Contents

Introduction

During the third quarter of 2001, the main efforts within the N_4 project have been concentrated to electric discharge excitation, ion-bombarding, microwave excitation and α-particle excitation experiments on cryogenic nitrogen-containing matrices in two different cryostats. Several synthesis attempts have been made using long integration times in order to suppress random noise. A time-of-flight mass spectrometer has been set up for CO_2 laser decomposition experiments on high-nitrogen compounds, previously synthesized and characterized through Raman spectroscopy. Capillary experiments of liquid nitrogen with multiphoton excitation at three different UV wavelengths have been prepared for. Initial experiments on SERS (Surface-enhanced Raman spectroscopy) have been made on previously known substances.

Synthesis experiments in cryogenic matrices

As mentioned in Ref. [1], the most important conclusion from the experiments carried out so far is that we have been able to deposit, excite and manipulate nitrogen 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 $N_4(T_d)$ through the combined and spontaneous process:

1. $N(^4S) + N(^4S) \rightarrow N_2(A^3\Sigma_u^+)$
2. $N_2(A^3\Sigma_u^+) + N(^4S) \rightarrow N_2(X^1\Sigma_g^+) + N(^2D)$
3. $N_2(X^1\Sigma_g^+) + N(^2D) \rightarrow N_3(C_{2v})$
4. $N_3(C_{2v}) + N(^2D) \rightarrow N_4(T_d)$

Long-time experiments, described in Ref. [1] have been continued using isotopic substitution. The question of the complexity of the δ' group in the near infrared has been further addressed through additional long-time and warming-up experiments on matrices containing atomic nitrogen. A recent isotopic substitution experiment on the δ' group is shown in Figs. 1-3.

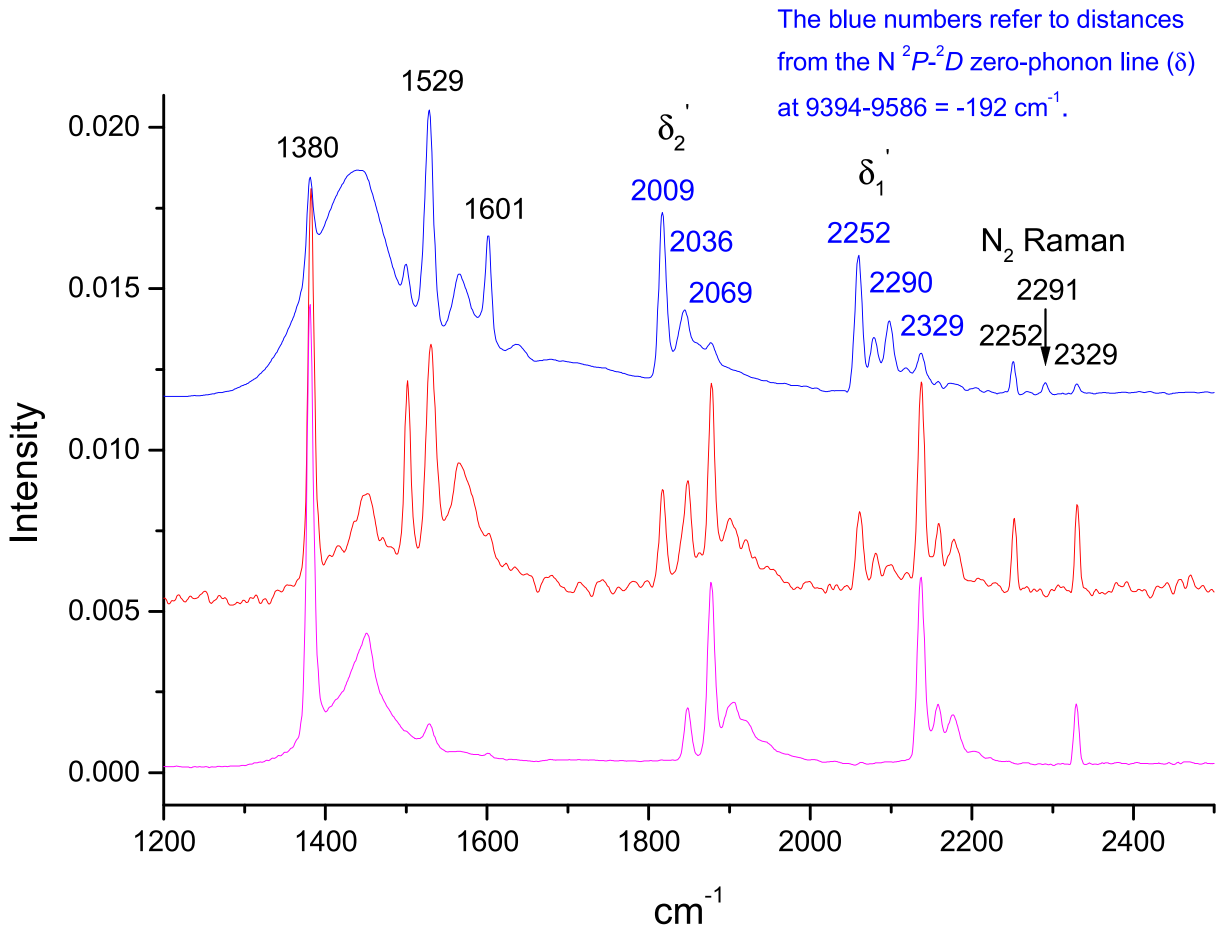


Fig. 1. Isotopic substitution experiment on the δ' group in a nitrogen matrix (cf. Fig. 21 in Ref [1]). The present spectra were recorded during the warm-up phase of two matrices, built up using a microwave discharge in pure $^{14}N_2$ (magenta) and in mixtures of $^{14}N_2$ and $^{15}N_2$ (red and blue). In the blue spectrum, we now have a substantial concentration of $^{14}N^{15}N$ in the matrix, as seen by its Raman line at 2291 cm^{-1}. Observe that the blue numbers in the spectra are measured from a different origin (-192 cm^{-1}). The Raman lines at 2252, 2291 and 2329 are due to the $^{15}N_2$, $^{14}N^{15}N$ and $^{14}N_2$ species, respectively. The intensity enhancements in the δ'_1 subgroup at 2290 and 2329 cm^{-1} (in blue) are consistent with the $^{14}N^{15}N$ and $^{15}N_2$ Raman intensities, while the δ'_2 subgroup is difficult to interpret. The features at 1529 and 1601 cm^{-1} are due to the YAG-excited $a^1\Delta_g \rightarrow X^3\Sigma_g^-$ bands of O_2, often present as impurity due to quartz tubing of the discharge.

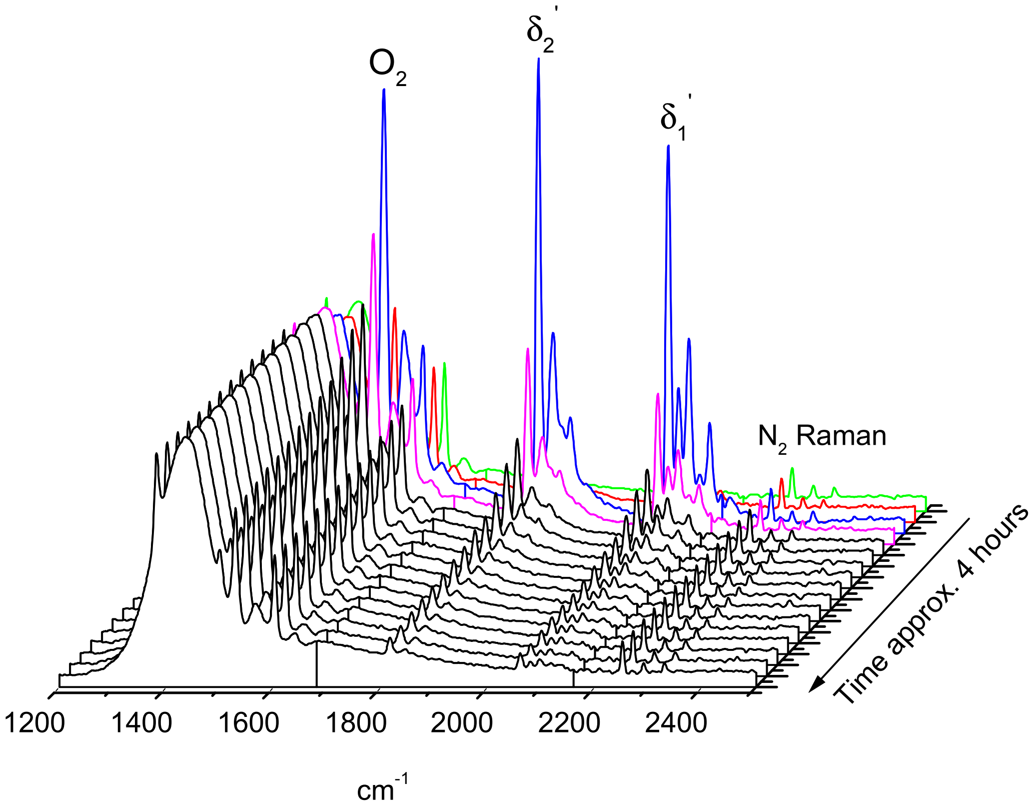


Fig. 2. Time evolution in the blue spectrum of Fig. 1. Each spectrum was recorded during 15 minutes. The first one at a temperature of 12.3 K, the second one at 13.5 K and the remaining spectra (beginning from the blue one) at 15.0 K. Note that the O_2 impurity is also consumed during the process, although less rapidly than the N-atoms.

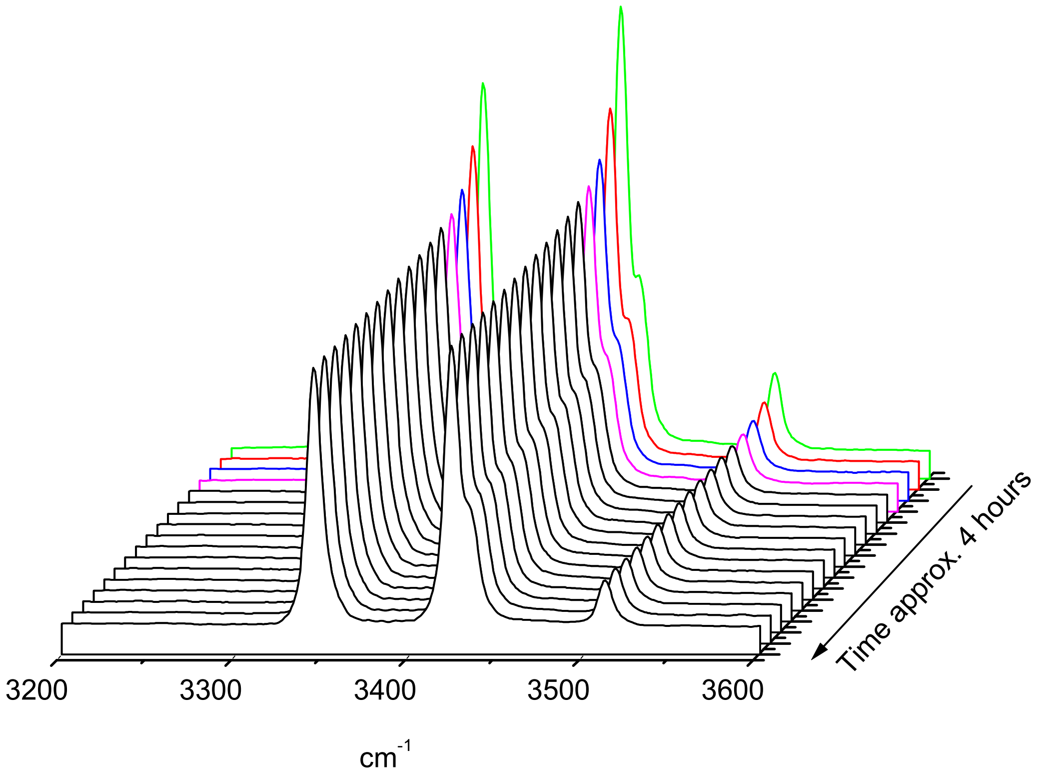


Fig. 3. Time evolution of the unidentified doublet in the same recording as in Fig. 2. Clearly, the doublet intensity is affected only marginally by the processes shown in Fig. 2, except for the initial minor decrease. Note that the second doublet due to ^{15}N (cf. Fig. 8 in Ref [2]) is negligible in the present recording, despite the fact that species due to ^{15}N dominate in Fig. 2.

Laser-excitation of liquid nitrogen

The concept of laser synthesis of $N_4(T_d)$ in liquid nitrogen is based on the assumption that the process $N_2 + N_2^* \rightarrow N_4(T_d)$ is a possible way of producing tetrahedral N_4. Here, N_2^* designates a nitrogen molecule in an excited state with an energy of at least 87000 cm^{-1} (11 eV) above the ground state. Ten possible excitation schemes have been suggested in Ref. [3].

We are now using three of these schemes (5, 7 and 9) in experiments, where the UV laser beam is sent through a capillary with an inner diameter of 1 mm, immersed in liquid nitrogen. The capillary is fixed in a vertical position, and imaged onto the entrance slit of a 1 m monochromator (SPEX 1000M). Our primary goal is to monitor a successful multiphoton excitation of liquid nitrogen through gated fluorescence. Since the actual detection threshold of $N_4(T_d)$ through Raman spectroscopy is quite high, the experiment is set up so that long-time integration is possible.

Experiments in a temperature-controlled cryostat

The set-up of the CRYOCOOLER cryostat for Raman measurements with an Ar^+-laser so far gives poor Raman signals, probably due to lack of incident power on the matrix. Changes of the setup will be (and partly have been) performed in order to enhance the power that reaches the matrix and to focus the energy to a small spot. This includes changing to a more suitable optical fiber and to get a coupling of the fiber to the inside of the vacuum chamber in order to decrease the distance to the matrix as well as mounting a focussing lens at the fiber end.

In the meantime a few more experiments have been made studying the laser induced fluorescence previously reported [1] from matrices deposited through a microwave discharge. These bands are still unassigned, but it has been shown that they must originate from N_2 since they appear also from a matrix of N_2 and Ar directly deposited on a sapphire window. It has been checked that the window itself does not generate these bands. The bands are broadened in a matrix with higher nitrogen content (Fig. 4) which is consistent with the fact that nitrogen molecules interact more with each other in such a matrix.

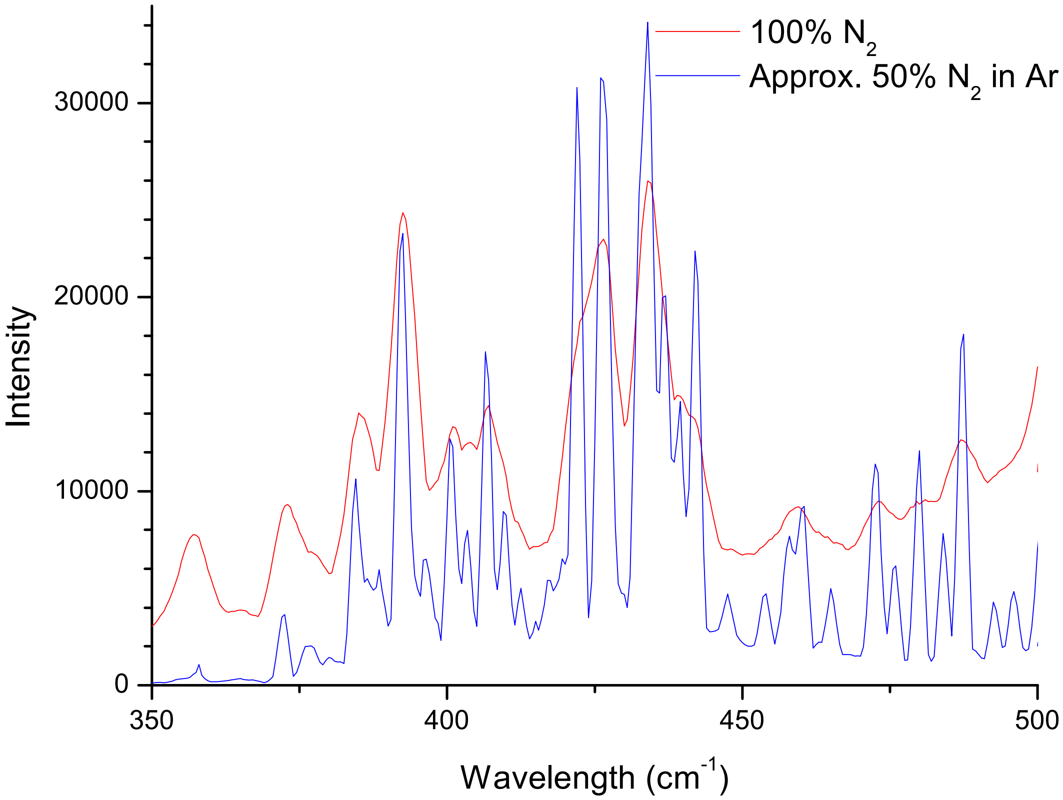


Fig. 4. Fluorescence spectra of solid nitrogen excited by the 514.5 nm line of an Ar^+ laser. All bands are laser-excited and still unassigned.

Calculations show that combination of two nitrogen molecules in the $A^3\Sigma_u^+$ state is favorable for the formation of N_4. A problem with this in an experimental approach is of course to obtain large enough population in the $A^3\Sigma_u^+$ state to make the process likely. If this could be achieved, however, this would be an alternative synthesis route to N_4. Therefore some attempts to optimize the concentration of molecules in the $A^3\Sigma_u^+$ state have been made.

It has been found before [2] that α-particle bombardment of the matrix results in a high population of the v=0 level of the $A^3\Sigma_u^+$ state. It can be argued that the population is still far too low to make the combination of two nitrogen molecules in the $A^3\Sigma_u^+$ state likely. However considering that the α-particles that create these nitrogen molecules in the $A^3\Sigma_u^+$ state will deposit its energy along a trace in the matrix, it is likely that these molecules are found next to each other. It may therefore be of interest to investigate this further.

Recent experiments with α-particle bombardment of the matrix have revealed that the intensity of the Vegard-Kaplan bands ($A^3\Sigma_u^+$- $X^1\Sigma_g^+$) is strongly dependent on the temperature (Fig. 5). The intensity curve may differ slightly in shape, but always seems to have a maximum intensity around 32 K and dies off to about the same intensity as in the 18 K matrix at about 37-38 K. The process is reversible. Since the mechanism is not yet known the reasons for this behavior cannot be proven, but it is reasonable to assume that the increase of intensity with increased temperature is due to the increased mobility of the molecules involved. It is also worth noticing that nitrogen has a phase transition at 37 K.

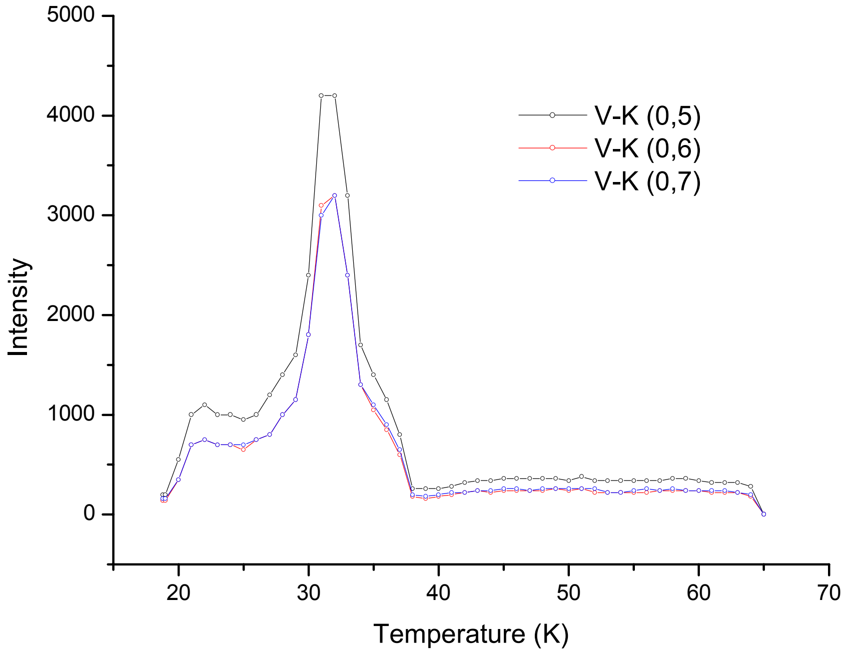


Fig. 5. The temperature dependence of the (0,5), (0,6) and (0,7) bands of the $A^3\Sigma_u^+$- $X^1\Sigma_g^+$ transition.

Bombarding the matrix with nitrogen ions from the ion gun also gives the Vegard-Kaplan bands under certain conditions. The bands are then very much stronger than what can be obtained with α-particle bombardment. The conditions under which the Vegard-Kaplan bands are strongest must be optimized. It has been seen that a slight alteration of the experimental conditions may make the Vegard-Kaplan bands disappear completely in favor of other, yet unidentified, bands.

In future experiments we plan to put a filament near the matrix in order to spray the matrix with electrons and see whether this has any similar effects. We will also try to measure the lifetime of the $A^3\Sigma_u^+$ state in the matrix. An accurate value is needed in order to be able to estimate the concentration of molecules in the $A^3\Sigma_u^+$ state. A preliminary estimate of the molar concentration, assuming that the lifetime is identical to the gas-phase value (1.9 s) gives a value of 10^{-8}, with an estimated inaccuracy of at least 1 order of magnitude.

We are not yet certain of the mechanism giving the $A^3\Sigma_u^+$- $X^1\Sigma_g^+$ transition. A VUV study of the matrix during ion bombardment is also planned. In order to optimize the concentration of molecules in the $A^3\Sigma_u^+$ state it is helpful to understand the process leading to it. Knowing if any higher energy transitions are present may help to do so. We plan to make a long time synthesis experiment with this setup before the end of the year.

Decomposition of high nitrogen content materials

Vapour deposition of 5-t-butyl-1H-tetrazole onto a sapphire window.

During the previous attachment 5-t-butyltetrazole was subjected to a number of high-energy techniques such as UV photon excitation, microwave irradiation and nitrogen ion bombardment to determine whether any decomposition or structural rearrangements took place with the possibility of producing new nitrogen cages or structures [2]. In all the experiments carried out the sample was in the form of a solid pellet or confined in a capillary.

Initial work for this attachment was to repeat the results obtained from the previous visit except the sample of 5-t-butyl-1H-tetrazole would not be a solid disc but either a fine vapour deposited layer or an intimate tetrazole/nitrogen mixture deposited on a sapphire window. This would allow for direct irradiation of the sample to take place while Raman spectra were being recorded. This would allow for a more dilute sample to be studied that may have given some insight into any reaction mechanisms occurring during excitation.

Three methods were attempted to vapour deposit the 5-t-butyl-1H-tetrazole onto the sapphire window: -

i) The sublimation of 5-t-butyl-1H-tetrazole at room temperature at a pressure of 3-8x10^{-7} mbar onto a cold head at 12K. On leaving the sample for several hours the tetrazole appeared to have migrated from the sample holder into the main chamber. There was visible evidence of a white deposit on the copper cold head and also a build up of a white solid at the end of the stainless steel inlet tube leading from the sample chamber to the main chamber (Fig. 6). On analysing the deposit on the sapphire window using Raman spectroscopy the only signals observed were due to the impurities and the continuum of the sapphire window.

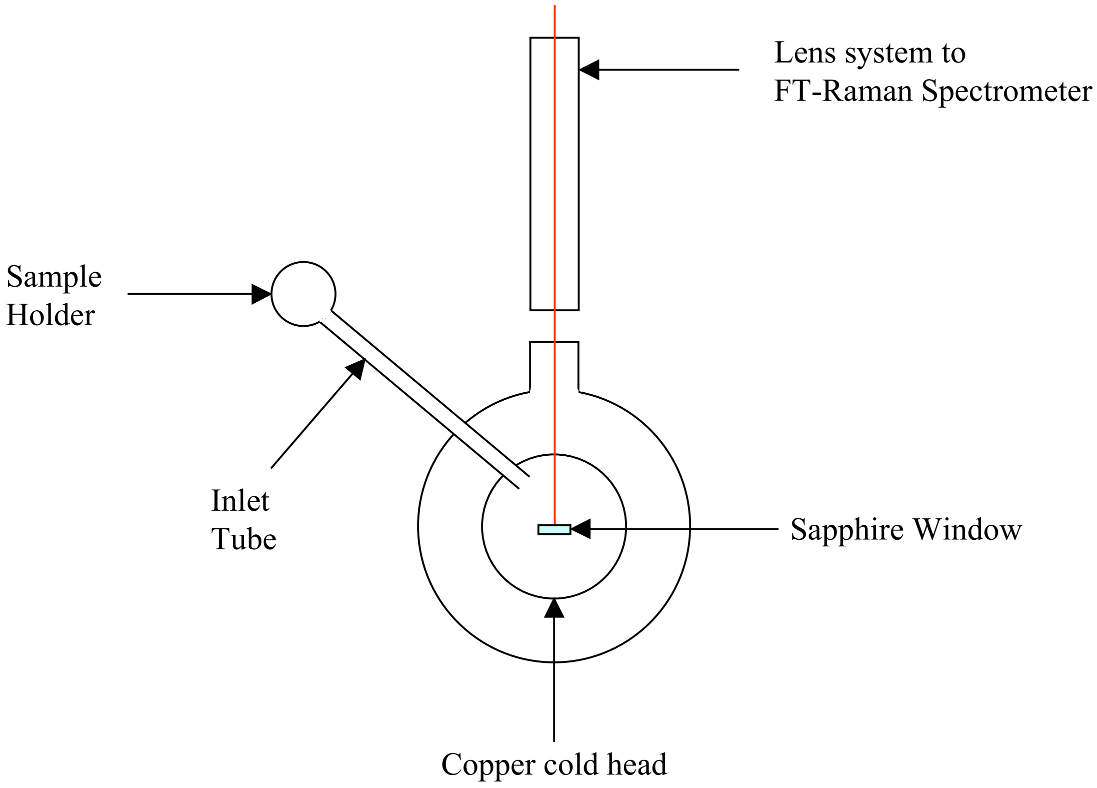


Fig. 6. Top view of the vapour deposition experimental set-up.

ii) Similar to the method above except that the external surfaces of the inlet system and the sample chamber were heated using heating tape. A temperature of 60°C was chosen. It was envisaged that thermal conduction through the metal surfaces would increase the rate of migration of the 5-t-butyl-1H-tetrazole through the system and increase the amount of deposition onto the sapphire window. The rate of sublimation increased, as did the amount of white deposit observed on the copper cold head and at the end of the inlet tube however, the sapphire window showed no evidence of any deposited material.

iii) This method involved passing nitrogen gas through the heated sample to act as a carrier gas and a medium to trap the 5-t-butyl-1H-tetrazole on the sapphire window. On passing the nitrogen through the sample for several hours a white deposit had formed over the cold head and the sapphire window. On examination of the deposit on the window using Raman spectroscopy a number of new signals were observed. Analysis of the spectrum assigned the signals as being due to oxygen impurity. The oxygen was introduced from a small leak in the gas chamber. There was no evidence of any 5-t-butyl-1H-tetrazole trapped within the matrix.

The vapour deposition of the 5-t-butyl-1H-tetrazole was proving to be more difficult than expected and owing to the time constraints on the attachment further efforts were not pursued.

Microwave irradiation of a pressed disk of 5-t-butyl-1H-tetrazole in a copper holder was carried out. The sample was cooled to 12K and then irradiated for several minutes by a neon plasma. The sample was then analysed by Raman spectroscopy.

Initial spectra were dominated by black body radiation caused by the heating effect of the microwave radiation. As the sample and the surroundings cooled the black body radiation reduced and the spectra due to the sample dominated. On comparing the Raman spectra of the material before and after the microwave irradiation the spectra were identical and there was no evidence of any decomposition occurring. However on irradiation of the sample with the Raman YAG laser after the microwave irradiation did cause a broad band to appear in the region 3500-2250 cm^{-1} that may be caused by LIF of a very low concentration species which could not be detected under the conditions that were used.

Further work has to be carried out on these experiments to try to determine what species is giving rise to these emissions.

UV decomposition studies of high nitrogen content materials in a mass spectrometer.

A recently published Japanese Patent [9] reports the formation of a number of nitrogen species N_x (where x = 4,5,6,..,10) by the decomposition of cyanuric azide using UV photolysis in a mass spectrometer. The laboratory at FOI has commissioned a mass spectrometer that is now capable of repeating the work carried out in this patent.

A time of flight spectrometer will be used with a window to allow a beam from a CO_2 laser to photolyse the material (Fig. 7). The products produced by the photolysis will be ionised by a filament and the corresponding ions detected by a dual multichannel plate detector and the output monitored using a LeCroy LC684DL 1.5 GHz oscilloscope. The output can be analysed using either Excel or LabView routines.

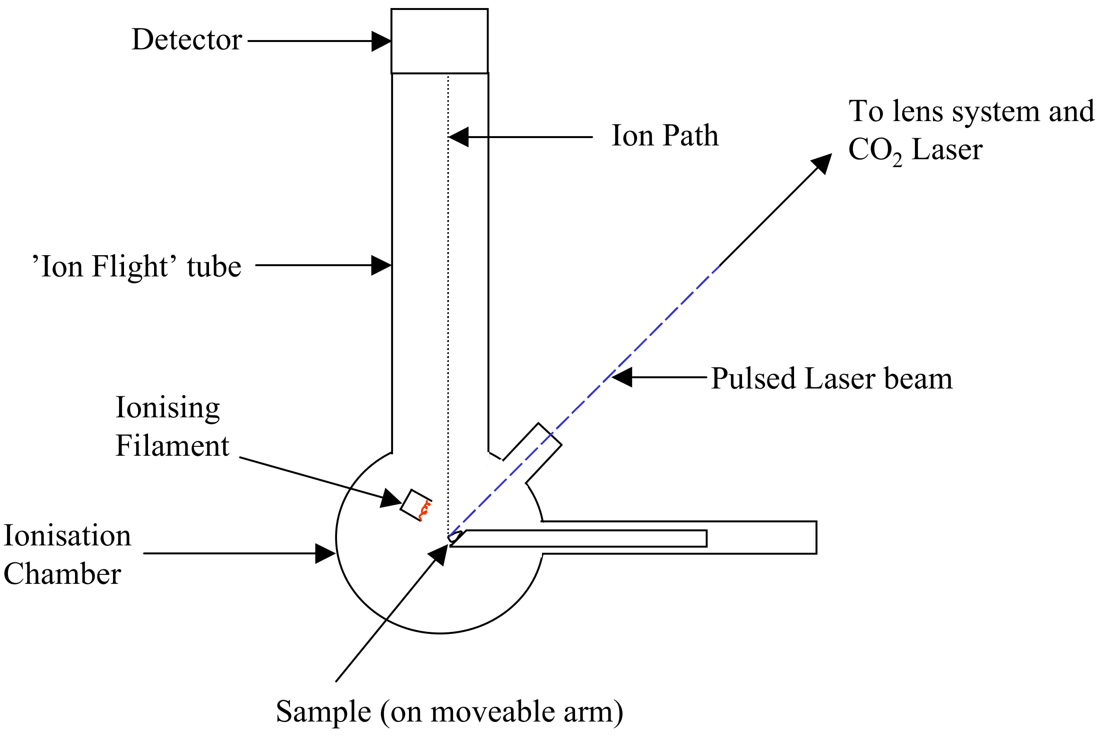


Fig. 7. Top view of the experimental set-up for the time of flight mass spectrometer decomposition experiments.

Decomposition studies have recently started on 5-t-butyl-1H-tetrazole and it is hoped that these will be extended to include cyanuric azide, phenyl pentazole and π–cyclopentadienyl cobalt (1,4-dimethyl tetraazadiene).

A typical mass spectrum obtained from the UV photolysis of 5-t-butyl-1H-tetrazole is shown in Fig. 8 with a potential fragmentation scheme outlined in Fig. 9. It is hoped that by increasing laser power the sample will undergo different fragmentation pathways. If the sample can be detonated it is hoped that the recombination of excited nitrogen atoms may bring about the formation of the nitrogen species observed in the Japanese work [9].

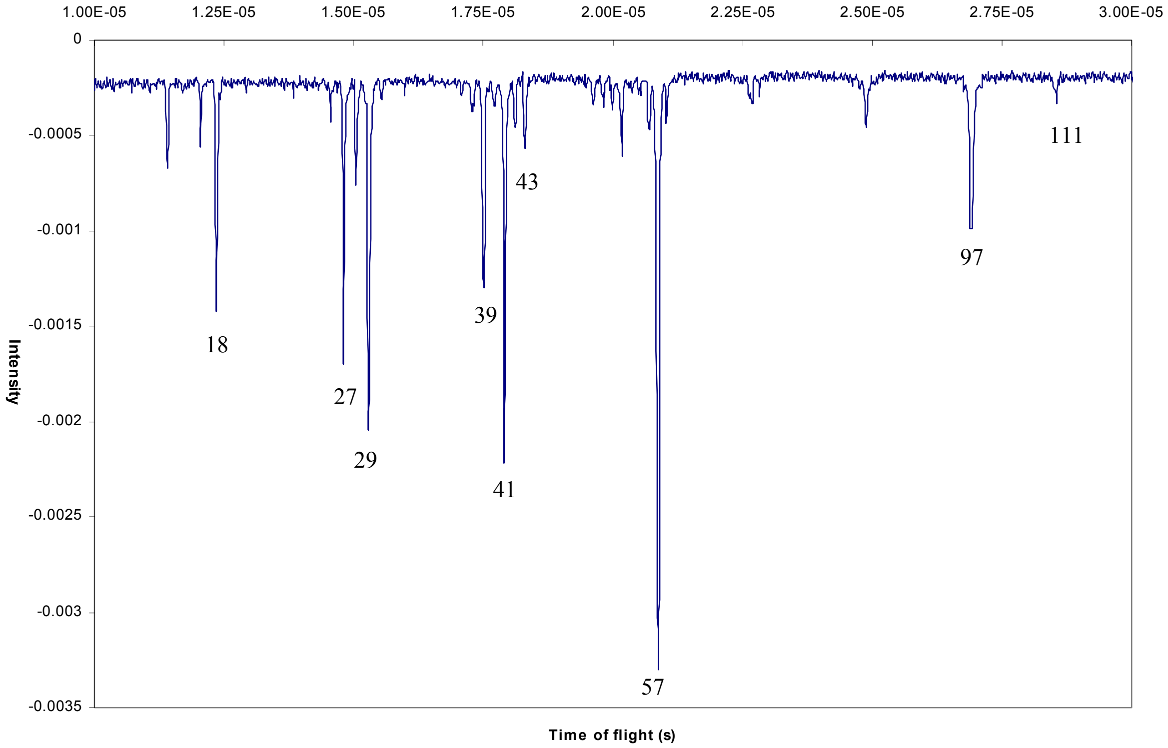
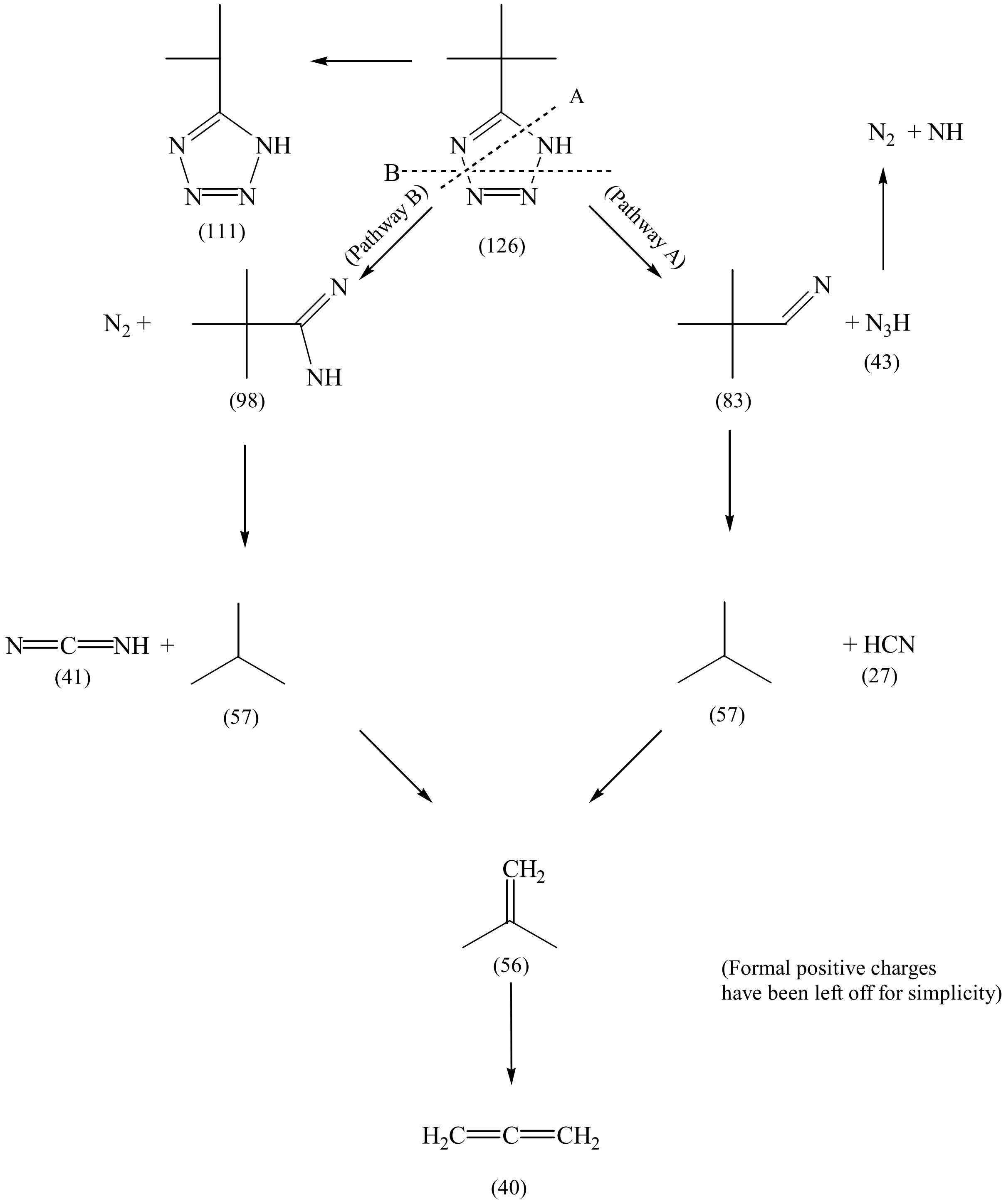


Fig. 8 Mass Spectrum for the UV decomposition of 5-t-butyl-1H-tetrazole.



(Formal positive charges
have been left off for simplicity)

Fig. 9. Suggested fragmentation scheme of 5-t-butyl-1H-tetrazole.

A potential problem of identifying mass fragments for example N_4 and t-butyl fragment [9], which both have molecular peaks m/z 56 should be overcome by increasing the resolution power of the mass spectrometer. The spectrometer has the ability to distinguish between carbon monoxide and molecular nitrogen which both have a molecular weight of 28.

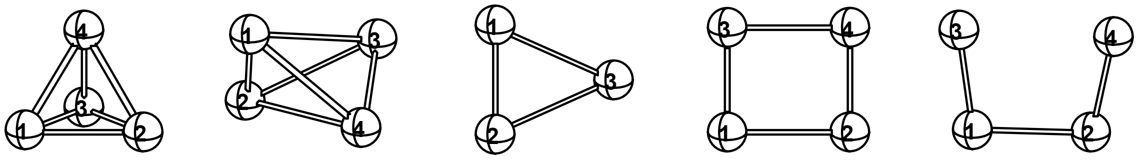
Ab initio [10] calculations on N_4^+ have shown this species to be sufficiently stable to be analysed by mass spectrometry. The ion is predicted to have D_{2d} symmetry with a partially distorted bond angle of 67º.

By varying the ionisation voltage of the ion source it could be possible to distinguish between N_4^+ as the linear, cyclic or tetrahedral species.

Work on the mass spectrometry studies is at a very early stage and further results will be discussed in subsequent reports.

Theoretical studies

Parallel to the experimental work theoretical studies have been performed with the objective to provide information that can aid the synthesis efforts. In an earlier study [4] we investigated the triplet N_4 potential energy surface using density functional theory (DFT) and high level ab initio methods, e.g. CASSCF, MRCI, and CCSD(T). We discussed the stability of the stationary points relative to the tetrahedral form of N_4. In particular, one stable triplet isomer of N_4 of D_{2d} symmetry was identified and characterized, and it was concluded that this isomer is likely to be an intermediate in synthetic routes which involve the formation of N_4 (T_d) from triplet excited states of N_2.



$N_4(T_d)$ **N_4^+ (D_{2d})** **$N_3(C_{2v})$** **$N_4(D_{2h})$** **$N_4(C_{2v})$ TS**

Fig 10. Optimized structure of stationary points discussed in this report in order of appearance.

One focal point of the continued work has been to identify alternative methods of detecting the N_4 isomers. We have previously determined the IR and Raman spectra of the two N_4 isomers and estimated their detection limits in Raman spectroscopy [5]. However, even with the use of high power lasers the detection limits for Raman spectroscopy are relatively high. Laser-induced fluorescence (LIF) is a much preferred method due to its higher sensitivity. In order to identify possible transitions to be used in LIF spectroscopy, the vertical electronic excitation energies for the lowest 11 singlet states of N_4 (T_d) were evaluated using time dependent DFT with the B3LYP functional and using EOM-CCSD (equation-of-motion CCSD) theory [7]. The EOM-CCSD/d-AVDZ calculations predict that there are two optically accessible singlet states of T_2 symmetry at 10.26 eV and 10.56 eV. These transitions are relatively weak. The transition to the third T_2 state, which is predicted to lie 10.65 eV above the N_4 (T_d) ground state, is stronger by about one order of magnitude. However, this state is still hard to reach using one-photon absorption, since the low excitation wavelength precludes the use of a high-power laser as the radiation source. We have therefore calculated the two-photon transition probabilities for excitation to the lowest lying states of N_4 (T_d) using the quadratic response CCSD (QR-CCSD) theory. The results from our calculations of both one-photon oscillator strengths and two-photon absorption probabilities are summarized in Table 1. It can be seen that some states that are one-photon dipole-forbidden are two-photon allowed, e.g. this is the case for the ^1E and $^1A_1$ states. However, for both one-photon and two-photon transitions the 3^1T_2 state is the most active. Since the ground state N_4 (T_d) molecule is strongly bound and, since the transition to the 3^1T_2 state is of Rydberg character, we believe this state to be bound. This fact together with the sizeable two-photon absorption probability is likely to make the 3^1T_2 state useful for detection by LIF spectroscopy.

Table 1. EOM-CCSD/d-AVDZ vertical excitation energies (ΔE_{vexc}) (in eV) and one photon oscillator strengths (*f*), and QR-CCSD/d-AVDZ two-photon transition probabilities (TPA) (in atomic units) for N_4 (T_d).

State	**ΔE_{vexc}**	*f*	**TPA**
1^1T_1	9.65	0.0	0.0
1^1T_2	10.26	0.0336	0.761
1^1E	10.28	0.0	15.818
2^1T_1	10.30	0.0	0.0
2^1T_2	10.56	0.0005	0.083
3^1T_1	10.60	0.0	0.0
3^1T_2	10.65	0.1974	253.6
4^1T_1	10.67	0.0	0.0
1^1A_1	10.75	0.0	12.44

Mass spectrometry with ion-detection may be an alternative method for detecting N_4 (T_d). However, this method requires that the formed N_4^+ cation is sufficiently stable to survive until detection. We have therefore investigated the tetrahedral region of N_4^+ potential energy surface. A stable D_{2d} minimum ($^2A_2$), which is slightly distorted from T_d symmetry, has been identified. The structural parameters, vibrational frequencies and ionization potentials are collected in Table 2.

Table 2. Equilibrium structure (Å, deg), harmonic frequencies (cm^{-1}), for N_4^+ (D_{2d},$^2A_2$), and the adiabatic ionization potential (eV) for N_4(T_d).

Method	R_{12}	R_{13}	α_{123}	$\omega_1(b_1)$	$\omega_2(e)$	$\omega_3(a_1)$	$\omega_4(b_1)$	$\omega_5(a_1)$	IP_{adiab}
CAS(12,11)/VTZ	1.295	1.686	67.4	362	543	570	1131	1371	
CCSD(T)/ VTZ	1.289	1.679	67.4						12.37

The energy of the N_4 (T_d) molecule relative to two N_2 molecules has been estimated to be 183 kcal/mol from CCSD(T)/VTZ calculations. This large energy difference makes it difficult to synthesize N_4 (T_d) using N_2 molecules as the reactants. We have therefore investigated the possibility of making N_4 (T_d) from nitrogen atoms and N_3 radicals. Electronically excited nitrogen atoms (^{2}D, ^{2}P) can be generated in a cryogenic environment. A suitable N_3 radical should have an appropriate geometrical configuration of the atoms in order to facilitate the generation of N_4 (T_d). The ground electronic state of the N_3 radical has a linear form and is not likely to be suitable for formation of N_4 (T_d). We have studied some other N_3 isomers hitherto not reported experimentally at various computational levels. These calculations indicate that a stable ring N_3 (C_{2v}) isomer should exist with a $^2B_1$ electronic state. This isomer has similar bond lengths and bond angles as N_4 (T_d), which indicates that it can be a suitable precursor for the N_4 (T_d) synthesis according to the scheme: $N_3(^2B_1)+N(^2D)\rightarrow N_4(^1A_1)$. Vibrational frequencies, IR and Raman intensities that can be useful for the detection of N_3 (C_{2v}) are presented in Table 3.

Table 3. Equilibrium structure (Å, deg), harmonic frequencies (cm^{-1}), zero point energy (kcal/mol), energy difference (eV), IR and Raman intensities (km/mol) for the ring N_3 (C_{2v},$^2B_1$) radical.

Method	R_{13}	R_{12}	α_{132}	$\omega_1(b_2)$	$\omega_2(a_1)$	$\omega_1(a_1)$
CAS(15,12)/ **VTZ**	1.483	1.232	49.1	285	826	1632
B3LYP/ **AVDZ**	1.457	1.229	49.9	351 [12.88]^a (13.56)^b	905 [0.24]^a (13.46)^b	1729 [4.19]^a (27.13)^b
CCSD(T)/ **AVDZ**	1.478	1.247	49.9	510 [5.62]^a	859 [0.56]^a	1631 [3.77]^a

[a] IR intensities, [b]Raman intensities

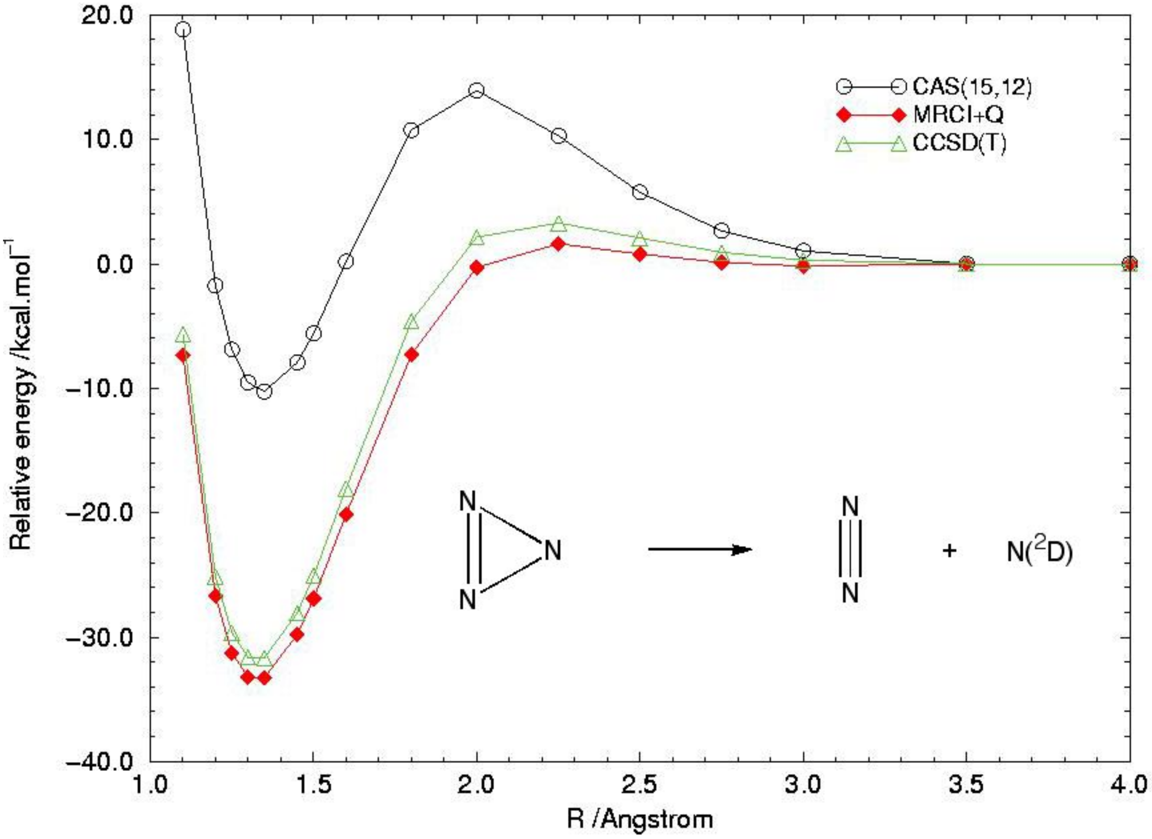


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Fig 11. The dissociation pathway of N_3(C_{2v}) calculated at various computational levels

The N_3 (C_{2v}) radical can be generated by the association of N(^{2}D) and ground state N_2. An analysis of the N_3 (C_{2v}) dissociation pathway at the MR-CISD(Q) level indicates that N_3 (C_{2v}) can be formed from these reactants with an activation energy of less than 1.5 kcal/mol. The dissociation energy of N_3 (C_{2v}) is close to 23 kcal/mol, which makes it sufficiently stable to be used as a precursor in N_4 (T_d) synthesis. The isomerization barrier for formation of the linear N_3 radical is also relatively high, 32 kcal/mol. However, it should be noted that also linear N_3 can be formed from N(^{2}D) and N_2 in a process with near zero barrier. In addition, our calculations indicate that reactive cross section for this process is larger than for the formation of N_3 (C_{2v}). Thus, it can be expected that N_3 (C_{2v}) will only be formed in relatively low concentrations.

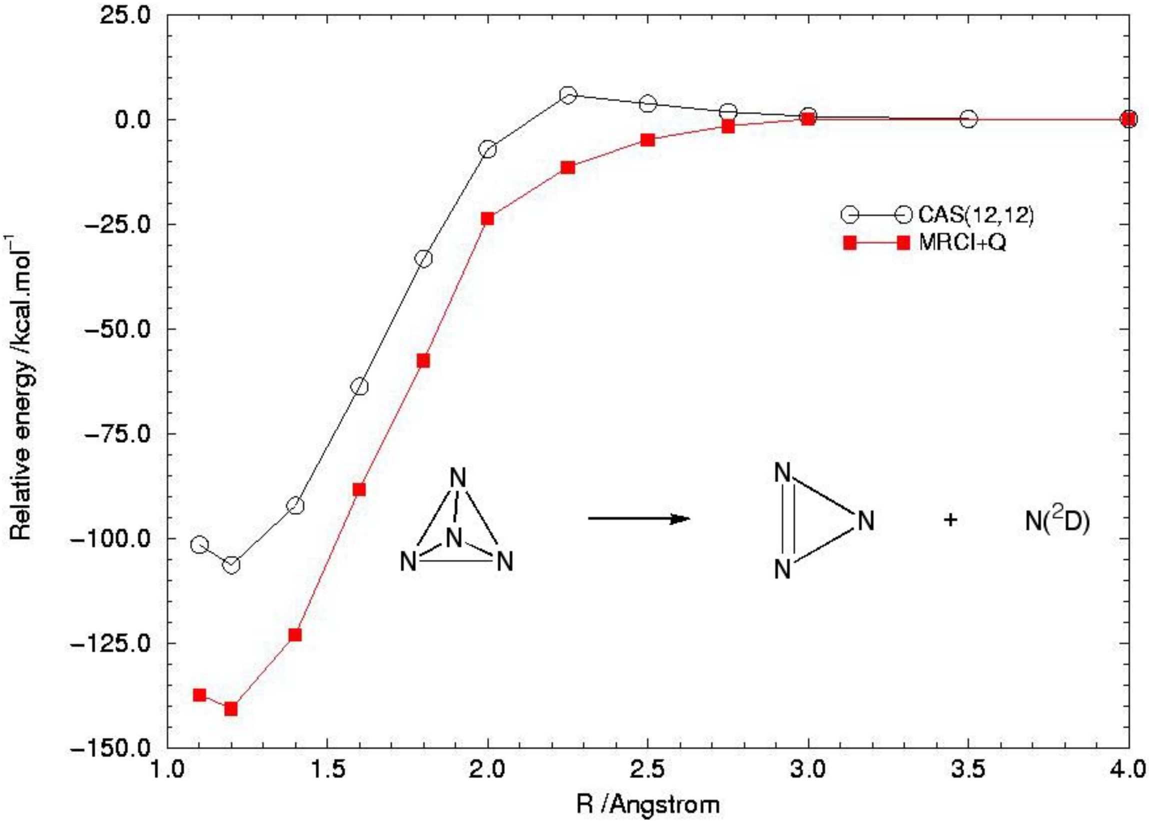


Fig 12. Reaction pathway for the dissociation of N_4 (T_d) to N_3 (C_{2v}) and N(^{2}D) computed at the CAS(12,12)/VTZ and MRCI(Q)/VTZ levels of theory.

In the next step we investigated the reaction of N_3 (C_{2v}) with N(^{2}D) to form N_4 (T_d). A scan of the potential energy surface at the CAS(12,12) level indicates that a perpendicular approach of N(^{2}D) towards the N_3 (C_{2v}) molecular plane is most favorable for reaction. This can also be rationalized from an analysis of the occupied orbitals in the two species. The N_4 (T_d) dissociation pathway calculated at the MR-CISD(Q) level indicates that N_4 (T_d) can be formed from N_3 (C_{2v}) and N(^{2}D) in a barrierless reaction, as is expected for a radical recombination process. However, the scan of the potential energy surface shows that the reaction channel is rather narrow and that N_2 molecules may be formed in a competing process.

The possible existence of other stable N_4 isomers than N_4 (T_d) is of particular interest. We have recently reinvestigated the rectangular N_4 (D_{2h}) molecule using high level *ab initio* methods [8]. Our study indicates that this isomer is of similar energy as N_4 (T_d), but much less stable. A C_{2v} transition state towards dissociation (N_4 (D_{2h}) → 2 N_2) was located and characterized at the CAS(12,12)/VTZ level of theory. The effective dissociation barrier was estimated to 6.5 kcal/mol from MR-AQCC/VTZ calculations. This shows that N_4 (D_{2h}) is considerably more stable than was indicated in an earlier study, and that it may be possible to synthesize and isolate at low temperatures.

In order to produce reference data for optical detection we calculated vertical excitation energies and oscillator strengths for the lowest 20 singlet states of N_4 (D_{2h}) using the EOM-CCSD method. The lowest excited state (1^1B_{3u}), which also is the first optically accessible state, lies about 1.6 eV above the ground state. This excited state was optimized and found to be bound at a wide variety of computational levels, e.g. CASSCF, TD-B3LYP and EOM-CCSD. Its geometry is very similar to the ground state (Table 4), which results in large Frank-Condon factors for transitions between the two states. This fact, together with the very low excitation energy, indicates that the 1^1B_{3u} state will be useful for detection of N_4 (D_{2h}) by means of LIF spectroscopy.

Table 4. (EOM)-CCSD/AVDZ equilibrium structures (Å), harmonic frequencies (cm^{-1}), and excitation energies (eV) for the ground state and the first excited state of N_4 (D_{2h}).

State	Ground state (^1A_g)	First excited state ($^1B_{3u}$)
R_{12}	1.540	1.517
R_{13}	1.269	1.264
$\omega_1(a_u)$	489	606
$\omega_2(b_{2u})$	580	586
$\omega_3(a_g)$	957	980
$\omega_4(b_{3g})$	1048	580
$\omega_5(b_{1u})$	1421	1300
$\omega_6(a_g)$	1625	1650
ΔE_{vexc}	0.0	1.62
ΔE_{0-0}	0.0	1.60

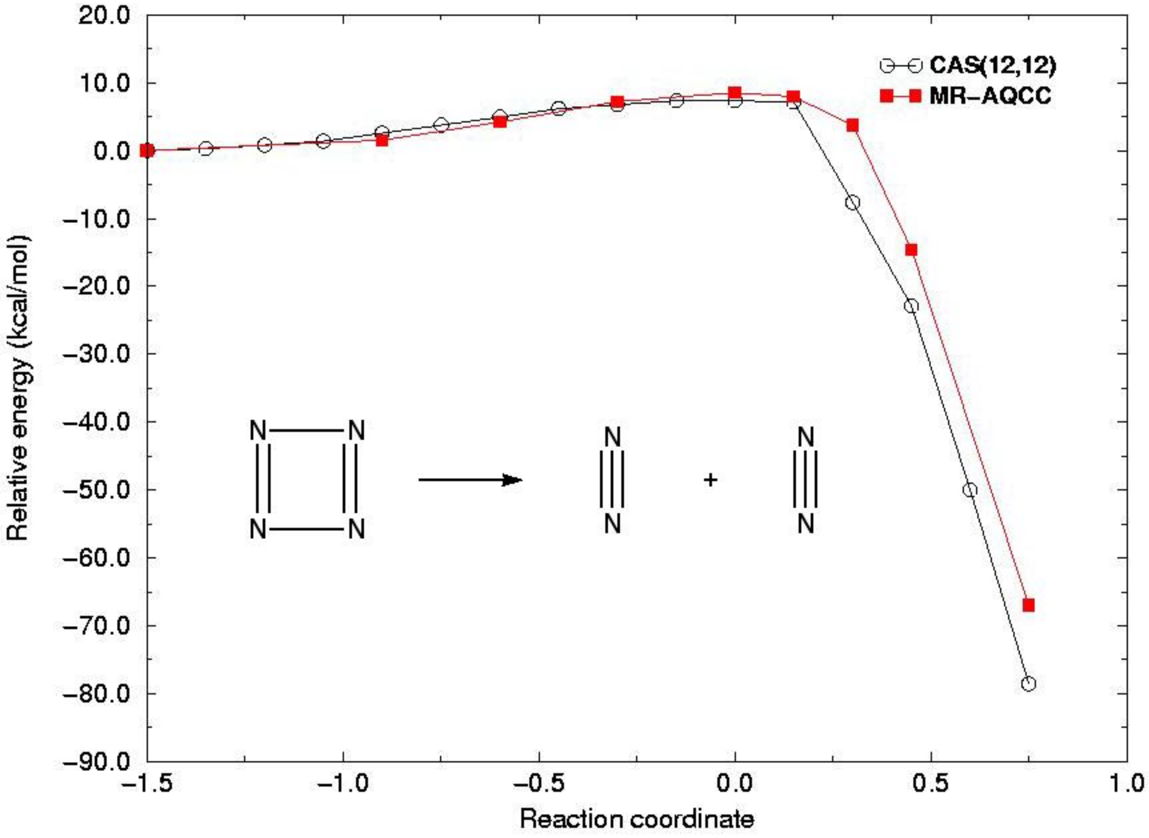
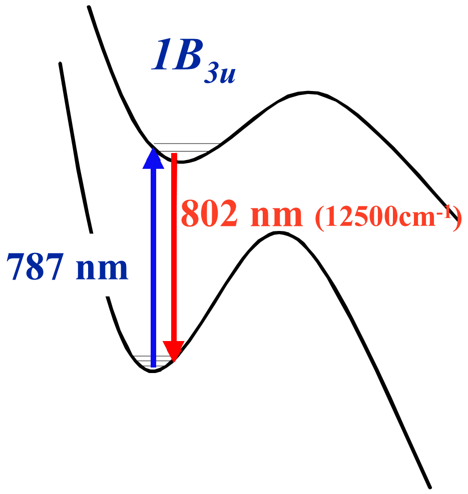


Fig 13. The dissociation pathway of N_4 (D_{2h}) calculated at the CAS(12,12)/VTZ and MR-AQCC/VTZ levels.



State	*Excitation Energy*[1] *(eV)*	*Oscillator Strength*[1]
$1B_{3u}$	**1.57**	**0.0033**
$2B_{3u}$	**7.22**	**0.0008**
$1B_{2u}$	**8.58**	**0.0075**
$1B_{1u}$	**10.04**	**0.1883**

[1)] EOM-CCSD / AVTZ

Fig. 14. Proposed LIF detection scheme for the rectangular $N_4(D_{2h})$ species.

Plan for the fourth quarter of 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 start in October 2001. We will use three excitation schemes (5, 7 and 9 in Ref [3]) 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 fourth quarter of 2001, we will perform SERS experiments on cryogenic matrices, as well as further decomposition experiments on heterocyclic compounds using a time of flight mass spectrometer.

The temperature-controlled cryostat experiments will continue. The experiments will utilize the CRYOCOOLER cryostat in combination with a SPEX 500M monochromator, an ion gun, an e^- filament, an Ar^+ laser and an optical multichannel analyzer. A MacPherson VUV spectrometer will also be used in order to study processes in excited matrices in the high-energy region.

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 two cryostats. Several synthesis experiments with long integration times have been carried out.
- Temperature-controlled matrix excitation experiments with Raman detection using the 514.5 nm line of an Ar^+ laser have been performed.
- Preparations have been made on multiphoton excitation of liquid nitrogen in a capillary with a tunable dye laser.
- Decomposition experiments on heterocyclic high-nitrogen compounds have been carried out using detection with a time of flight mass spectrometer.
- Initial SERS experiments have been performed on previously characterized substances.

Progress:

- A number of unassigned features have been observed in ion bombarding, microwave-excitation and hollow-cathode excitation experiments on nitrogen-containing matrices.
- The Vegard-Kaplan bands of nitrogen have been produced at very high intensity levels in nitrogen and mixed argon-nitrogen matrices using ion gun excitation.
- The tetrahedral N_4^+ ion has been found to be stable in *ab initio* calculations.
- The rectangular $N_4(D_{2h})$ species has been found to be stable in *ab initio* calculations, and a LIF detection scheme has been proposed for its detection.

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.
- SERS experiments will be carried out at cryogenic temperatures.
- And of course our ultimate goal: The successful synthesis and detection of N_4.

Reports:

- One report has been written (Ref. 1 in the reference list).
- One article has been published. (Ref. 8 in the reference list).

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