the same cryochamber and can be used in parallel. Figs. 1 and 2 show pictures of the cryostat with the microwave discharge running on pure neon.

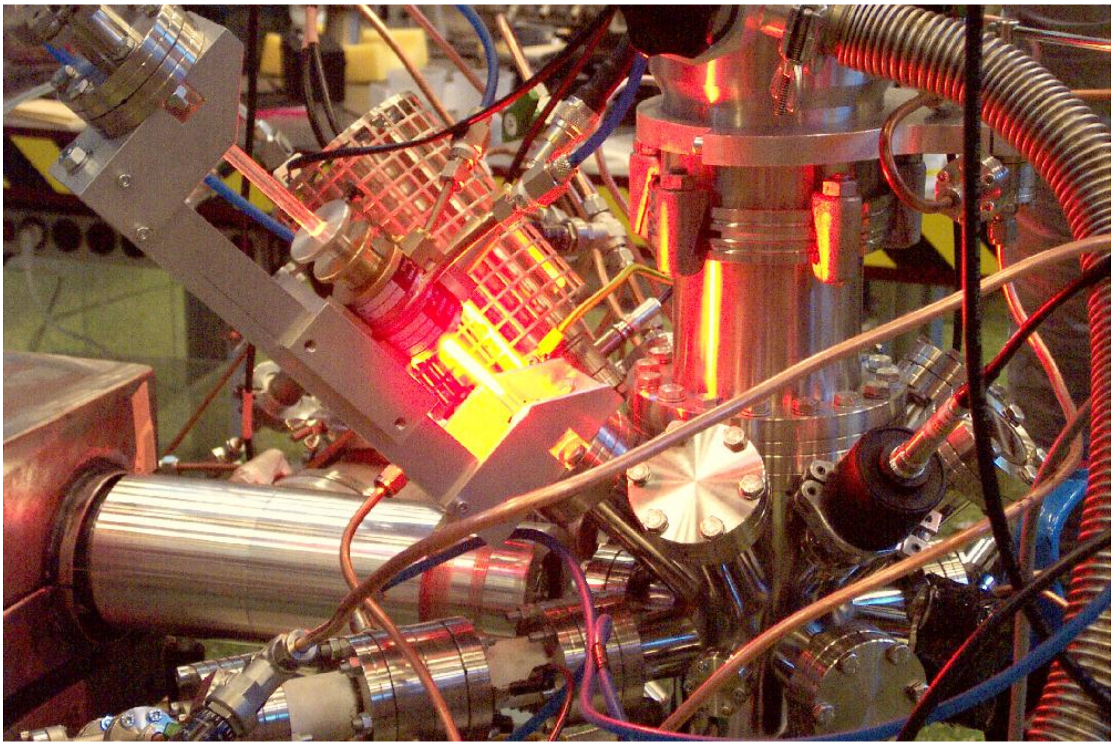

Fig. 1. Three matrix excitation devices, mounted on the same cryostat. The miniature hollow cathode is seen in the lower left. In the middle, the microwave cavity is seen running on pure neon. The protection shield of the ion gun is seen behind the discharge. The aluminum tube below the ion gun contains the lens system (cf. Fig. 3)

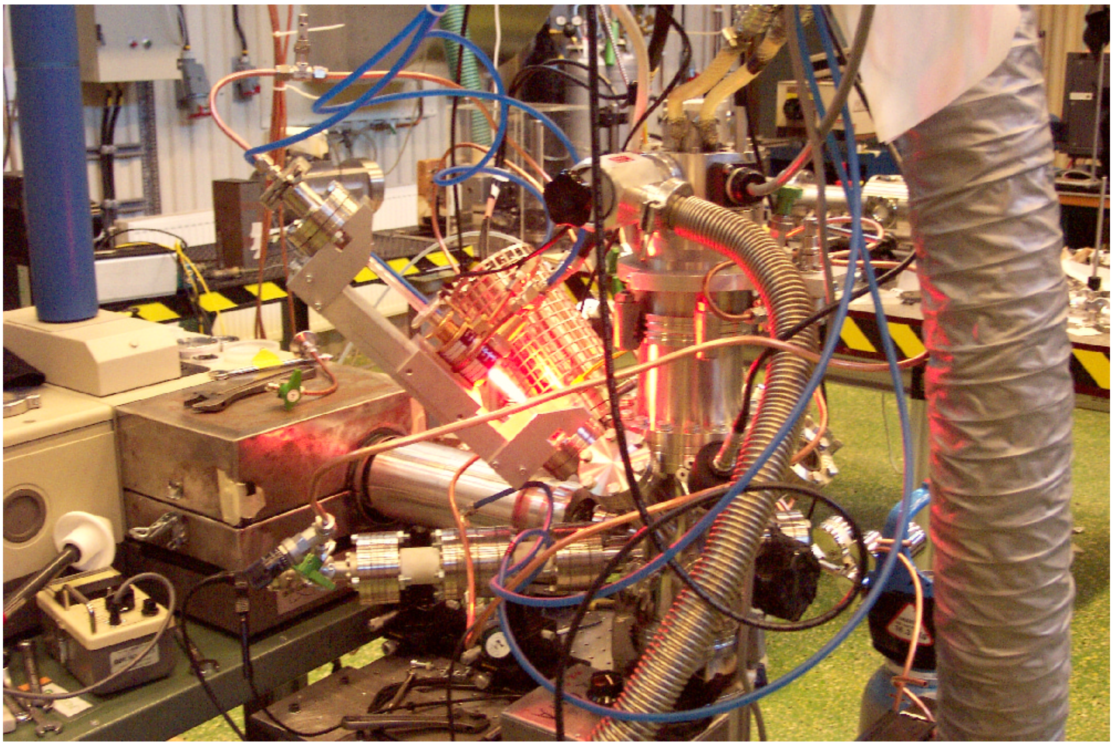

Fig. 2. Another view of the cryostat. The FT-Raman interferometer (Bruker IFS55/FRA106) is seen to the left.

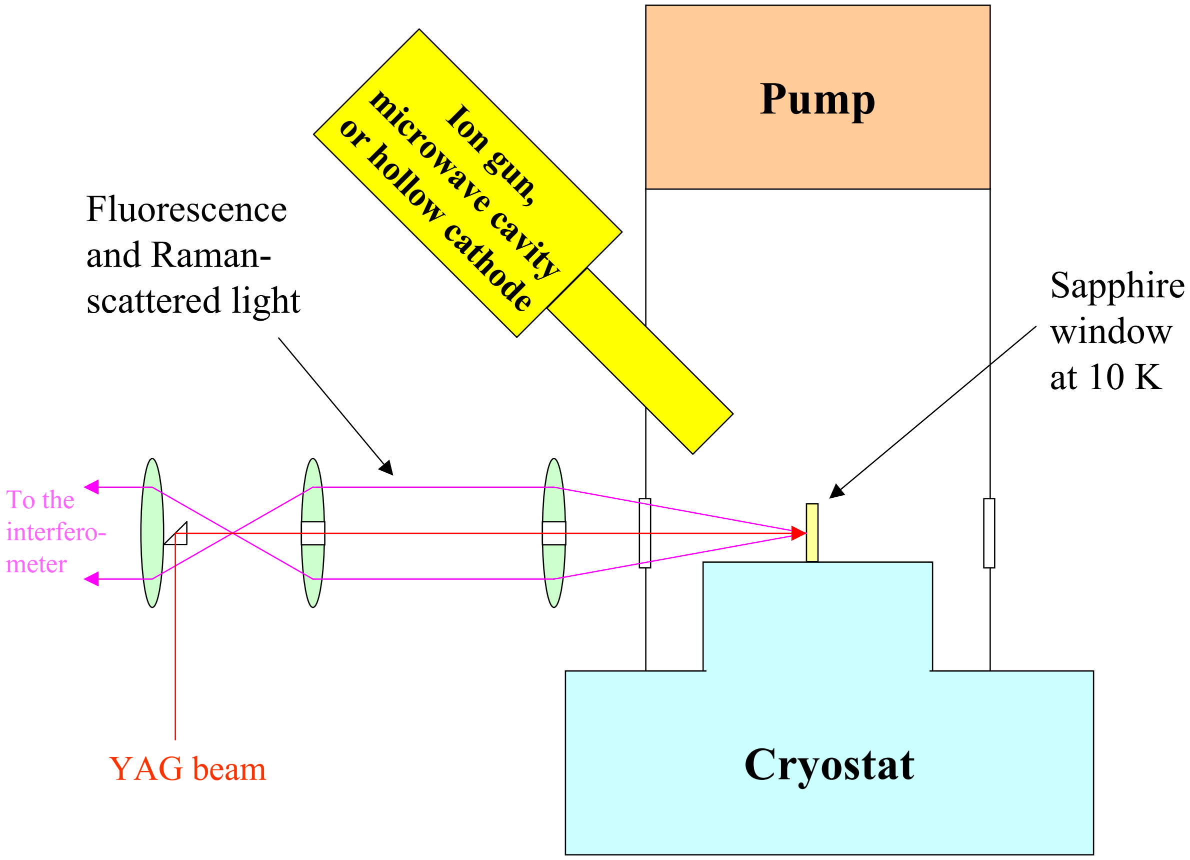

Fig. 3. Schematic arrangement of the matrix excitation experiments. A cryogenic matrix, consisting of pure nitrogen or a mixture of nitrogen with different nitrogen-containing species is first deposited on the sapphire window. During the deposition, the Raman signal is continuously monitored with a FT-Raman interferometer. When a desired matrix thickness has been reached, the matrix is bombarded with ions (N_2^+, N^+, Ar^+, Ne^+ or He^+) or corresponding products from a microwave or a hollow cathode discharge. The resulting matrix fluorescence is monitored with an IFS55/FRA106 FT-Raman interferometer and a Mechelle 900 UV-VIS-NIR spectrometer.

When the cryostat cold finger is cooled and when the discharge contains enough nitrogen, the deposited nitrogen glows in bright green (Fig. 4)

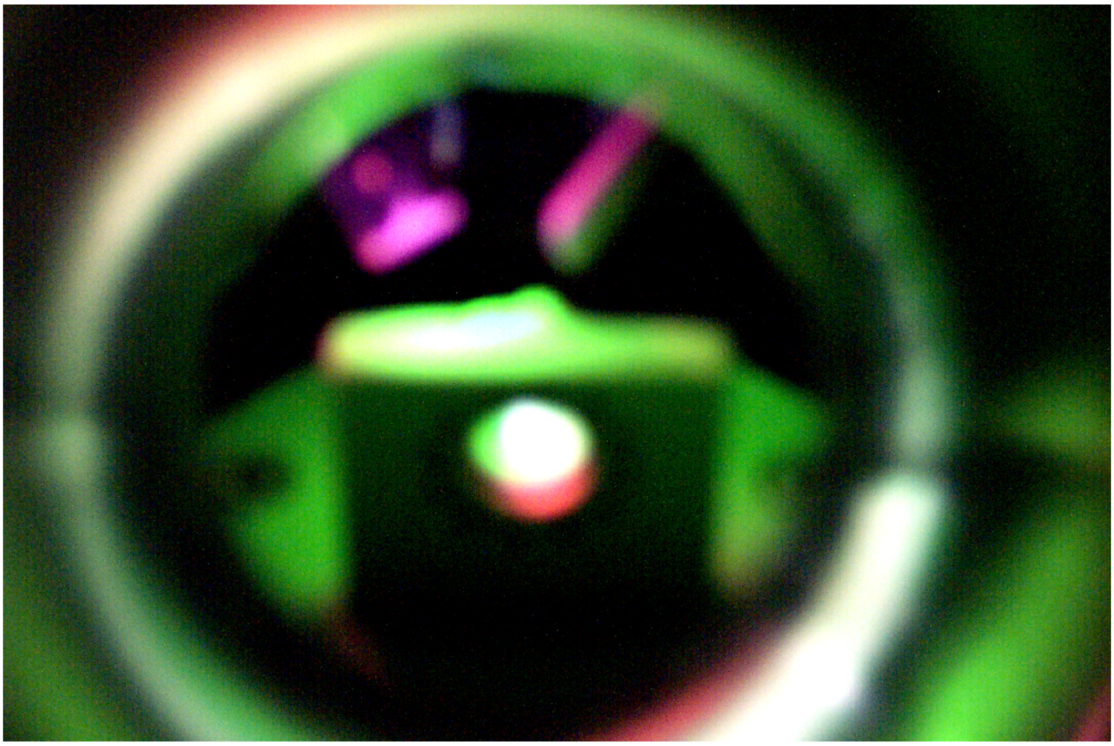

Fig. 4. The cryostat sapphire window, photographed under nitrogen deposition from microwave discharge. The sapphire window is located in the circular aperture of the rectangular copper block, mounted on the cryotip. The transparent, very thin nitrogen matrix is photographed from behind. The magenta-colored orifice of the microwave capillary is seen to the upper left. The green color arises from a ${}^2D$-${}^4S$ transition in nitrogen atoms in the deposited solid, while the magenta color of the capillary tube is due to the $C^3\Pi_u$-$B^3\Pi_g$ and $B^3\Pi_g$-$A^3\Sigma_u^+$ emissions in N_2.

Numerous synthesis experiments have been carried out on excited, nitrogen-containing matrices during the first half of 2001. All three excitation devices mounted on the cryostat have been used in these experiments. Four different types of recordings have been made:

1. *Recordings of a matrix during the excitation phase (relatively short recordings during several hours of matrix build-up).*
2. *Long-time recordings of the matrix after excitation (FT-Raman)*
3. *Short time series during rapid warm-up of the excited matrix.*
4. *Extended time series during gradual stepwise warm-up of the excited matrix.*

Different types of information can be collected in these experiments. During the excitation phase, mixed spectra of gas-phase and matrix processes are obtained with the FT-Raman instrument either in Raman mode (laser on) or in infrared emission mode (laser nearly off). Simultaneous spectra are recorded with the Mechelle 900 UV-VIS-NIR spectrometer. Together, these instruments cover the wavelength range of 200-1800 nm. The gas phase spectra most often consist of well-known molecular N_2 or N_2^+ bands, together with rare gas atomic emission spectra in the cases where mixtures of rare gases and N_2 have been used. In the case of microwave discharges, the $B^3\Pi_g$-$A^3\Sigma_u^+$ system of N_2 usually dominates, while the hollow cathode device also gives N_2^+, as well as higher-lying excited states of N_2. An example can be seen in Fig. 5.

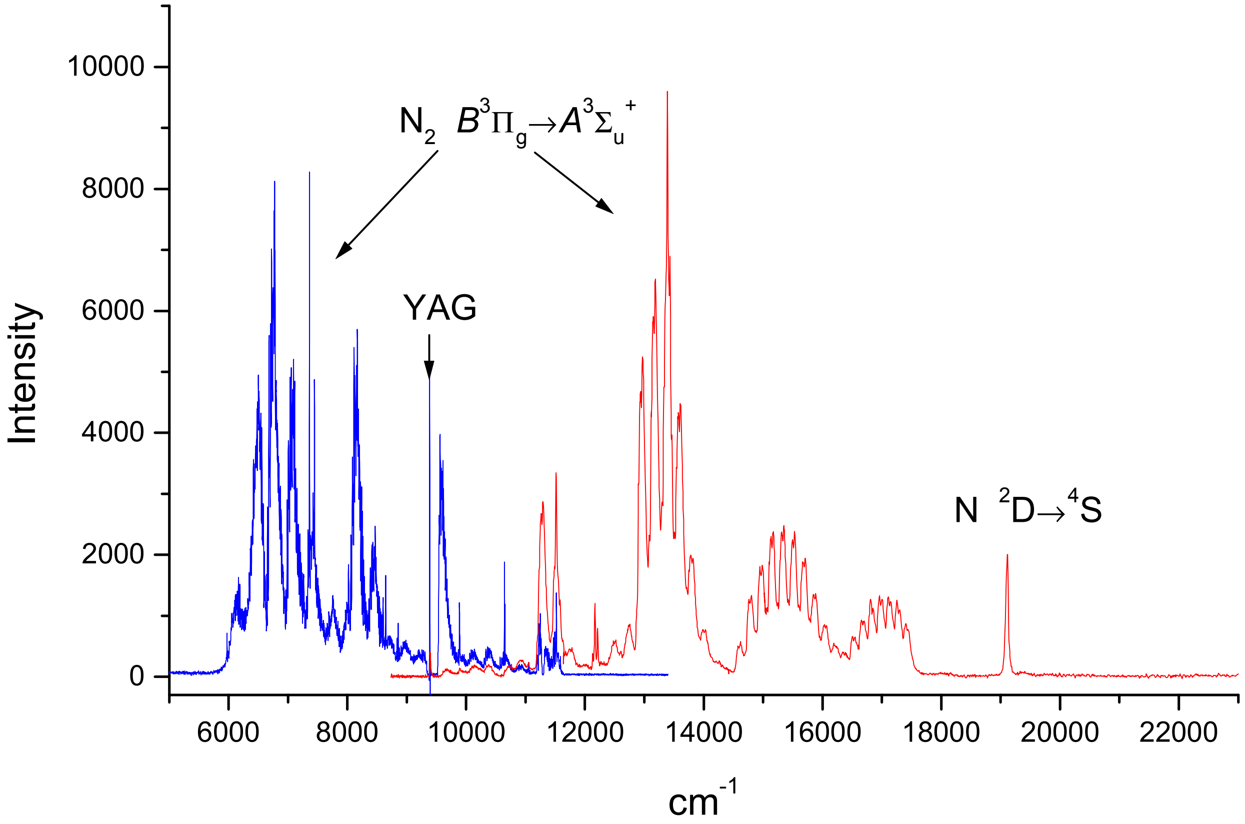

Fig. 5. A short (350 scans) simultaneous FT-Raman/Mechelle recording of a N_2 matrix during deposition from a microwave discharge (200 W). The molecular bands are due to the $B^3\Pi_g$-$A^3\Sigma_u^+$ system of N_2. The YAG power was 500 mW and resolution 4 cm^{-1}.

In the long-time recordings (exceeding 14 hours), mostly the FT-Raman instrument has been used. These recordings give highly puzzling spectra, where the most dominating features are still unassigned. One of the unassigned features is a characteristic triplet, consisting of two close-lying strong lines and a weaker one, shown in Fig. 6.

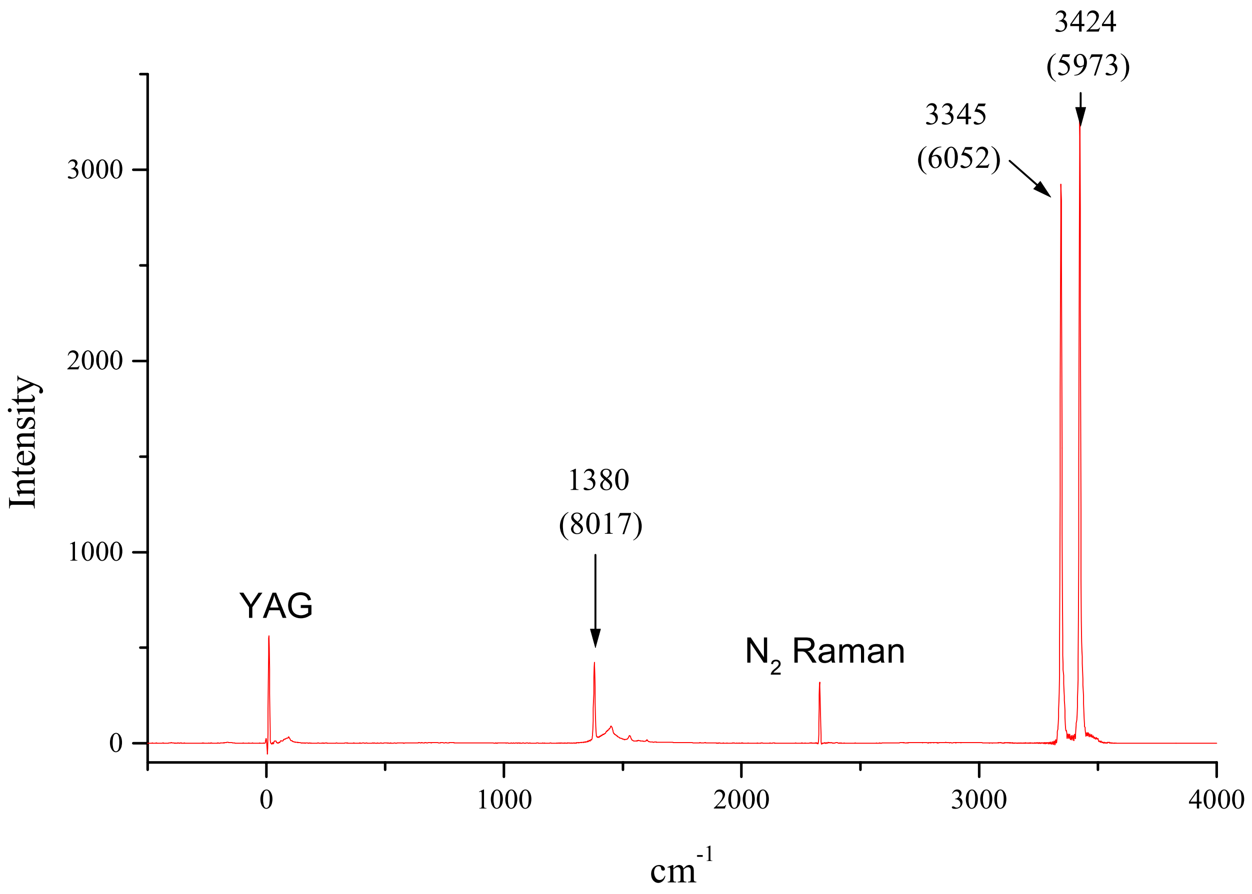

Fig. 6. A long-time FT-Raman recording (28000 scans in 14 hours) of a microwave discharge-excited N_2 matrix. The apparent wavenumbers of the triplet are shown, as given by the interferometer software, together with the true fluorescence wavenumbers in parenthesis. The YAG power was 500 mW and the resolution 4 cm^{-1}.

This triplet is laser-induced, and its intensity is linearly dependent on the YAG power (Fig. 7).

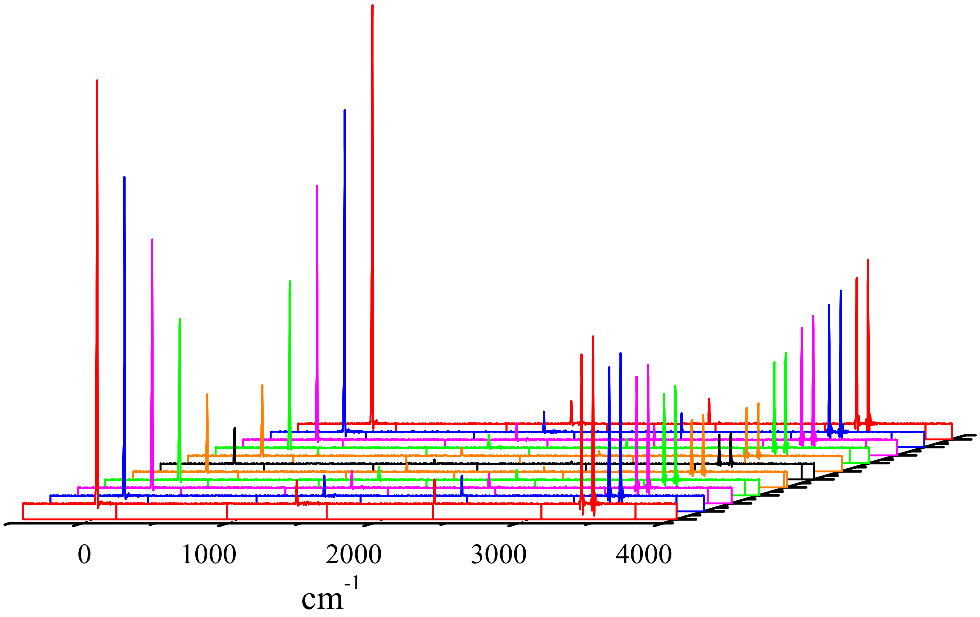

Fig. 7. The laser power dependence of the unassigned triplet. The YAG power was varied between 50 mW and 500 mW. As can be seen, the two strong lines of the triplet follow the laser intensity linearly. The sample is the same as in Fig. 6, but the imaging was inferior, the signal containing more scattered laser light from the lens system. Very slight saturation of the fluorescence signal occurs at the higher power levels.

This behavior suggests that the excitation is due to a one-photon process. However, in matrix environment this conclusion might be erroneous. Clearly, the triplet is not due to a Raman process, as has been shown in isotopic substitution experiments (Fig. 8).

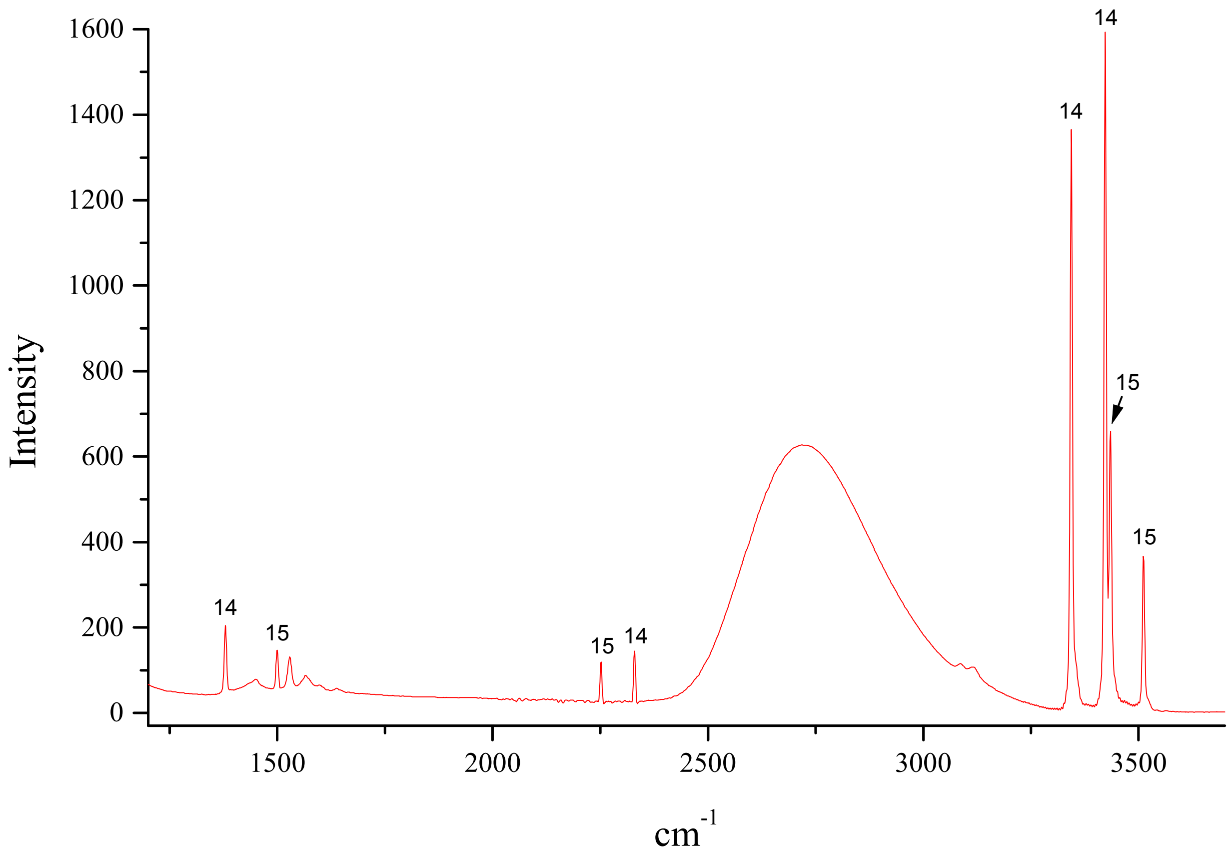

Fig. 8. Long-time FT-Raman recording (33000 scans in 16½ hours) of a $^{14}N_2$+$^{15}N_2$ matrix, excited by ion gun, running on pure $^{14}N_2$, pure $^{15}N_2$ and on a mixture of these. The two lines in the 2300 cm^{-1} region are the N_2 Raman lines for both isotopomers. No sign of $^{14}N^{15}N$ was seen. The fact that the triplet lines move to higher (apparent) wavenumbers, means that they cannot be Raman lines. The YAG power was 500 mW and the resolution 4 cm^{-1}.

The triplet has been investigated more closely in an isotopic replacement experiment. The ion gun was first run with pure $^{14}N_2$ in order to establish proper conditions for the triplet build-up. When these conditions were found, pure $^{15}N_2$ was introduced in the ion gun. We observed that the N_2 Raman line moved as it should (towards lower Raman wavenumbers), while the triplet lines moved to the opposite direction (Fig. 8).

This behavior is consistent with the assumed fluorescence origin of the triplet. In the following table, the true wavenumbers are used for these lines.

σ_{14}	σ_{15}	σ_{14}/σ_{15}	**Commentary**
2329.29	2251.59	1.0345	N_2 Raman
8016.95	7897.07	1.0152	LIF (weak)
6052.33	5961.25	1.0153	LIF (strong)
5973.26	5884.51	1.0151	LIF (strong)

What could be considered as intriguing, is that only two different triplet spectra are observed, despite the fact that the matrix contains $^{14}N_2$ and $^{15}N_2$ in approximately equal concentrations, as can be seen by looking at the intensities of the N_2 Raman lines. According to our opinion, this clearly excludes N_4 as a carrier (rectangular or tetrahedral), since such a molecule should occur in at least three different isotopic configurations in the matrix ($^{14}N_2$+$^{14}N_2$, $^{14}N_2$+$^{15}N_2$ and $^{15}N_2$+$^{15}N_2$), which should result in three distinct spectra. On the other hand, the carrier must contain nitrogen in a rather tightly bound position, because the isotopic shift is quite substantial. A comparison with diatomics shows that the CN radical has a similar isotopic shift (1.5 per cent). There is always a possibility for the occurrence of CN in ion gun spectra, since the gun contains a carbon disk in the discharge cell. The CN assignment, however, is not supported by data from carbon-free experiments (microwave- and hollow cathode-discharge), where the triplet is actually even stronger than in the ion gun experiments.

In this context, we should mention that the weak LIF line at 8016.95 cm^{-1} is always accompanied by a broad satellite on the low wavenumber side at 7946.53 cm^{-1}. It might be tempting to assume that this satellite is simply predissociated or otherwise broadened, and that we are actually having a quadruplet and not a triplet of LIF lines. However, a severe objection to this conclusion is that the intensity of this broad feature varies between different experiments, while the relative intensities of the remaining three lines remain unaffected, corrections having been made for the different sensitivity of the Ge detector in different temperatures (see below).

In Ref. [7], an absorption spectrum of water in a N_2 matrix has been published. In Fig. 1 of this paper, a spectrum is shown, where two weak absorption lines are located at 5964 and 6056 cm^{-1}, respectively. The lines are assigned as combination lines ($H_2O(\nu_1)+N_2$ and $H_2O(\nu_3)+N_2$). Comparing with our results 5973 and 6052 cm^{-1}, respectively, the discrepancy with Ref. [7] seems to be too large to be conclusive. However, allowing for the possible influence of matrix effects (which can affect the different vibrational modes in different ways), it is nevertheless interesting to note that the respective *intensities* of these two lines coincide with our values, using the corrected intensity distribution of the triplet (see below).

For this reason, we decided to perform a different experiment. For a long time, we have been aware of two strong continua, always obtained when mixtures of Ar and N_2 are deposited through a hollow cathode, microwave discharge or an ion gun (Fig 9). Accidentally, one of these broad bands happens to coincide with the 1.38 μ band of water. Within these continua, it is therefore possible to perform absorption experiments on the matrix without having to use external light sources. Fig 10 shows one such spectrum, obtained during the melting phase of a matrix, deposited through a hollow cathode, run with a mixture of N_2 and Ar. This spectrum clearly indicates that we had a substantial amount of H_2O in that particular matrix. The temperature profile of the 1.38 μ band is a composite one (it is actually a combination of room-temperature atmospheric water and cold water in the matrix). The water probably comes from a direct reaction between hydrogen (always present) and oxygen (from the quartz tube). However, this observation still does not mean that our unassigned triplet has the same origin.

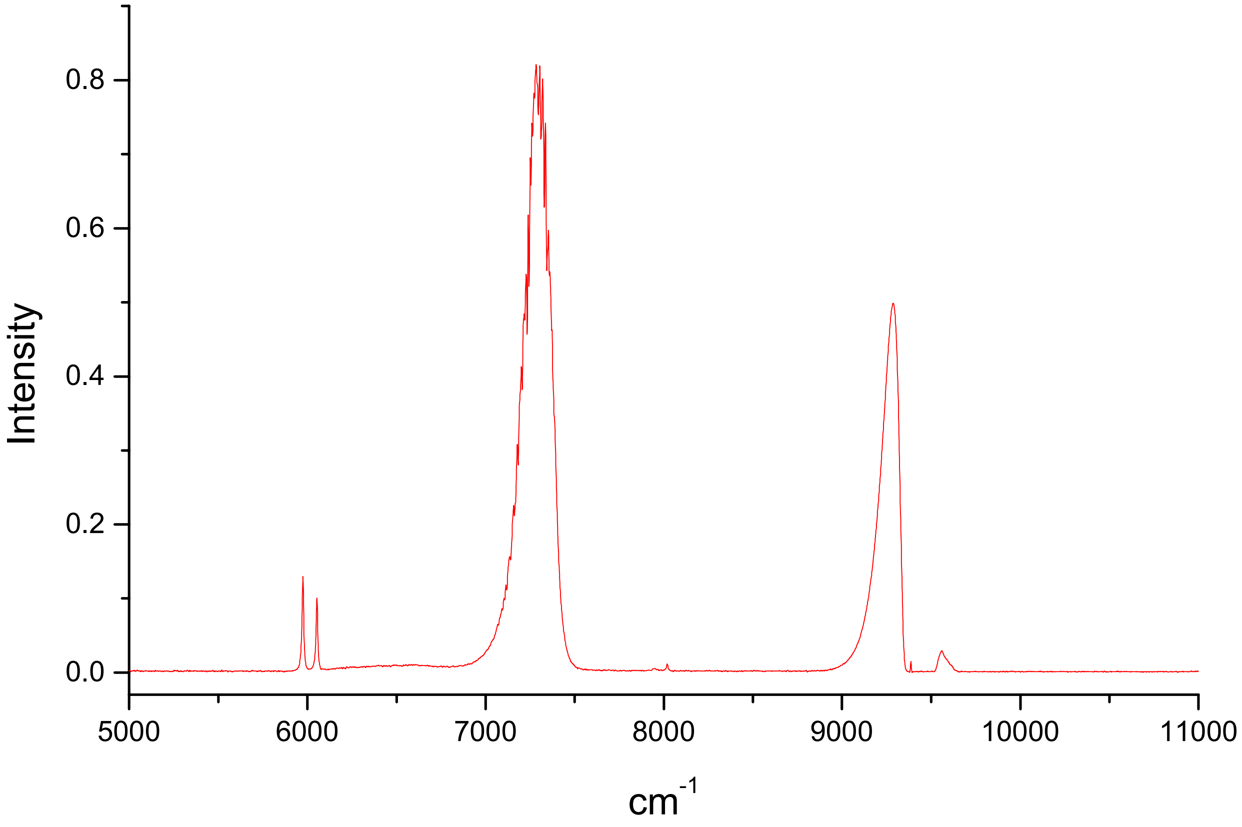

Fig. 9. The two unassigned broad bands in a matrix, deposited through a hollow cathode, using a mixture of N_2 and Ar. The spectrum is an average of 200 scans, recorded with a resolution of 4 cm^{-1}. The laser power was 500 mW

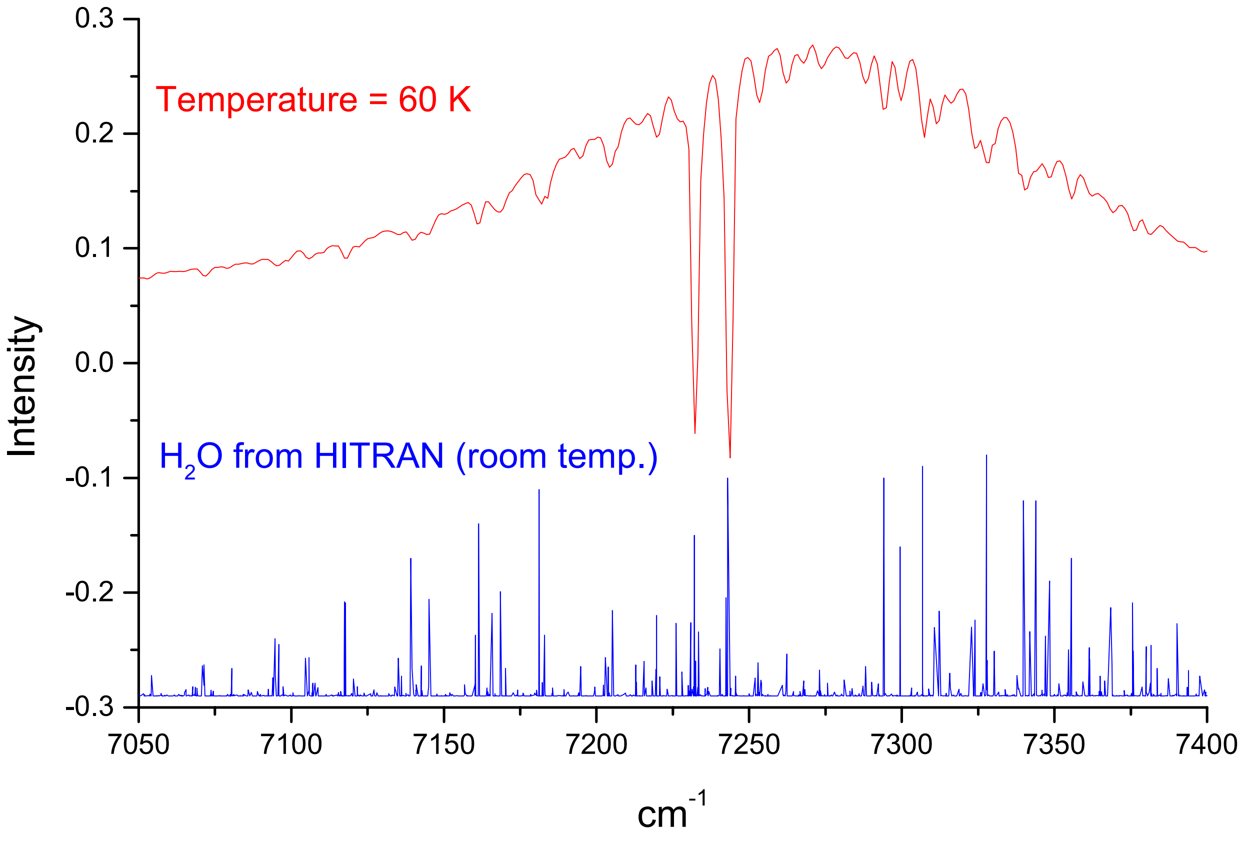

Fig. 10. Upper trace: A portion of an absorption spectrum on a matrix, deposited through a hollow cathode, run with a mixture of N_2 and Ar. The spectrum was recorded during the meltdown phase of the matrix. Lower trace: A room temperature H_2O spectrum from the HITRAN database.

In previous reports, we have reported anomalous intensity behavior for the two strong lines of the triplet (Fig. 28 in Ref. [1], Fig 9 in Ref. [5]). This behavior has now been shown to be due to enhanced sensitivity of the Ge-detector at temperatures slightly above 77 K. This increased sensitivity in the 1.66 μ region is due to a shift of the detector curve towards longer wavelengths, verified using a white-light source. Since the long wavelength flank of the detector curve is rather steep, the increased temperature results in quite dramatic sensitivity enhancement for spectral lines lying on the flank (Fig. 11).

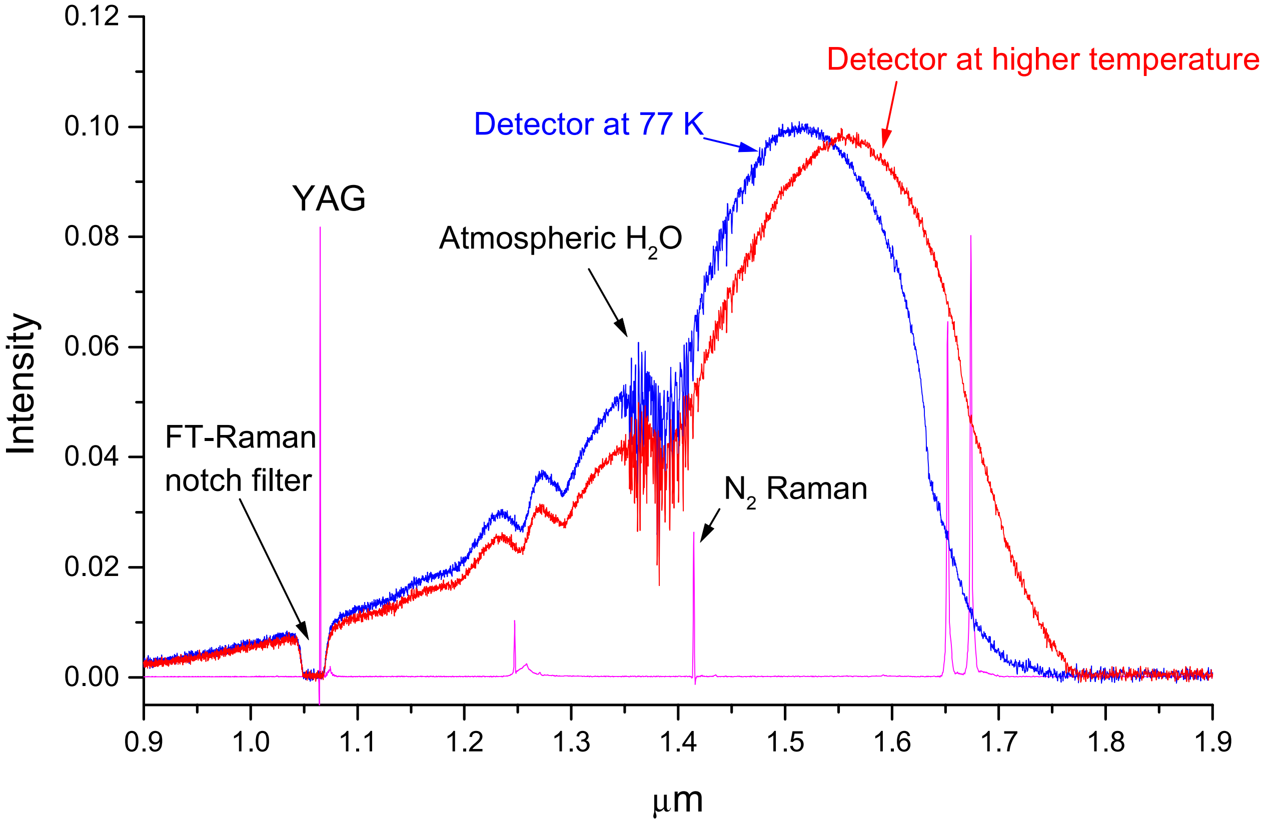

Fig. 11. Temperature-induced shift of the Ge detector in the 1.66 μ region, causing a dramatic enhancement of the doublet intensity upon increasing detector temperature. The blue and red curves were recorded without laser excitation, the matrix being illuminated by a quartz halogen lamp only. The magenta curve represents a corresponding recording with laser (500 mW), but without white light illumination.

The unassigned triplet occurs in all three investigated types of excitation, being strongest in hollow cathode- and microwave-excited matrices. In Ref. [5], the relative intensities within the triplet were given as 5, 44 and 51 percent of the total intensity carried by the triplet. In these values, the influence of the detector response curve had not been taken into account. The above measurements with a white light source show now that the correct numbers are actually 5, 28 and 67 per cent, respectively. In Ref. [5], a comparison was also made between the intensity carried by the N_2 Raman line and the total intensity of the triplet. If the obtained result (3 per cent) is corrected with respect to the detector curve, we now obtain only 1 per cent for the contribution of the N_2 Raman line as compared to the triplet. This result is even more remarkable than the previous one, and certainly warrants a thorough examination.

The third type of experiment consists of heating the matrix from 10 K to 30 K by gradually applying an increasing current to a resistor, in thermal contact with the matrix. These experiments often give characteristic structured emissions in the infrared and in the visible. The matrix emission mostly consists of atomic N spectra (^2P-^2D and ^2D-^4S), bearing witness of atom-matrix interactions through the occurrence of characteristic vibron- and phonon-induced sidebands. The processes can largely be explained by recombination schemes, where free nitrogen atoms are involved. A pair of ^4S nitrogen atoms lies at an energy of 9.8 eV, compared with a N_2 molecule in the ground state. A process like $N(^4S) + N(^4S) \rightarrow N_2(A^3\Sigma_u^+)$ is exothermal by several eV. The 6.2 eV energy stored in $N_2(A^3\Sigma_u^+)$ is subsequently used to pump up N atoms to the ^2D or ^2P states at 2.4 and 3.6 eV, respectively, causing the intensive green ($^2D \rightarrow {}^4S$) and IR ($^2P \rightarrow {}^2D$) emissions, which persist as long as fresh $N(^4S)$ supply is guaranteed. Another aspect of this process, dealing with α-particle excitation of N_2, has been described in Ref. [1]. Many features in the warm-up spectra coincide with the spectra recorded under excitation, although the relative intensities differ considerably.

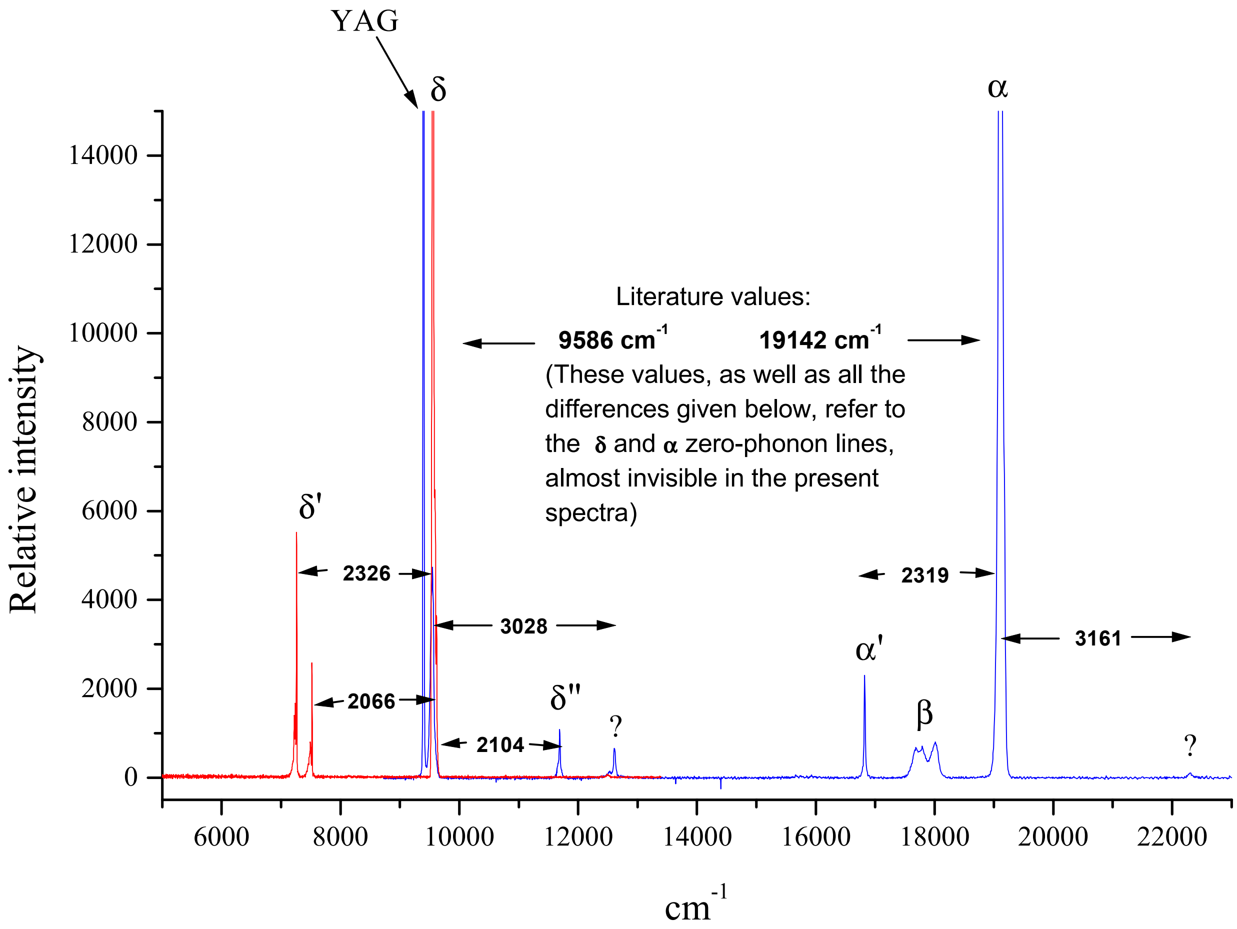

Fig. 12. Combined FT- and Mechelle-spectra during the warm-up of a nitrogen matrix. The α and δ lines correspond to the atomic nitrogen ^2D-^4S and ^2P-^2D transitions, respectively. The α' and δ' lines are corresponding vibrational satellites. Several weaker lines near the δ line have not been assigned. The β line has been assigned as a ^1S-^1D transition in atomic oxygen. The oxygen atoms are presumably released from the quartz capillary through the influence of the discharge. The YAG power was very low (8 mW). The integration time was 30 s.

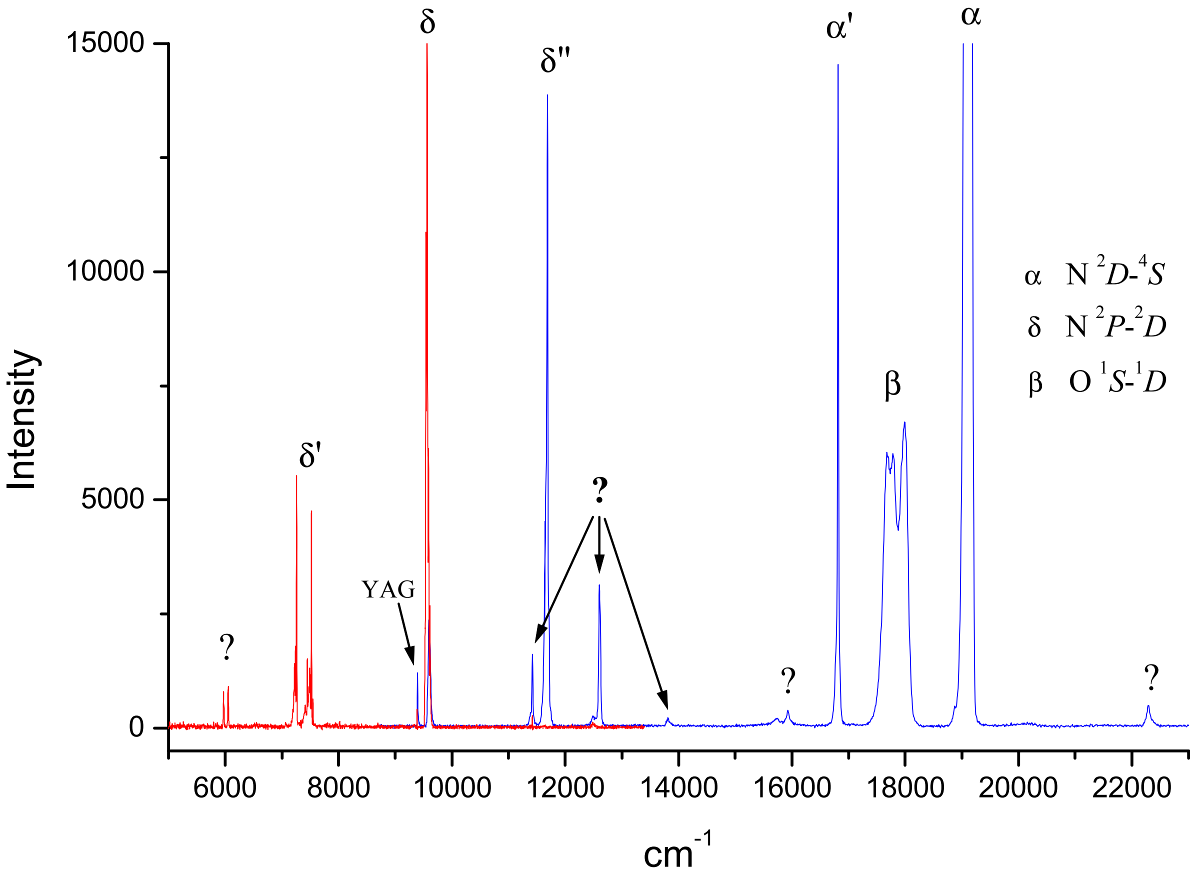

Fig. 13. Combined FT- and Mechelle-spectra during the warm-up of a nitrogen matrix. The spectra were recorded in similar conditions as in Fig. 12, with the exception that the laser power was now 500 mW. Notch filters were used in both recordings, resulting in a better suppression of the exciting laser line. Among the unidentified lines seen in these spectra, the doublet at 6000 cm^{-1} is identical with the one discussed above. The integration time was 30 s.

In Figs. 14 and 15, another type of experiment is shown. This warming-up spectrum was recorded using a three-layer N_2 matrix, deposited with neutral, hollow-cathode excited and neutral layers, respectively. This experiment was performed in order to investigate the possibility of surface phenomena as being the cause of the occurrence of the triplet.

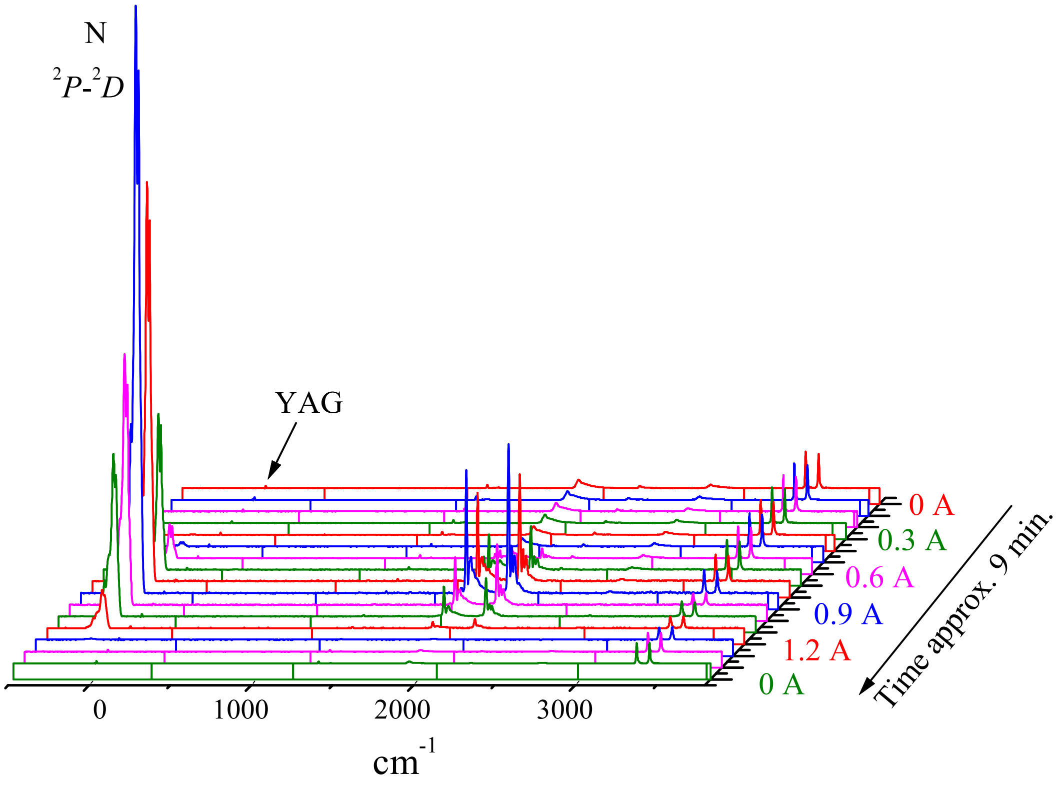

Fig. 14. A warming-up series of a hollow-cathode excited, layered N_2 matrix. The matrix was constructed by deposition of consecutive neutral, excited and neutral N_2 layers, respectively. The atomic N signal was unusually strong in this recording, as can be seen upon comparison with the residual YAG line. The laser power was 500 mW and resolution 4 cm^{-1}.

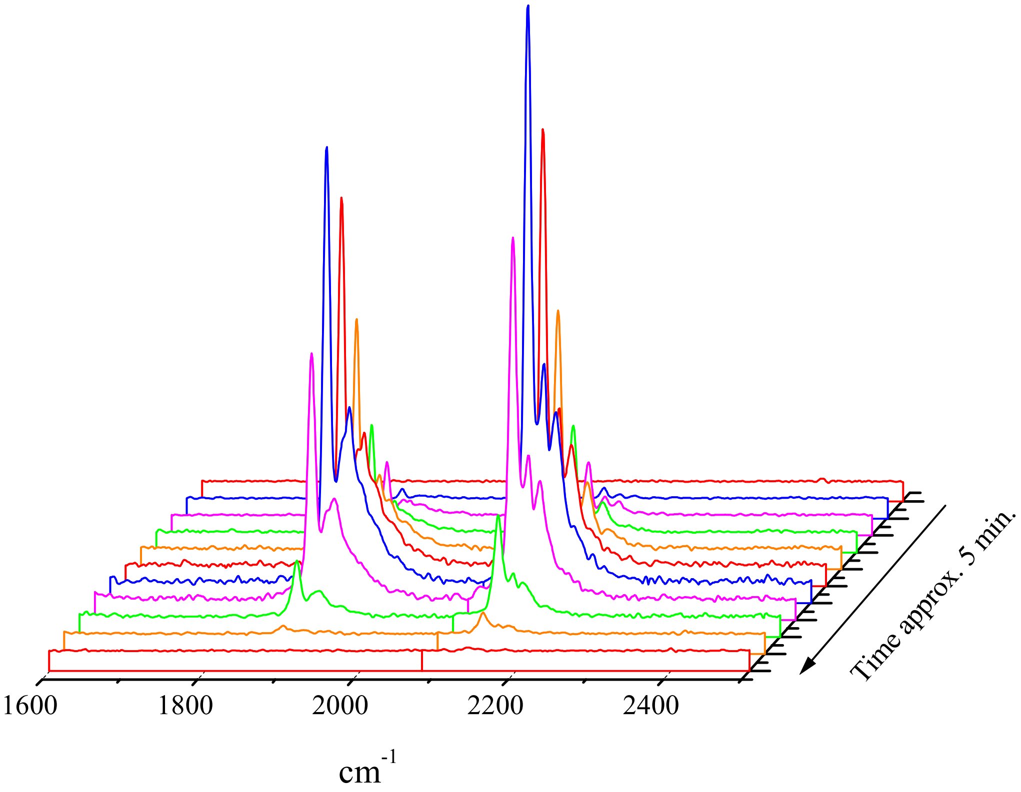

Fig. 15. Portion of a warming-up spectrum of a microwave-excited N_2 matrix. Compare the relative intensities of the two bands with those of Fig. 16.

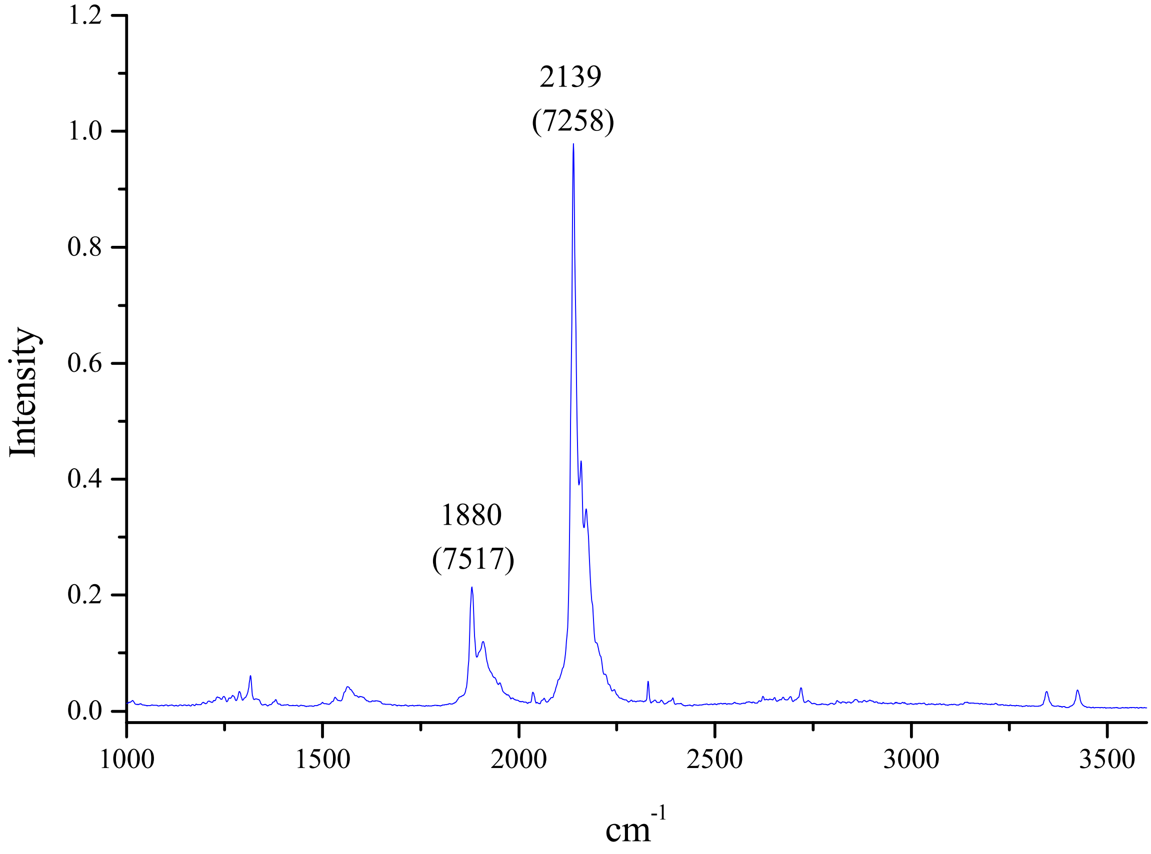

Fig. 16. Spectrum of an ion-gun excited N_2 matrix during the excitation phase. Compare the relative intensities of the two bands with those of Fig. 15.

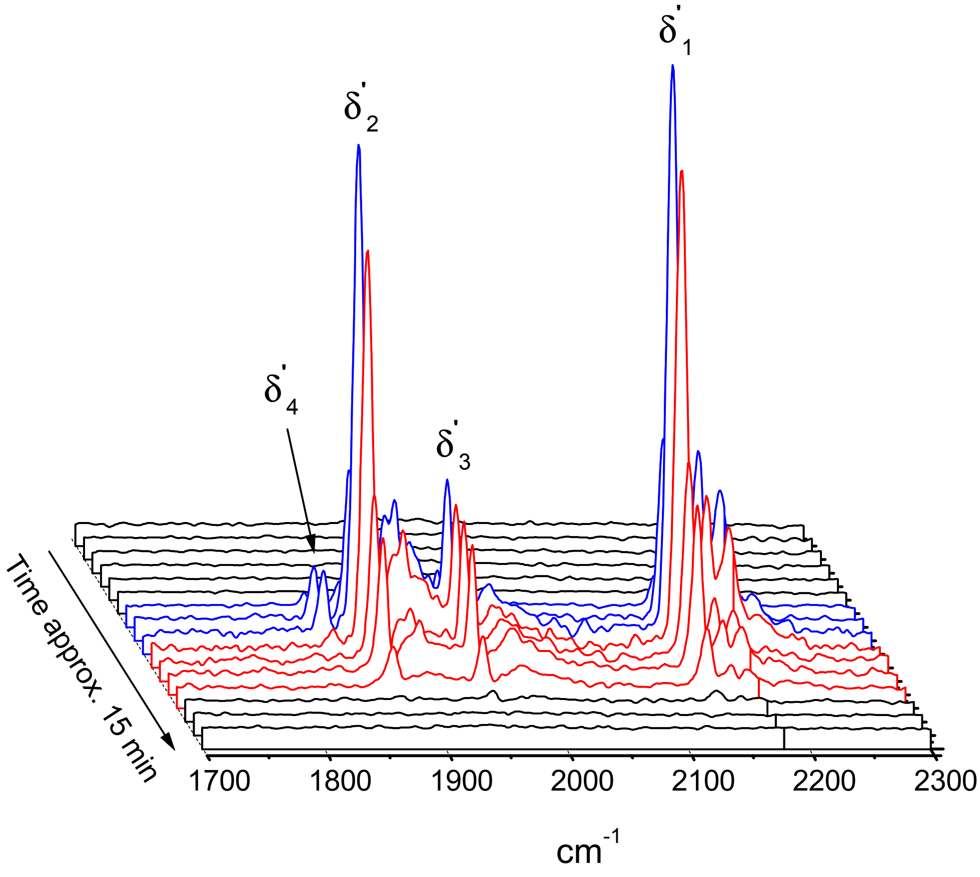

Fig. 17. A warm-up spectrum of the δ' group in a nitrogen matrix. The matrix was built up during 2½ hours using a hollow cathode discharge in pure N_2. The δ_1' band is attributed to the ^2P-^2D transition in nitrogen atom, combined with a simultaneous vibrational excitation of a neighboring N_2 molecule. The remaining bands are unassigned so far. An isotopic substitution experiment on the δ' group is shown in Fig. 21.

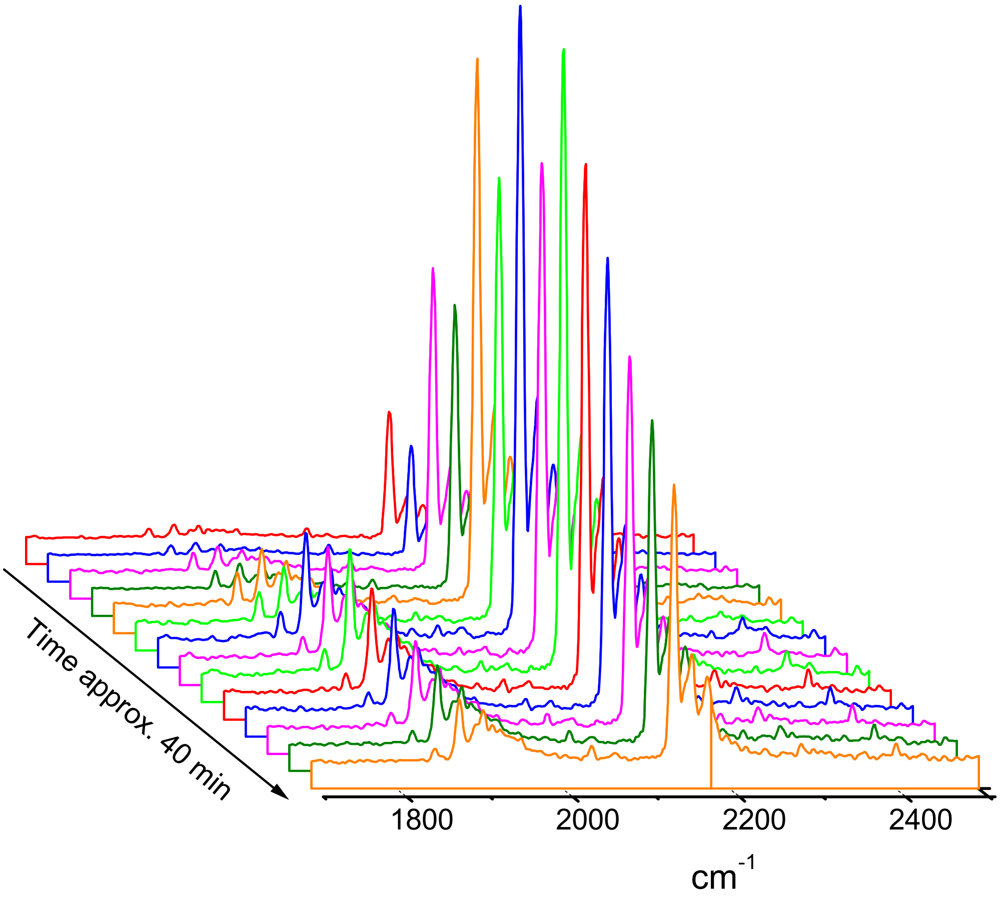

Fig. 18. Spectra of an excited N_2 matrix during the build-up phase in the δ'-region. The matrix was built up using a Ne/N_2 mixture in a microwave discharge, starting with a Ne-concentration of about 20 per cent. Several consecutive refills with pure N_2 were then made, causing strong intensity fluctuations of the δ_2' band at 1880 cm^{-1}. Compare with Fig. 19.

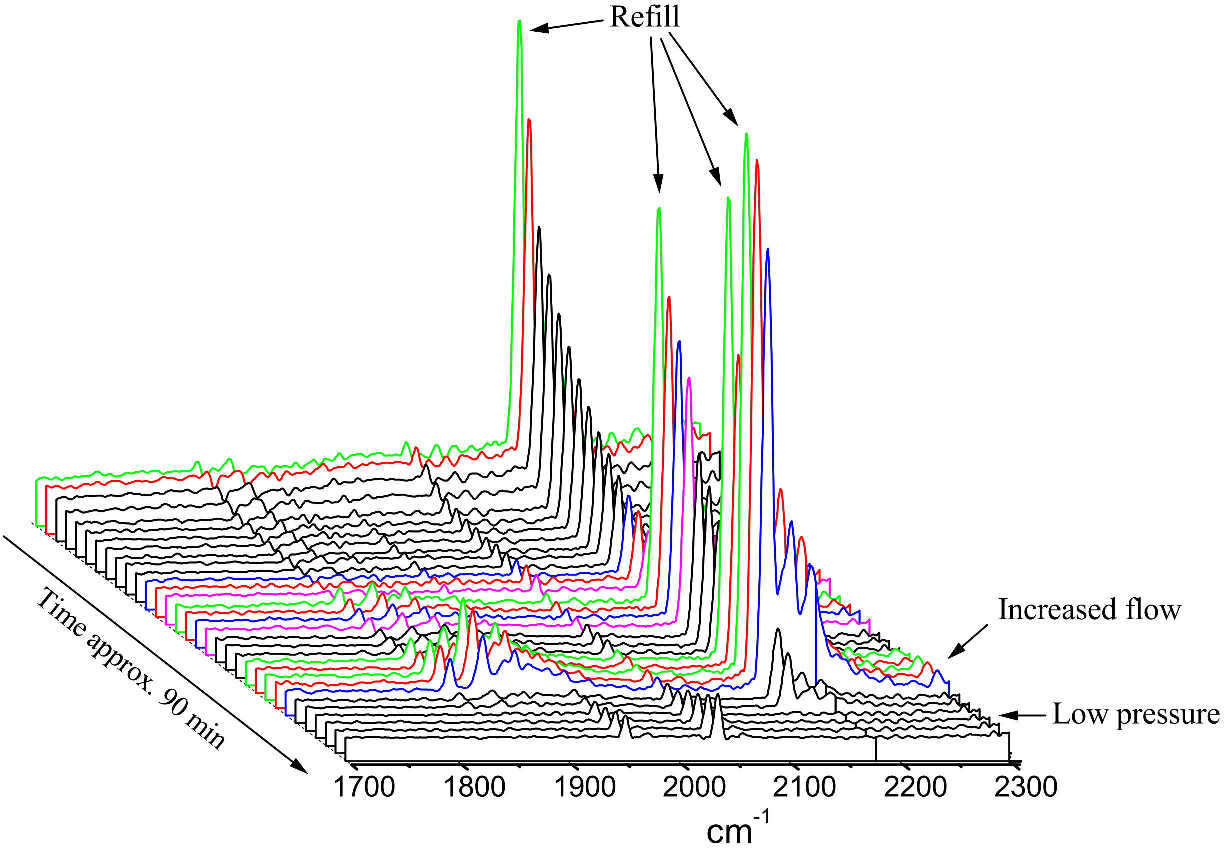

Fig. 19. Spectra of an excited N_2 matrix during the build-up phase in the δ'-region. The matrix was built up using a He/N_2 mixture in a microwave discharge, starting with a He-concentration of nearly 50 per cent. Several consecutive refills with pure N_2 were then made, causing strong intensity fluctuations of the δ_2' band at 1880 cm^{-1}. Compare with Fig. 18.

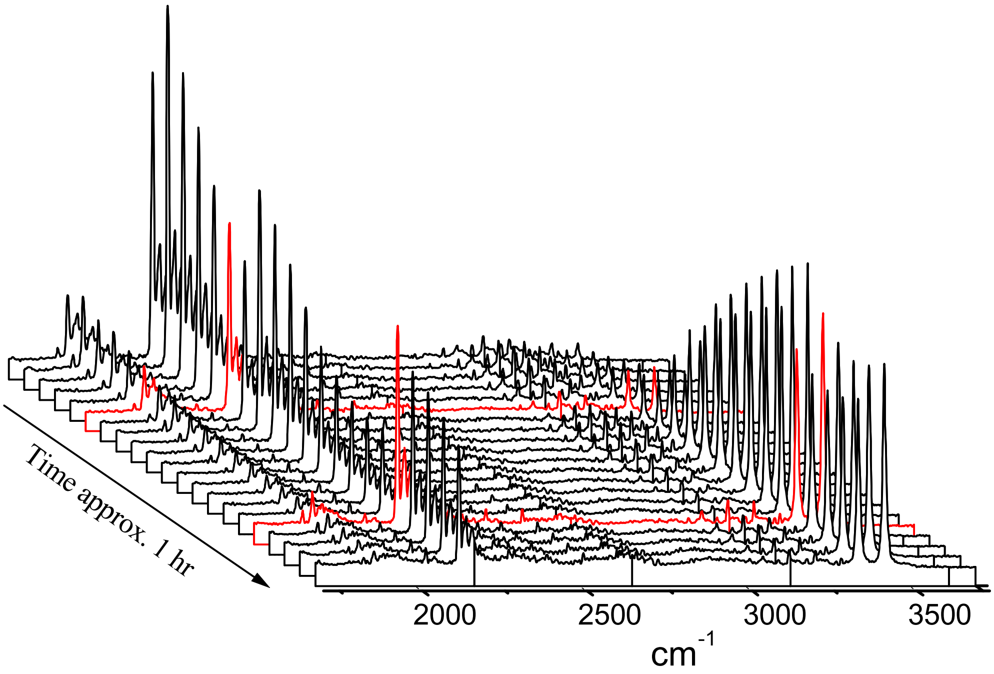

Fig. 20. The δ' group in a nitrogen matrix and the unassigned laser-excited doublet at 3400 cm^{-1}, recorded during matrix build-up through a microwave discharge in N_2, with a small amount of Ne. The spectra were taken using a resolution of 4 cm^{-1} with a laser power of 500 mW. It is evident from these spectra that there is no correlation between the δ' group and the unassigned doublet.

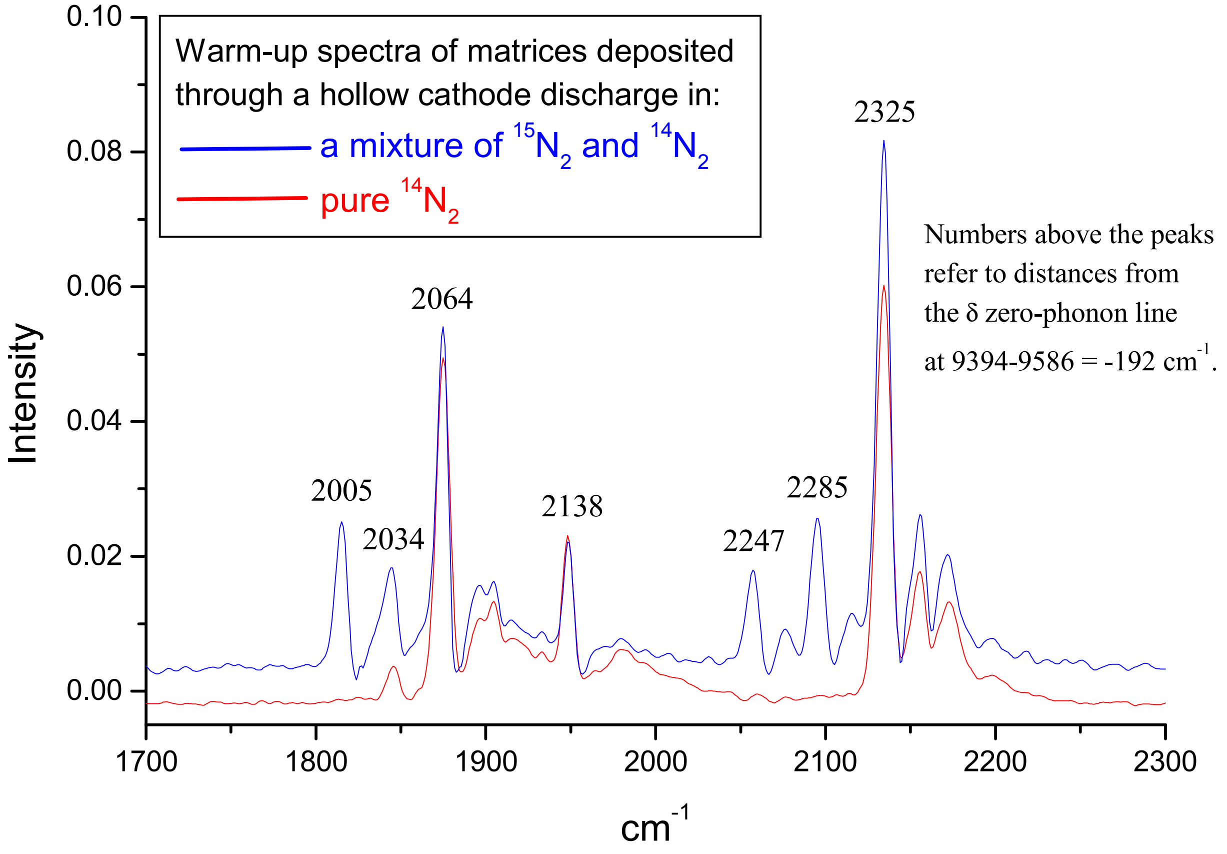

Fig. 21. Isotopic substitution experiment on the δ' group in a nitrogen matrix. The spectra were recorded during the warm-up phase of two matrices, built up using a hollow cathode discharge in pure $^{14}N_2$ (red) and in a mixture of $^{14}N_2$ and $^{15}N_2$ (blue). The isotope behavior of the δ_1' subgroup (cf. Fig. 17) can be understood by comparison with theoretically expected vibrational shifts. It is interesting to note that the line marked with '2285' is located exactly where it would be expected to be, if it is assumed that the vibrational shift arises from interaction of the N ^2P-^2D transition with a neighboring $^{14}N^{15}N$ molecule. However, while this conclusion seems *á priori* plausible, it is contradicted by the non-observation of the $^{14}N^{15}N$ Raman line in the matrix in question. The behavior of the remaining subgroups is also puzzling: The location of the line marked with '2005' clearly excludes interaction with $^{15}N_2$. The correct interpretation might be either a matrix site-effect or a similar atom-molecule interaction within a loosely bound N_3 molecule.

Yet another type of experiment consists of switching off the excitation source and recording time series (Fig. 22). Long integration times can be used since some of the de-excitation processes are very slow (30-100 s). An average of two of the spectra of the time series of Fig. 22 is shown in Fig. 23. The unassigned features in these spectra are probably due to different species.

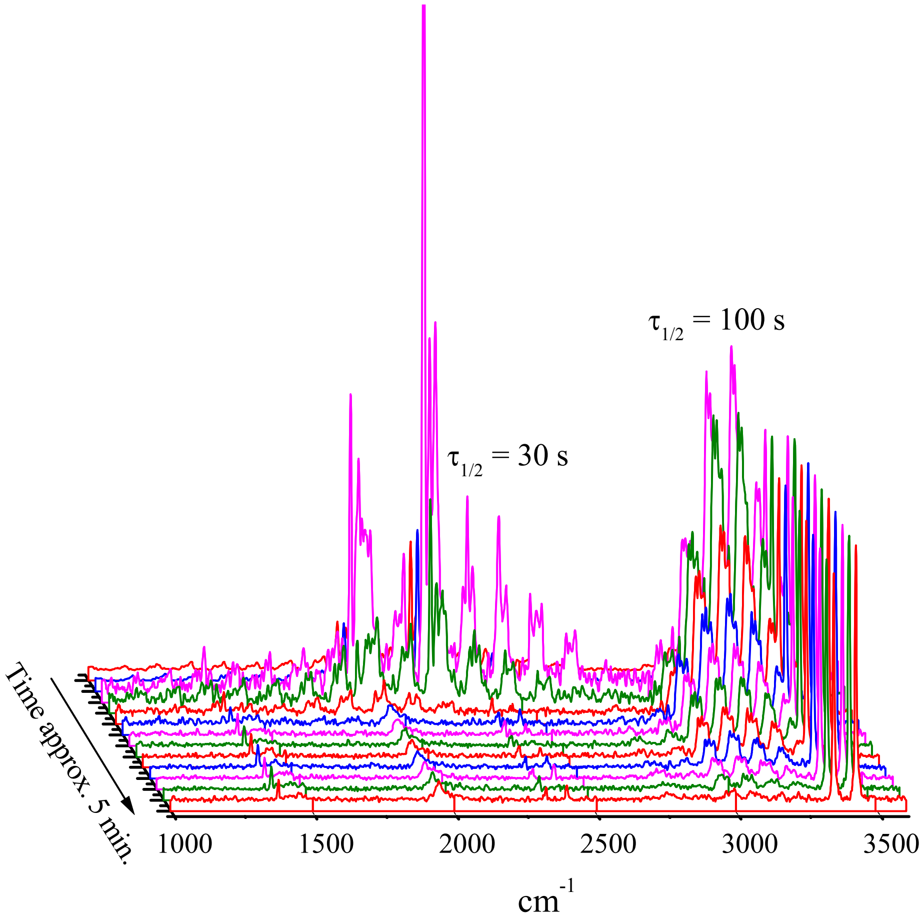

Fig. 22. A time series of excited N_2 matrix at 10 K, recorded after sudden switching-off of the hollow cathode excitation discharge. The spectra represent consecutive 20-scan FT-Raman recordings with a YAG power of 500 mW and resolution 4 cm^{-1}. Two characteristic decay times are observed for the two different (unassigned) band systems in the 2000 cm^{-1} and 3200 cm^{-1} regions, respectively. The conclusion is that there are two different carriers involved.

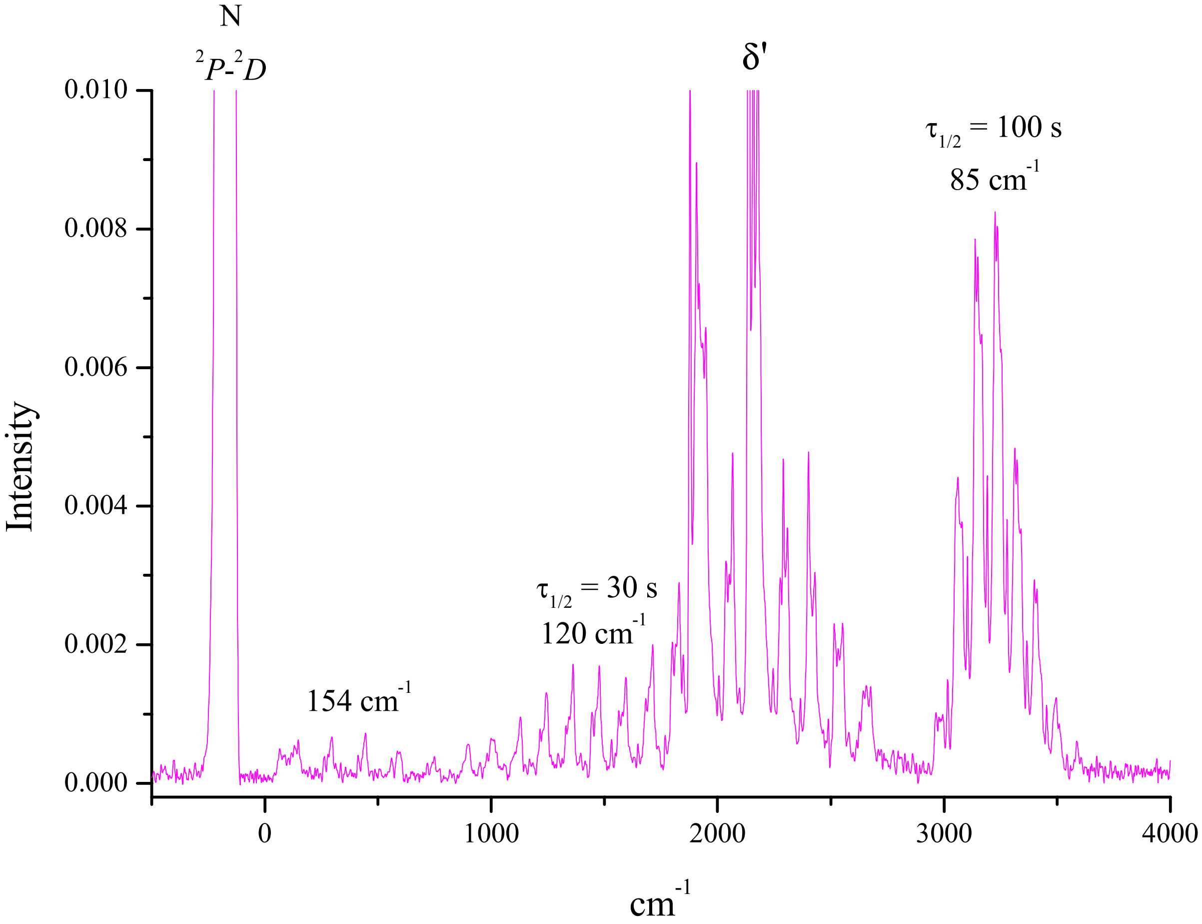

Fig. 23. An average of two of the spectra in the time series of Fig. 22. The wavenumber designations in the spectra refer to the characteristic sub-band separations within the corresponding band systems. In the case of the 3200 cm^{-1} band system, the sub-bands can be fitted to a first-degree polynomial, while a second-degree polynomial is needed for the 2000 cm^{-1} system.

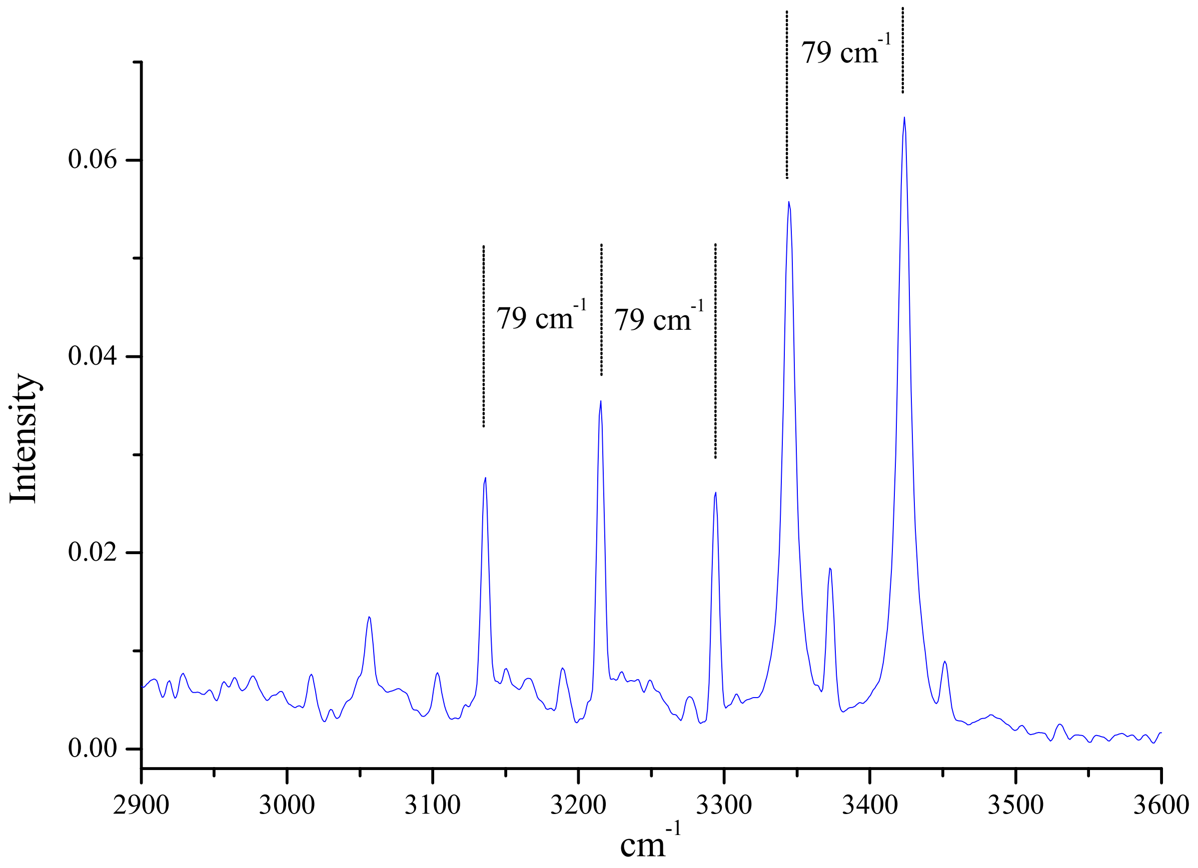

Fig. 24. Unassigned structures in a FT-Raman recording during matrix build-up from a microwave discharge. The spectrum is an average of 900 scans, recorded during approximately 30 minutes at a resolution of 4 cm^{-1} and slightly varying conditions. The broad and narrow lines do not appear to be related, despite the identical 79 cm^{-1} separations. See further in Fig. 25.

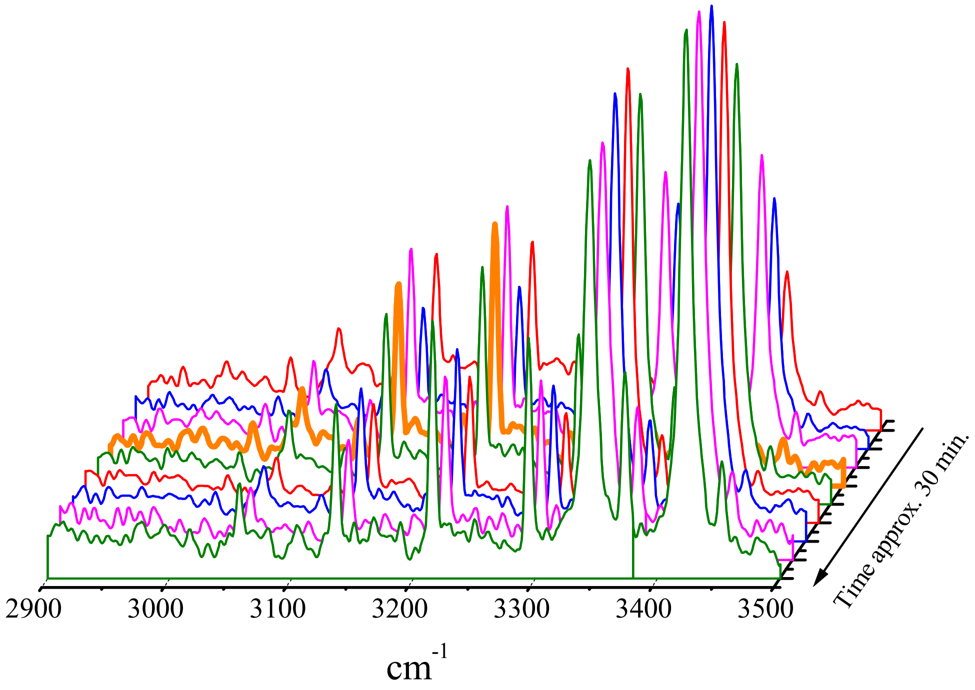

Fig. 25. A series of FT-Raman recordings (9x100 scans) of a microwave discharge-excited N_2 matrix during the matrix build-up phase. As can be seen, the time behaviors of the 3400 cm^{-1} doublet and the narrow lines in the 3200 cm^{-1} band are different. In fact, the intensity fluctuations of the narrow lines mirror exactly the fluctuations of the atomic ^2P-^2D line of nitrogen, not shown in this figure. The bold orange spectrum in the middle was recorded with low YAG power (5 mW), while the remaining spectra were taken at 500 mW laser power. The narrow lines are clearly not laser-induced.

Hollow-cathode discharge excitation of N_2 matrices gives rise to somewhat confusing spectra. In addition to the features occurring in microwave- and ion gun-excited matrices, several additional bands appear (Fig. 26). These bands are also laser-induced.

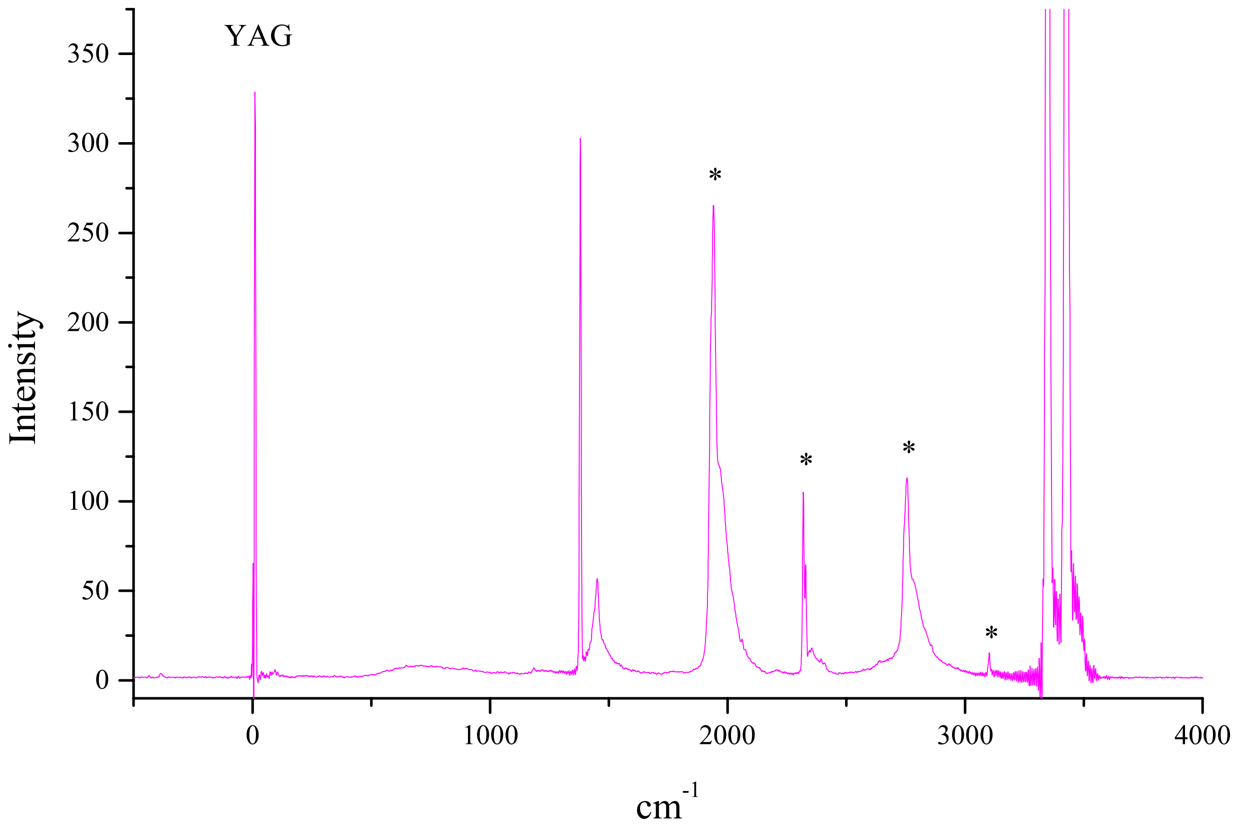

Fig. 26. New bands, marked with asterisks, appearing in hollow-cathode excited nitrogen matrices. The spectrum is an average of 36000 scans, recorded during 18 hours with a laser power of 500 mW at a resolution of 4 cm^{-1}. The spectrum has been expanded with a factor of 10 in the vertical direction.

Furthermore, the bands show a slow decay in long-time experiments, possibly related to diffusion-induced phenomena (Fig. 27).

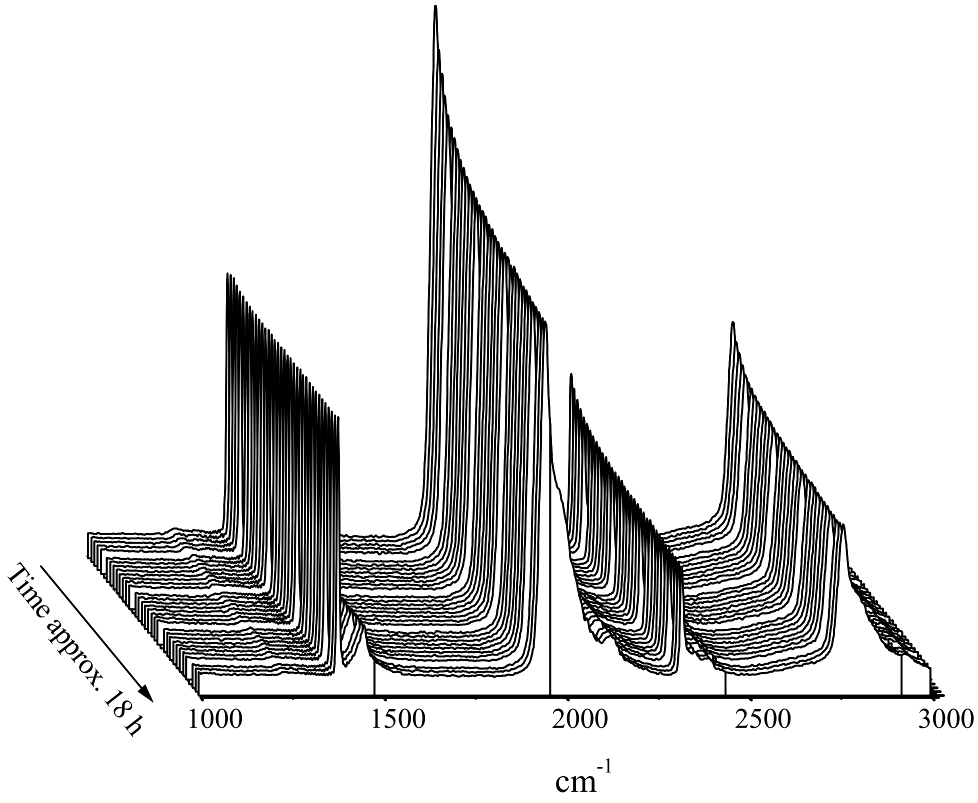

Fig. 27. Long time behavior of the hollow-cathode bands in N_2 matrix. Each spectrum is an average of 1000 scans, collected during 30 minutes. The laser power was 500 mW and resolution 4 cm^{-1}.

Upon annealing, the new bands disappear more readily than the triplet, which shows a temporary decrease, climbing up again to approximately 80 per cent of the original strength when the temperature is lowered (Figs. 28 and 29). The new bands, however, lose most of their intensity upon warming-up to 30 K. The triplet vanishes irreversibly at approximately 37 K, as can be seen in Fig. 30. Interestingly, this is approximately the temperature at which the α-nitrogen ceases to exist.

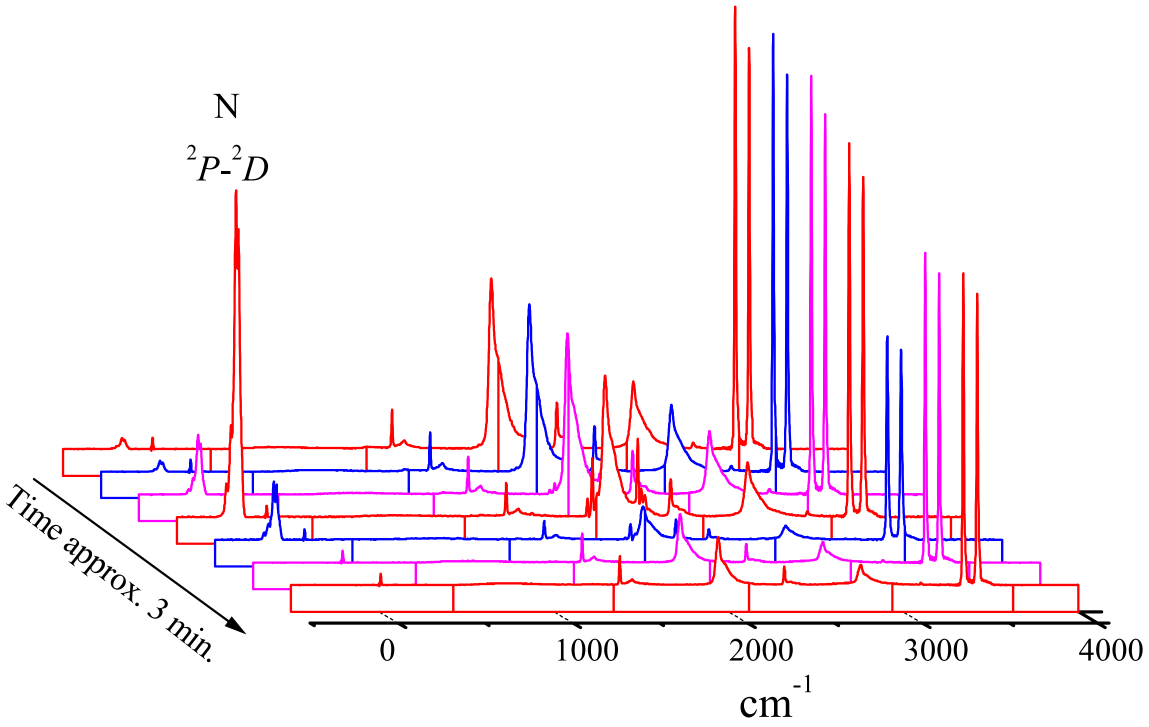

Fig. 28. A warming-up series (10 K → 30 K → 10 K) of a hollow-cathode excited N_2 matrix. The two broad bands at 2000 and 2800 cm^{-1} vanish more easily than the triplet lines. The laser power was 500 mW and resolution 4 cm^{-1}.

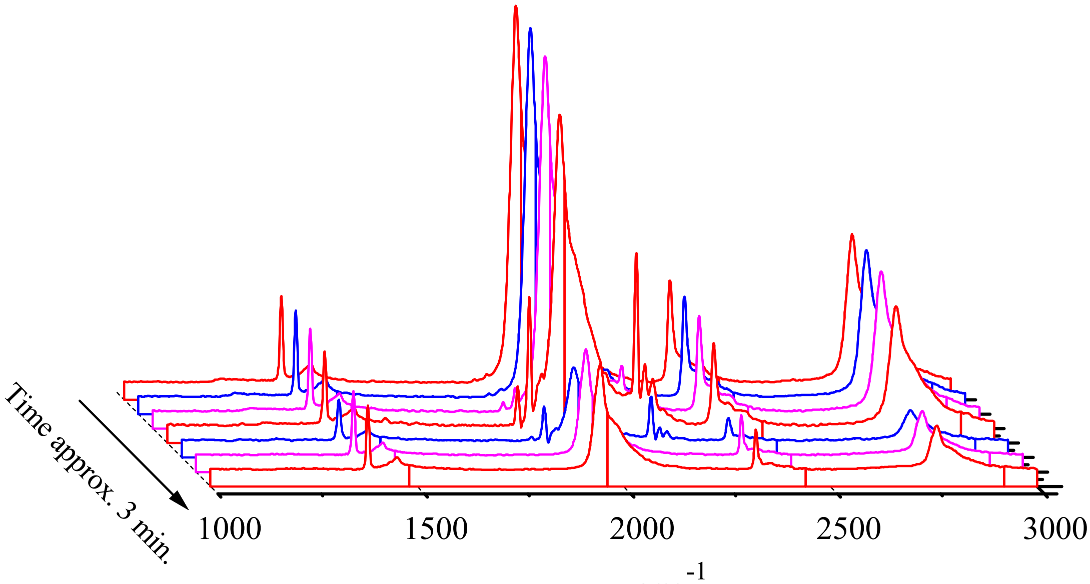

Fig. 29. A warm-up series (10 K → 30 K → 10 K) of a hollow-cathode excited N_2 matrix. The two broad bands at 2000 and 2800 cm^{-1} vanish more readily than the triplet line at 1380 cm^{-1}. The laser power was 500 mW and resolution 4 cm^{-1}.

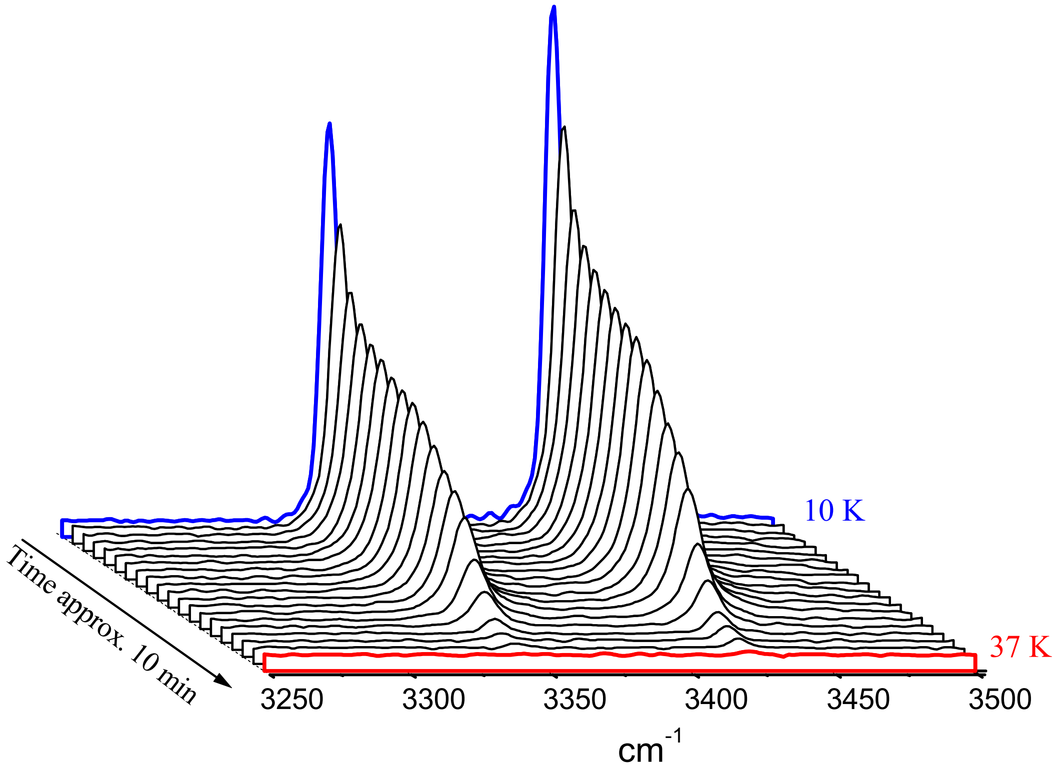

Fig. 30. The 3400 cm^{-1} doublet, recorded during 10 minutes after compressor shut-off. Each individual spectrum represents an average of 20 scans. The laser power was 500 mW and resolution 4 cm^{-1}.

We have now collected a rather large material on processes in excited cryogenic matrices. A critical evaluation of this material boils down to some important conclusions, regarding the possibility of a successful synthesis and detection of $N_4(T_d)$ in cryogenic matrices. First of all, some of the unassigned features shown above may constitute important precursors in the synthesis efforts. In particular, the origin of the mysterious triplet has to be established with certainty. Another important feature in the spectra is the unexpectedly complicated δ' group (Figs. 17-21). The unexplained lines in this group might in fact arise from a hitherto unknown carrier (possibly an isomer of N_3). The even more complicated features shown in Figs. 22-25 represent a veritable challenge, since they are difficult to reproduce and decay rapidly once the discharge is turned off. The "hollow cathode bands" of Figs. 26-29 constitute yet another conspicuously persistent feature, which we are unable to attribute to a specific carrier. We know from other experiments that a hollow cathode discharge contains a larger fraction of highly excited species (for instance N_2^+) than a microwave discharge. For this reason, the non-observation of these bands in microwave discharges is not necessarily surprising. On the other hand, we also know that sputtering phenomena are stronger in electric discharges than in microwave plasmas. This means that impurity bands are often difficult to suppress in hollow cathode discharges.

Perhaps the most important conclusion is that we have been able to deposit, excite and manipulate our matrices in a largely reproducible manner. This means that a foundation has now been laid for cryosynthesis experiments, where free nitrogen atoms are to be used as reactants in the continuing efforts to synthesize $N_4(T_d)$. A very important idea has arisen during the present experiments. This idea consists of trying to use triangular N_3 for this synthesis according to the scheme: $N_3(C_{2v}) + N(^2D) \rightarrow N_4(T_d)$.

A new synthesis route for $N_4(T_d)$

We have performed calculations on the hitherto not reported triangular $N_3(C_{2v})$ radical. Detailed calculations on this second species clearly show that this radical is bound. This means that we now have a new precursor for the $N_4(T_d)$ synthesis according to the scheme: $N_3(C_{2v}) + N(^2D) \rightarrow N_4(T_d)$.

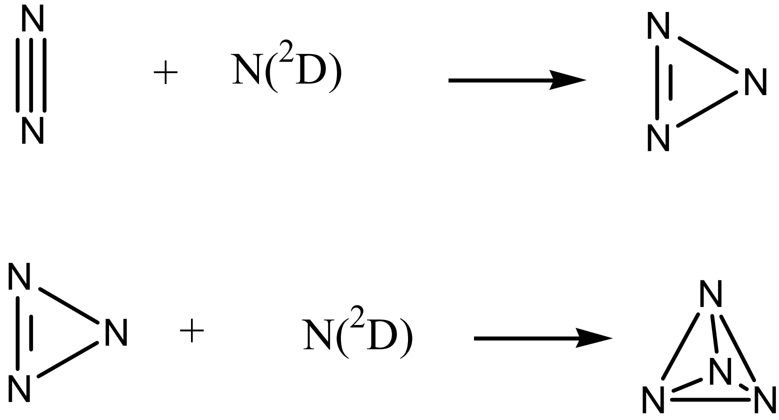

Fig. 31. A new proposed synthesis route for N_4. Both steps are fully symmetry-allowed and exothermal. The scheme works in cryogenic environments, where $N(^2D)$ can be generated from previously deposited ground state nitrogen atoms using the following two-step process: **1.** $N(^4S)+N(^4S) \rightarrow N_2(A^3\Sigma_u^+)$ **2.** $N_2(A^3\Sigma_u^+) + N(^4S) \rightarrow N_2(X^1\Sigma_g^+) + N(^2D)$.

For this scheme to be realistic, sufficient concentrations of nitrogen atoms must be available in the matrix [9]. If the matrix temperature is raised enough in order to allow sufficient diffusion of N atoms to take place (to 12-15 K), there will be enough time for the first reaction to occur easily, since the lifetime of $N(^2D)$ in a nitrogen matrix is very long (approximately 37 s). Thus, a small concentration of $N_3(C_{2v})$ will hopefully build up, along with the (probably unavoidable) linear $N_3(D_{\infty h})$ radical. The relative cross-sections of these two processes are not known at present. However, once the experimental vibrational frequencies of $N_3(C_{2v})$ have been experimentally measured, an absorption set-up can be used in order to monitor the respective concentrations of $N_3(C_{2v})$ and $N_3(D_{\infty h})$. The second step in the above scheme will be the overall rate-limiting one, since it involves two low-concentration species. However, if it can be experimentally verified that $N_3(C_{2v})$ can be obtained in measurable quantities in the first step, the second step to the detection of $N_4(T_d)$ will not be a long one.

The main processes to be considered are the following:

Step	Process	Energy release (eV)
1.	$N(^4S) + N(^4S) \rightarrow N_2(A^3\Sigma_u^+)$	3.6
2.	$N(^4S) + N(^4S) \rightarrow N_2(X^1\Sigma_g^+)$	9.8
3.	$N_2(A^3\Sigma_u^+) \rightarrow N_2(X^1\Sigma_g^+) + h\nu$	6.2
4.	$N_2(A^3\Sigma_u^+) + N(^4S) \rightarrow N_2(X^1\Sigma_g^+) + N(^2P)$	2.6
5.	$N_2(A^3\Sigma_u^+) + N(^4S) \rightarrow N_2(X^1\Sigma_g^+) + N(^2D)$	3.8
6.	$N(^2P) \rightarrow N(^2D) + h\nu$	1.2
7.	$N(^2D) \rightarrow N(^4S) + h\nu$	2.4
8.	$N_2(X^1\Sigma_g^+) + N(^2D) \rightarrow N_3(D_{\infty h})$	2.5
9.	$N_2(X^1\Sigma_g^+) + N(^2D) \rightarrow N_3(C_{2v})$	1.4
10.	$N_3(C_{2v}) + N(^2D) \rightarrow N_4(T_d)$	5.6

The overall reaction for the steps 1-7 is essentially: $2n\mathbf{N} \rightarrow n\mathbf{N_2}$ + photons. The number of emitted photons depends on the actual branching ratios for the steps in question. These ratios are not known at present. If only steps 1-7 are involved, all the energy initially stored in the N atoms is ultimately wasted, since it is converted to photons (in addition to some extent of warming of the matrix, due to vibrational relaxation processes). In order to synthesize N_4 in a matrix, it is therefore necessary to control the steps 8-10, especially the branching ratios involved in steps 8 and 9. This control is most conveniently performed using an absorption set-up for on-line monitoring of the $N_3(D_{\infty h})$ and $N_3(C_{2v})$ concentrations. A preliminary calculation on $N_3(C_{2v})$ at the B3LYP-AVDZ level gives the vibrational frequencies 351, 905 and 1729 cm^{-1}, with the corresponding IR intensities of 12.88, 0.24 and 4.19 km/mol, respectively. At the same level, the calculated frequencies of the linear $N_3(D_{\infty h})$ radical were 472, 1372 and 1714 cm^{-1}, with IR intensities 9.06, 0 and 222.41 km/mol, respectively. More detailed calculations are underway in order to determine the absorption spectrum of $N_3(C_{2v})$, as well as the relevant Raman and IR-absorption cross-sections for both N_3 species.

We have performed long-time diffusion experiments on N_2 matrices containing atomic nitrogen, deposited through a hollow cathode discharge. A typical long-time recording is shown in Fig. 32. In this experiment, the temperature of the matrix was kept at 12.5 K, which allowed some diffusion of N atoms to take place, which is manifested through the observed decay of the green N ^2D-^4S signal.

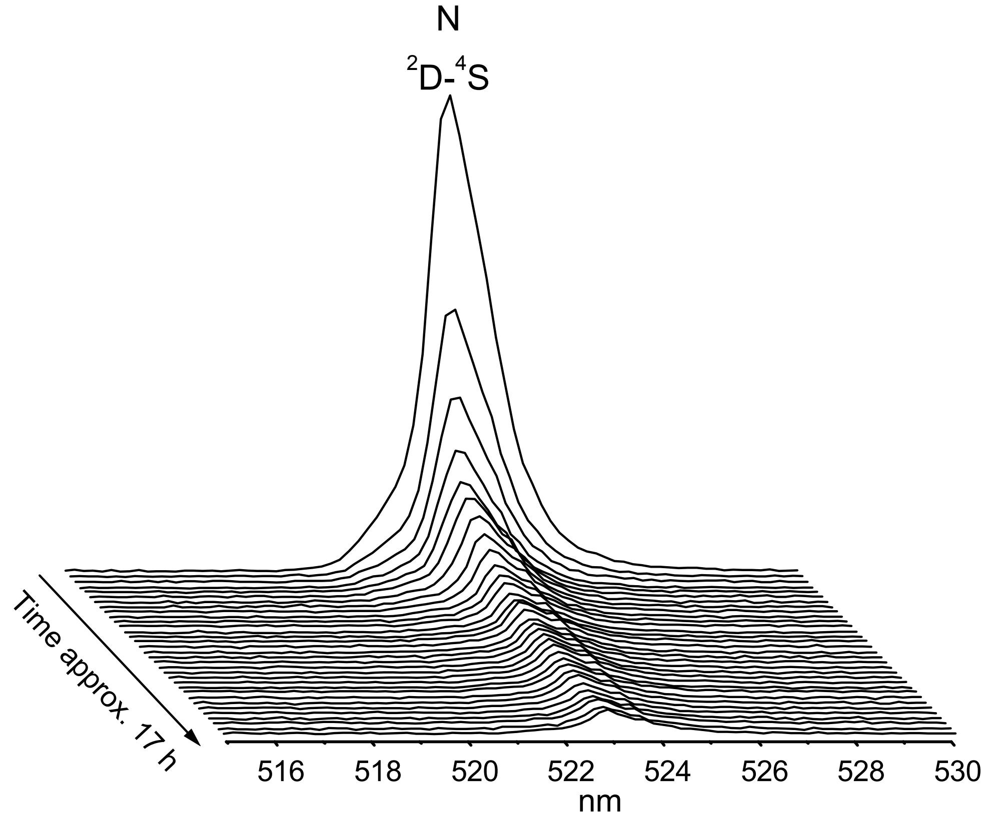

Fig. 32. A long-time recording of a slightly heated (12.5 K) nitrogen matrix, containing free N atoms. The peak shows the time decay of the green ^2D-^4S line of N

The decay of the N ^{2}D-^{4}S green line can be fitted to a double exponential (Fig 33). The actual meaning of the two characteristic decay times (30 and 165 minutes) is under investigation at present.

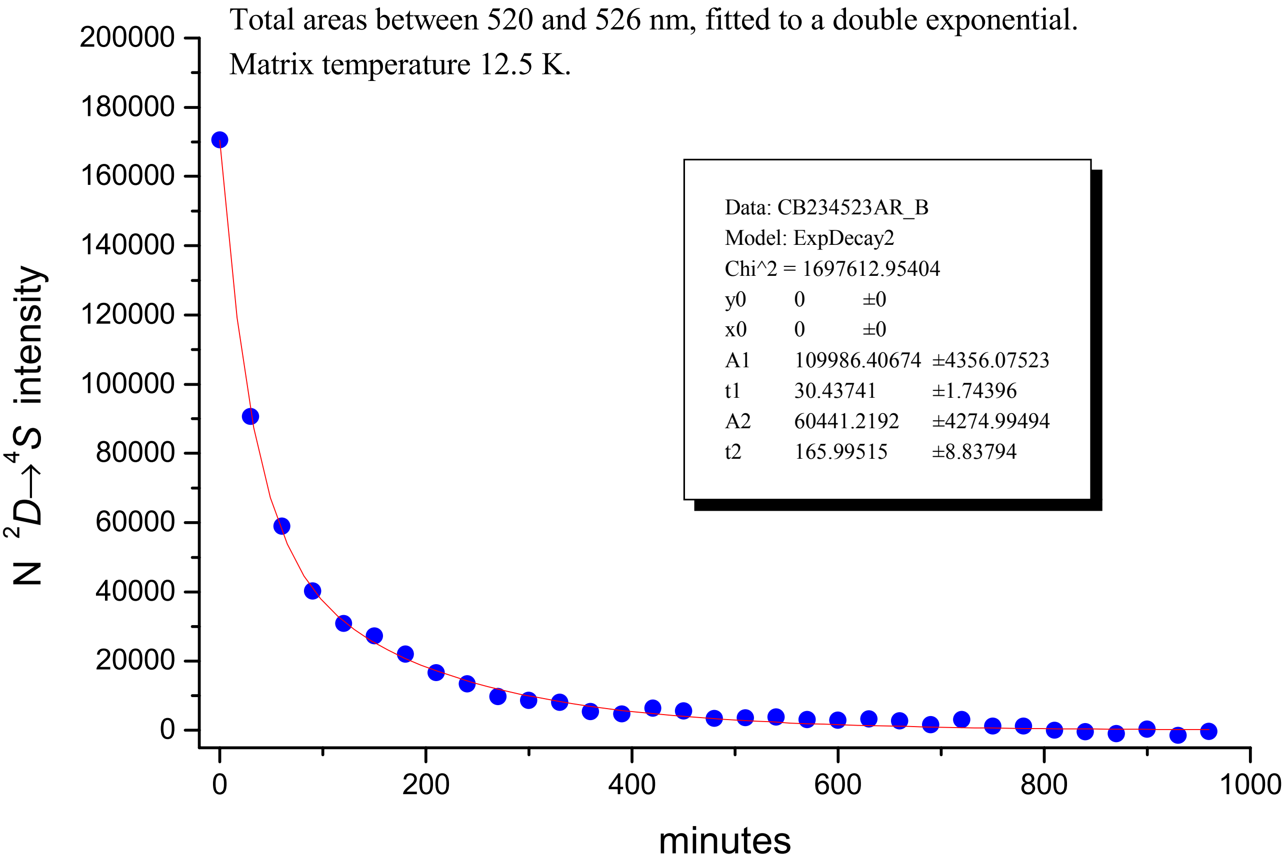

Fig. 33. Total peak areas of the N ^{2}D-^{4}S emission in Fig. 32, fitted to a double exponential. At this temperature (12.5 K), the characteristic decay times are 30 and 165 minutes, respectively.

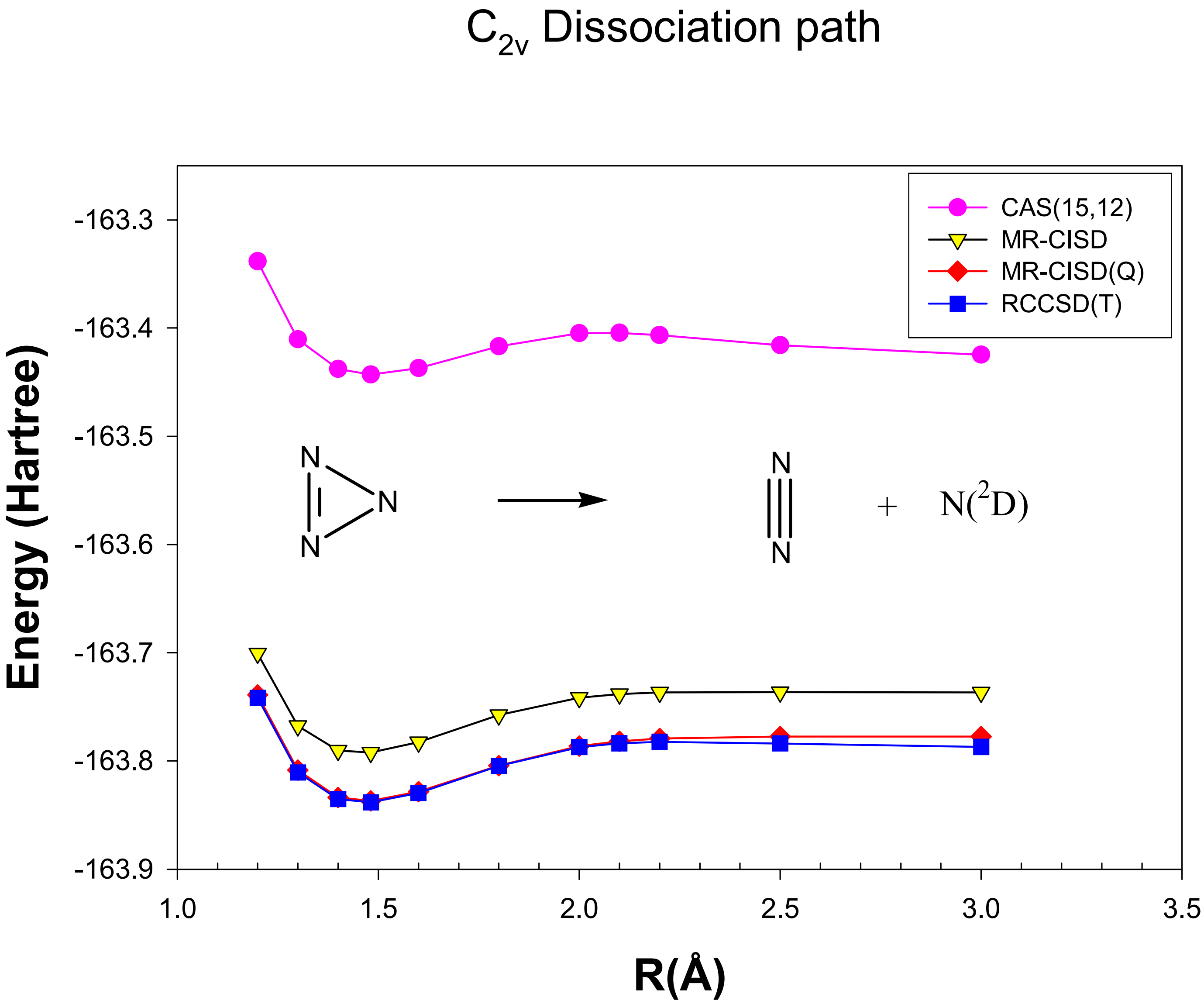

Fig. 34. QM calculations on the dissociation pathway of $N_3(C_{2v})$, performed at various levels. The dissociation energy is approximately 1 eV in all the calculations. This means that $N_3(C_{2v})$ is stable enough to be kept in cryogenic matrices as a precursor for the $N_4(T_d)$ synthesis.

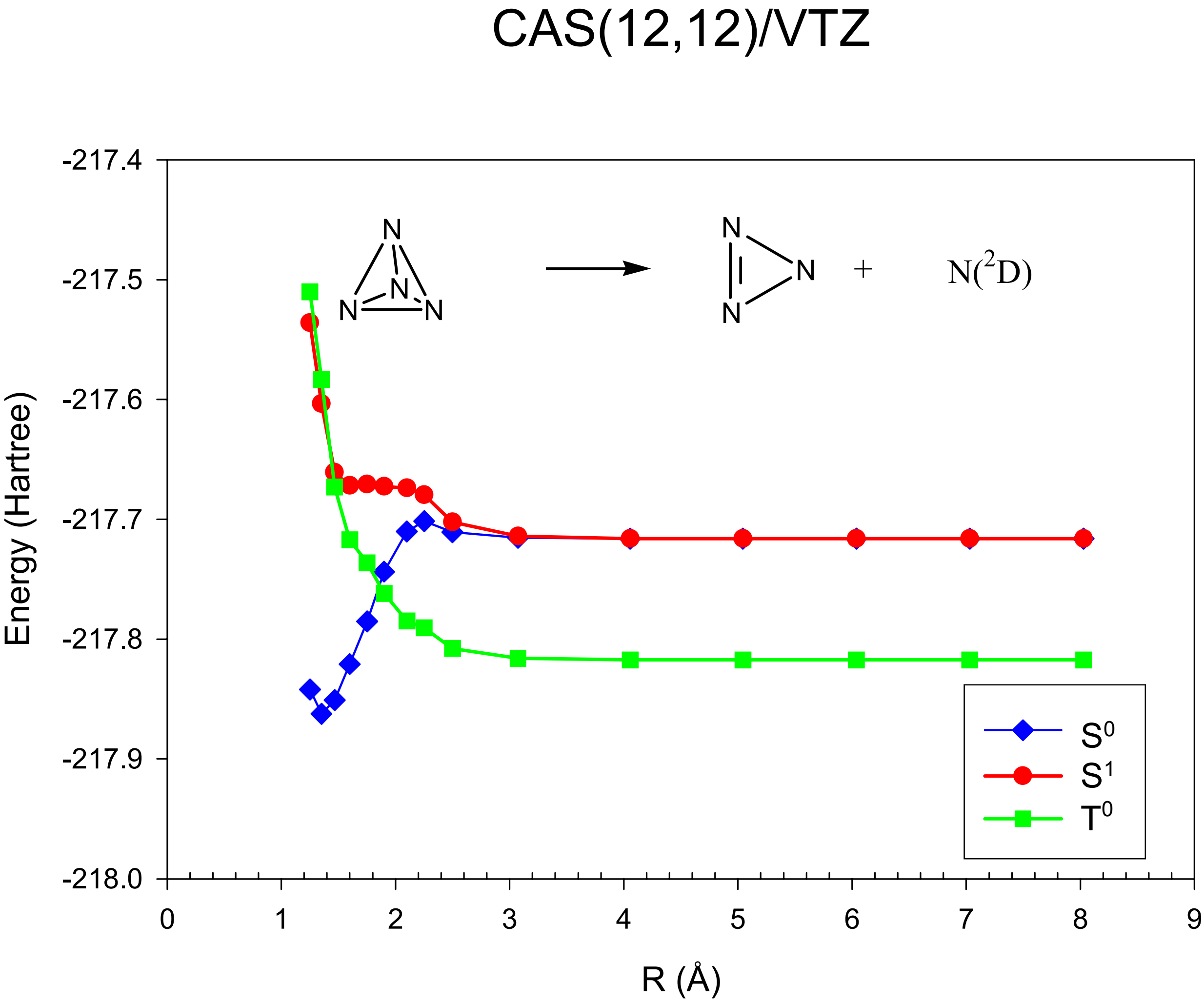

Fig. 35. QM calculations on the dissociation pathway of $N_4(T_d)$, performed at CAS(12,12) level. The dissociation energy of $N_4(T_d)$ in its singlet ground state (blue curve) is approximately 4.7 eV at this level.

Laser-excitation of liquid nitrogen

The experiments using multiphoton excitation of liquid nitrogen have continued with experiments with ArF excimer laser, operating at 193 nm. Although there are no allowed excitation schemes, the high power of this laser might be used in order to cause electric breakdown in liquid nitrogen. This process could subsequently have the potential of generating N_4. Obviously, the energy is not a problem here, since the breakdown processes easily ionize N_2. We have verified this by recording breakdown spectra in air (Fig. 36).

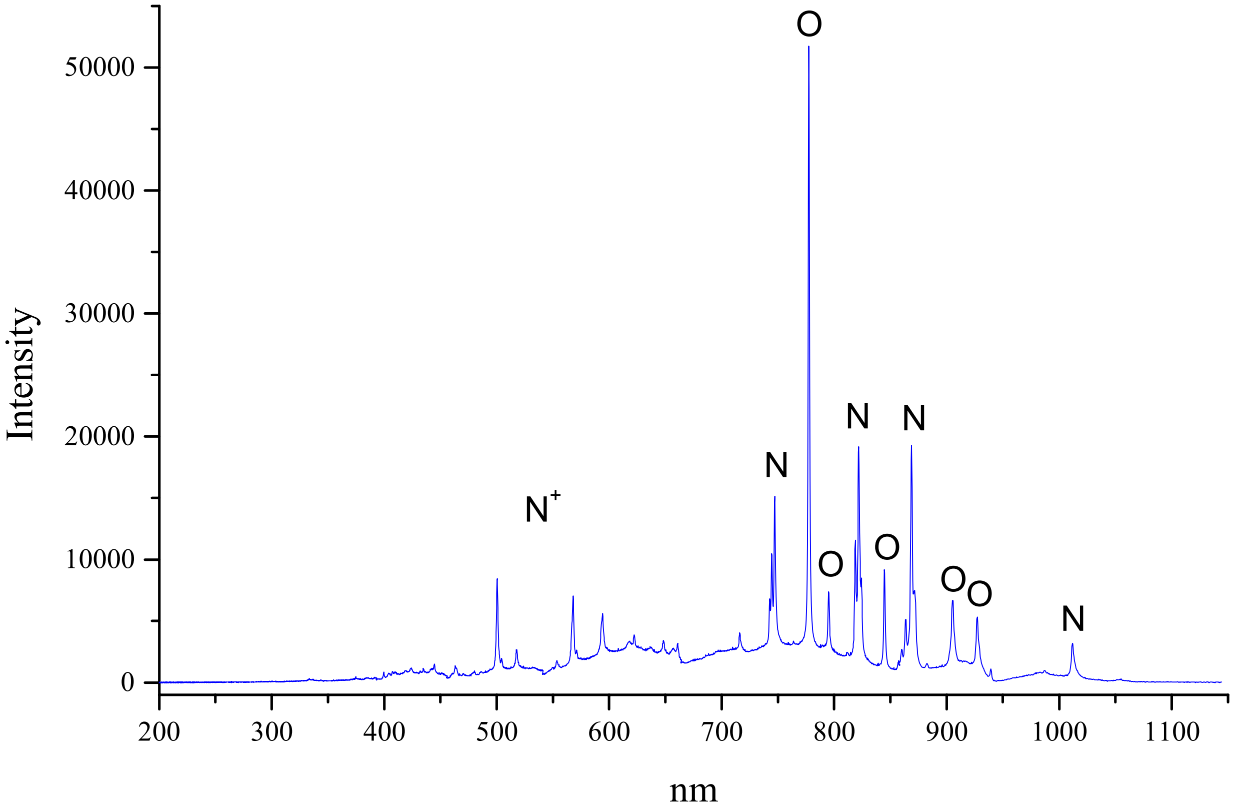

Fig. 36. Spectrum of laser-induced electric breakdown in air, using an ArF laser at 193 nm. The available energy at the focus was in the order of 100 mJ/pulse. The focal length of the lens was 7.5 cm. The exposure time was 100 s using a Mechelle 900 spectrometer. No molecular emission features are seen in this spectrum.

The experimental set-up for the liquid nitrogen breakdown experiments consists of a modified liquid nitrogen cryostat (JANIS), where a vertical, evacuated tube was inserted in order to minimize energy losses. A second reason for having the tube was the possibility of using short focal length lenses, necessary for small focal diameters. An overview of the experimental apparatus is shown in Fig. 37.

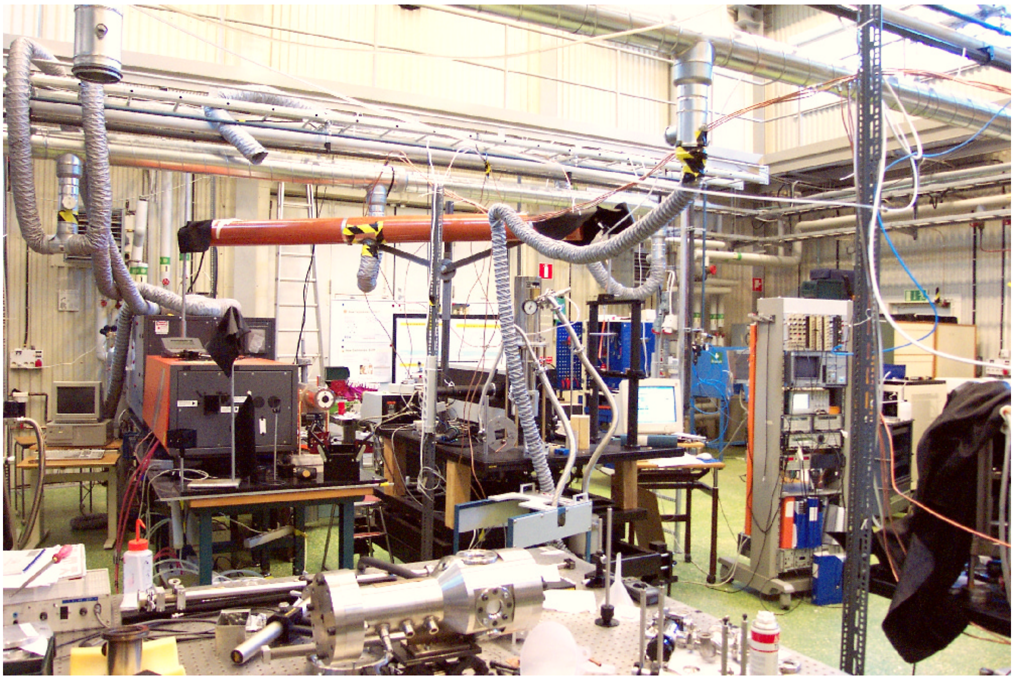

Fig. 37. The experimental equipment used in the liquid nitrogen experiments. *To the left:* The excimer laser in the background, the dye laser with orange cover in the foreground. *In the middle:* The cryostat and the SPEX 1000M spectrometer. *To the right:* The data collection equipment.

In the ArF liquid nitrogen experiments, we have not been able to see any electric breakdown in the liquid.

Experiments in a temperature-controlled cryostat

A CRYOCOOLER cryostat has been set up for temperature-controlled Raman experiments on matrices, built from microwave discharge products. The basic idea for these experiments is to avoid dilution of possible N_4 products through the excessive condensation of nitrogen, as is the case for the LEYBOLD cryostat experiments. The laser excitation experiments on solid nitrogen, mentioned in Ref. [1], can also be carried out using this set-up. The experimental equipment is shown in Fig. 38.

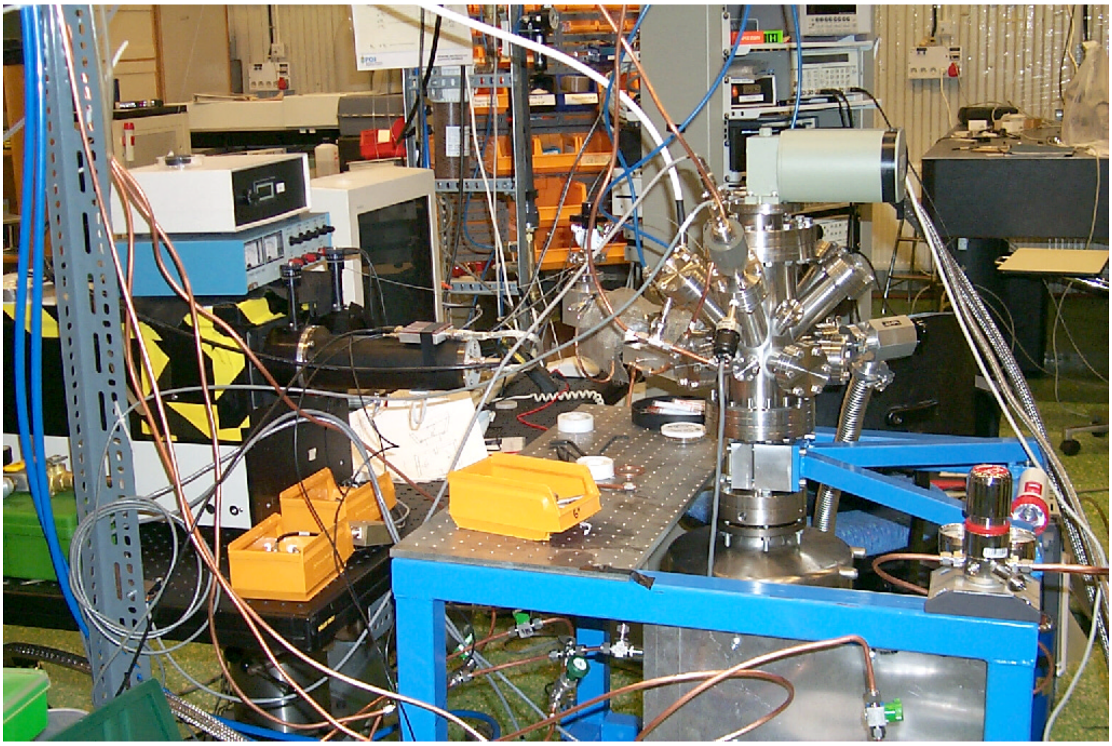

Fig. 38. The experimental set-up for the temperature-controlled experiments on cryogenic matrices. The cryostat and the microwave cavity, attached to a new cryochamber, are located to the right. The SPEX 500M monochromator is seen in the left part of the picture.

The equipment for the temperature-controlled experiments has now been set up. In these experiments, the microwave discharge will be run on different nitrogen-containing mixtures during extended periods of time, while keeping the sapphire window of the cryostat at a temperature above 77K, in order to avoid condensation of nitrogen. The deposited substances are subsequently analyzed using Raman spectroscopy with the 514.5 nm line of an Ar^+ laser, in combination with a notch filter (ORIEL 53682) with extinction of the laser light in the order of 10^{-6}. Several preparatory experiments have shown that the equipment is capable of running during extended periods of time (several days) without intervention. Fig. 39 shows the cryostat window during nitrogen deposition through a microwave discharge in one of the preparatory experiments at 20 K, with no warming being applied on the cryostat window.

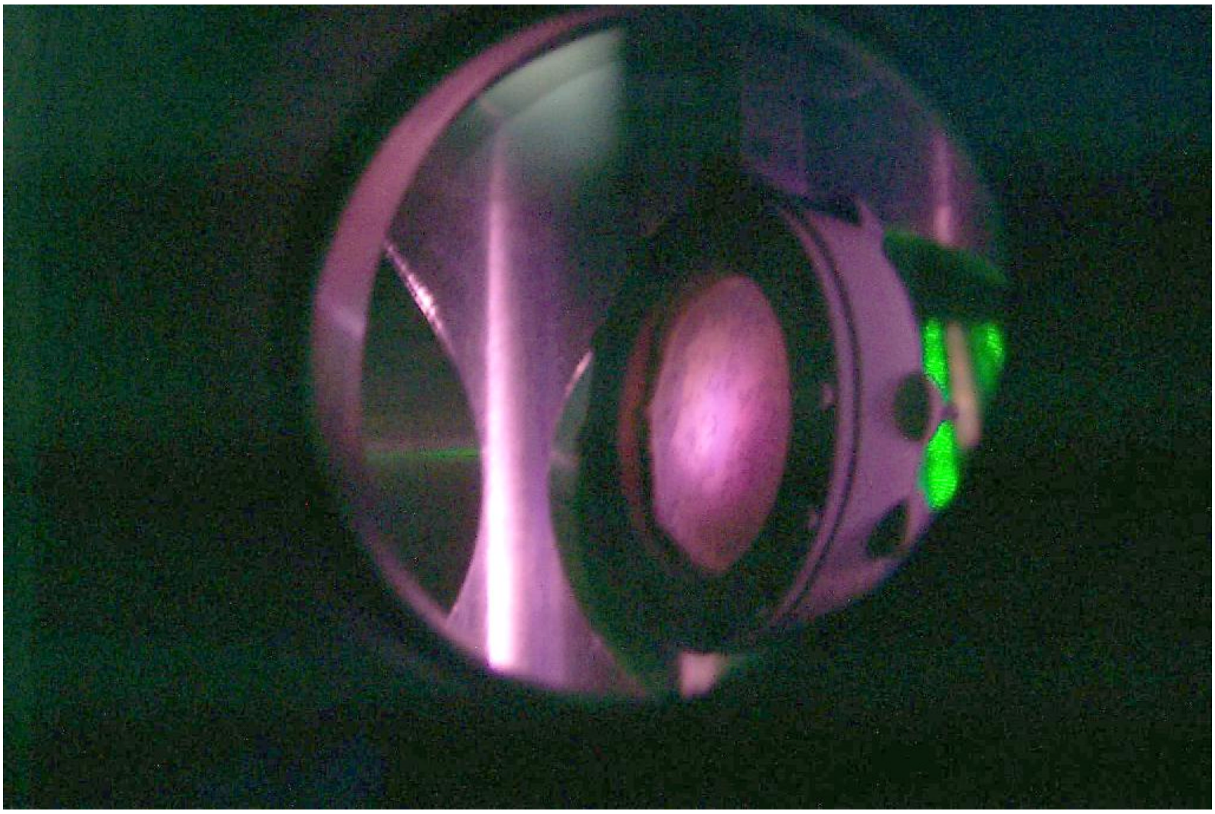

Fig. 39. The CRYOCOOLER cryostat window at 20 K during deposition of a 50/50 N_2/Ar mixture through a microwave discharge. The magenta color arises partly from nitrogen emission in the discharge tube (not shown). The green color is due to scattered light from the Ar^+ laser (blocked).

Fig. 40. The CRYOCOOLER cryostat window after several hours deposition of a 50/50 N_2/Ar mixture through a microwave discharge. The discharge was shut off while taking this picture. The origin of the magenta color of the matrix is not known at present.

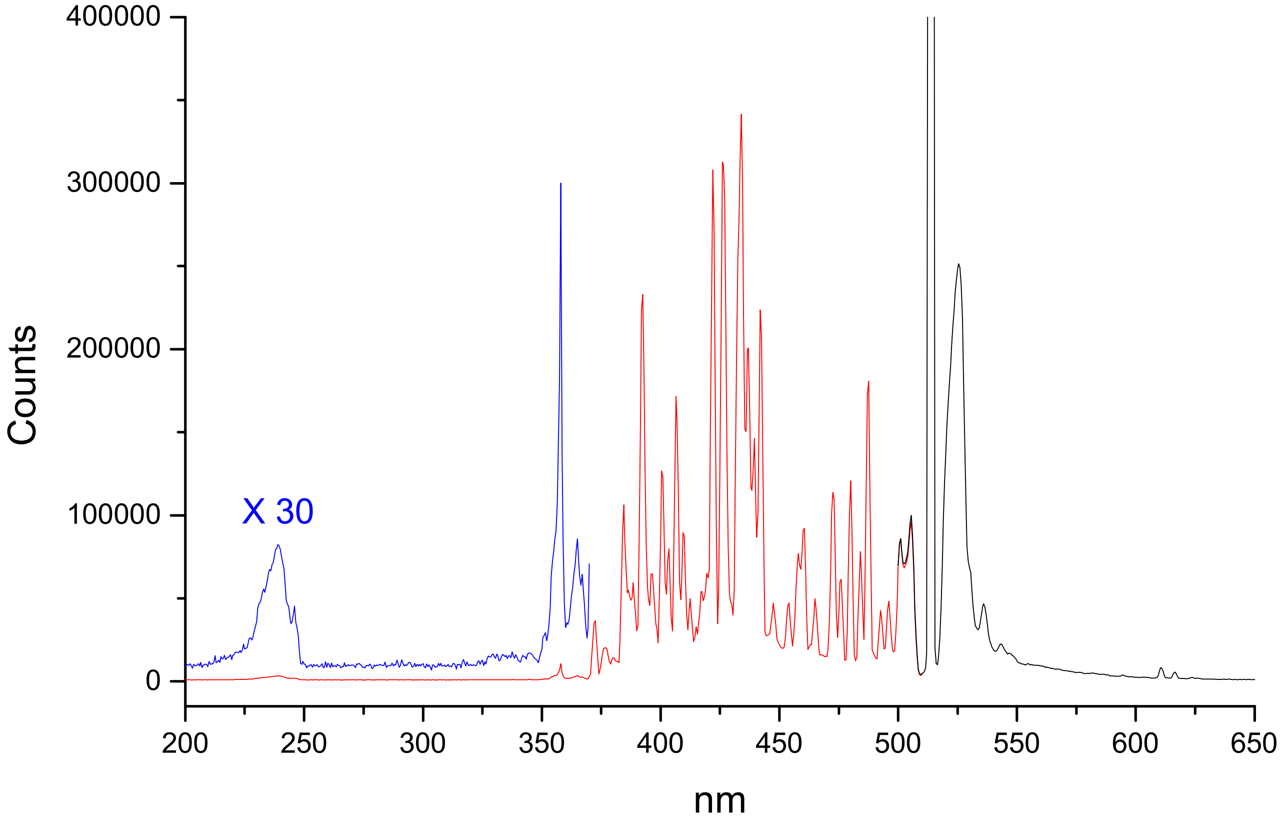

Fig. 41. Spectrum of the material deposited on the cryostat window of Fig. 40. The sample was excited by the 514.5 nm line of an Ar^+ laser, attenuated in this spectrum by a notch filter. The strong bands between 350 and 500 nm are all laser-excited and so far unassigned.

Theoretical calculation of the density of N_4

For theoretical estimates of the density of N_4, the program MOLPAK (MOLecular PAcKing) from University of Maryland [8] has been used. MOLPAK uses the calculated electrostatic potential surfaces from Gaussian 98 as a starting-point for the molecules to be packed. MOLPAK uses group theory to pack the molecules in 29 different space groups and the minimum energy is calculated for each space group. The space group which gives the lowest energy is considered as the most probable packing and the corresponding density is the estimated theoretical density. The MOLPAK program has not been written for pure nitrogen clusters, so there is an uncertainty in the prediction of the density. Especially for $N_4(D_{2h})$ one can choose between four different orbital bondings (atom code volume additivity). A more thorough evaluation of the space groups would lead to more accurate results.

Molecule	**Density (g/cm^3)**
$N_4(T_d)$	2.26
$N_4(D_{2h})$	2.17 – 2.62

The resulting calculated densities, extracted from MOLPAKs output data.

Plan for the second half of the year 2001

The main emphasis during the rest of the year 2001 will be on continued N_4 synthesis experiments with long integration times. The experiments will be carried out on liquid nitrogen samples, solid nitrogen matrices and samples containing heterocyclic high-nitrogen compounds at cryogenic and room temperatures.

The N_4 synthesis experiments using laser excitation of liquid nitrogen in capillary tubes will be set up starting from July 2001. We will use three excitation schemes (5, 7 and 9 in Ref [2]) with excitations at 208.8, 222.75 and 202.3 nm, respectively.

The cryogenic matrix bombarding experiments in the LEYBOLD cryostat will continue. During the second half of 2001, we will perform SERS experiments on cryogenic matrices, as well as further experiments on heterocyclic compounds

The temperature-controlled cryostat experiments will continue. The experiment will utilize the CRYOCOOLER cryostat in combination with a SPEX 500M monochromator, an Ar^+ laser and an optical multichannel analyzer.

LIF experiments on excited nitrogen matrices will be performed using pulsed lasers in combination with gated detection, in order to rationalize the large number of unassigned features presented in this report.

Summary

Activities:

- Ion bombardment, microwave-excitation and hollow-cathode excitation experiments of solid N_2 have been performed in the 16-port cryochamber. Several synthesis experiments with long integration times have been carried out.
- A second cryostat has been set up for laser excitation experiments and preparations have been made for temperature-controlled matrix excitation experiments with Raman detection using the 514.5 nm line of an Ar^+ laser.
- Initial tests have been made on excitation of liquid nitrogen with a 193 nm ArF laser.

Progress:

- A number of unassigned features have been observed in ion bombarding, microwave-excitation and hollow-cathode excitation experiments on nitrogen-containing matrices.

Expectations for the rest of the year 2001:

- Continued long-time experiments on different nitrogen-containing cryogenic matrices will hopefully reveal the carriers of the unassigned features observed so far.
- Laser excitation experiments of excited solid nitrogen in both cryostats will be carried out, envisaging the possibility of two-laser experiments.
- Capillary experiments will hopefully answer some of the questions in the laser excitation experiments on liquid nitrogen.

- A continuation of the experiments on the heterocyclic nitrogen-rich compounds is envisaged.
- And of course our ultimate goal: The successful synthesis and detection of N_4.

Reports:

- Two reports have been written (Refs. 1 and 5 in the reference list).
- Three articles have been published. (Refs 3, 4 and 6 in the reference list).

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Report title
The N_4 project. Activity report for the first half of the year 2001.

Abstract (not more than 200 words)

A summary of activities and achievements within the N_4 project during the first half of year 2001 is presented.

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En sammanfattning över aktiviteter och resultat inom N_4 projektet under det första halvåret av 2001 presenteras.

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