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13. ABSTRACT (Maximum 200 words) We have investigated several ways to prepare and characterize spectroscopically novel compounds of pure nitrogen:tetrazete N4 and pentazole anion N5. They are of interest to DARPA/AFOSR as potential new high energy density materials (HEDM)s and attractive propellants. Results of earlier, extensive theoretical work (quantum mechanical computations) consistently suggest that tetrazete should be a metastable compound with decomposition barrier of 60 kcal/mol, and it should contain 180 kcal/mol of energy with respect to the two dinitrogen molecules. We have carefully scrutinized several methods to prepare tetrazete and for its subsequent detection we have employed a number of spectroscopic techniques. Microwave, electrical discharge of gaseous nitrogen or fast atom bombardment of solid N2 (at 10K) produces highly reactive neutral and charged nitrogen fragments: N-atoms, N3 radicals and variety of ions. Majority of them recombine among themselves to form back dinitrogen or react will always-present trace amounts of impurities (mostly oxygen atoms) to produce nitrogen oxides. In our experiments we have condensed such mixtures on the low-temperature (5.6 -20K) spectroscopic targets (salt windows or Pt-plated copper). We have observed in IR absorption and Raman spectroscopy many lines characteristic for such compounds. In addition, we have detected absorption lines in the positions that are highly compatible with signals predicted by high-level quantum mechanical calculations for tetrazete. Due to the high symmetry of N4 only one IR absorption should be observable for a pure 14N4 or 15N4 isotopomers, making the convincing and unambiguous proof difficult on the basis of such observation alone.				
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PREPARATION OF NOVEL POLYAZETES
FINAL TECHNICAL REPORT
PATENT AND FISCAL REPORT

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I. FINAL TECHNICAL REPORT

PREPARATION OF NOVEL POLYAZETES

SUMMARY

We have investigated several ways to prepare and characterize spectroscopically novel compounds of pure nitrogen: tetrazete N_4 and pentazole anion N_5^- . They are of interest to DARPA/AFOSR as potential new high energy density materials (HEDM)s and attractive propellants. Results of earlier, extensive theoretical work (quantum mechanical computations) consistently suggest that tetrazete should be a metastable compound with decomposition barrier of 60 kcal/mol, and it should contain 180 kcal/mol of energy with respect to the two dinitrogen molecules. We have carefully scrutinized several methods to prepare tetrazete and for its subsequent detection we have employed a number of spectroscopic techniques. Microwave, electrical discharge of gaseous nitrogen or fast atom bombardment of solid N_2 (at 10 K) produces highly reactive neutral and charged nitrogen fragments: N-atoms, N_3 radicals and variety of ions. Majority of them recombine among themselves to form back dinitrogen or react with always-present trace amounts of impurities (mostly oxygen atoms) to produce nitrogen oxides. In our experiments we have condensed such mixtures on the low-temperature (5.6 –20 K) spectroscopic targets (salt windows or Pt-plated copper). We have observed in IR absorption and Raman spectroscopy many lines characteristic for such compounds. In addition, we have detected absorption lines in the positions that are highly compatible with signals predicted by high-level quantum mechanical calculations for tetrazete. Due to the high symmetry of N_4 only one IR absorption should be observable for a pure $^{14}N_4$ or $^{15}N_4$ isotopomers, making the convincing and unambiguous proof difficult on the basis of such observation alone. So far, we have not able to prepare samples of pure isotopomers concentrated enough for obtaining the clear-cut, reproducible Raman spectrum (that should contain 3 lines), nor samples of mixed $^{14-15}N_4$ isotopomers that should consist of multiple IR absorptions. The spectra that we were able to record, although very encouraging, suffer from low reproducibility and low signal-to-noise ratio. These basic findings were described in detail in our article in *Chem. Phys. Lett.* **2000**, 328, 227. The by-product of these attempts: the detailed spectroscopy of all twelve possible isotopomers of N_2O (consisting of ^{14}N , ^{15}N , ^{16}O , ^{17}O , and ^{18}O atoms) has been published in *J. Chem. Phys.* **2001**, 115, 1757.

The work aiming at the preparation of pentazole anion (N_5^-) and its chemistry is still in progress. The results of our initial attempts were published in three papers: *Tetrahedron*, **2002**, 58, 2085, *J. Org. Chem.* **2002**, 67, 1354, and *J. Am. Chem. Soc.* **2002**, 124, 14115. The forth paper is in final stages of preparation and we intend to submit it for publication later this year.

PREPARATION OF NOVEL POLYAZETES

Below we describe our activities and present results of our effort on this project.

Preparation of the new pure nitrogen compounds is exceedingly difficult, however we believe that we had made some first successful steps towards this goal. In the two-part technical section below we will describe work related to preparation of the tetrazete (N_4), and pentazole anion (N_5^-).

A. "Tetrazete - N_4 " (Tetrazatricyclo[1.1.0.0]^{2,4}butane).

Our efforts were focused on tetrazete, N_4 , and earlier also on pentazole anion, N_5^- . We have investigated several ways to prepare, detect and characterize them with optical spectroscopy tools. The work on N_4 was performed at our lab in Golden Colorado, and synthetic attempts were made in collaboration with Vanderbilt University group in their Nashville facility.

Tetrazete - N_4 (Tetrazatricyclo[1.1.0.0]^{2,4}butane) Preparation and Spectroscopy.

Results of earlier, extensive theoretical work consistently suggested that tetrazete should be a metastable compound with decomposition barrier of 60 kcal/mol, and it will accumulate 180 kcal/mol of energy with respect to the two dinitrogen molecules. N_4 should be observable by IR spectroscopy, if it is generated in sufficient concentrations. And it could be very attractive HEDM, very likely stable at room temperature.

We have carefully scrutinized several methods to prepare tetrazete. Microwave or electrical discharge, pulsed laser breakdown of gaseous nitrogen or fast atom bombardment of solid N_2 (at 10 K) produces highly reactive neutral and charged nitrogen fragments: N-atoms, N_3 radicals and variety of ions. Majority of them recombine among themselves to form back dinitrogen, N_2 or react with always-present trace amounts of impurities (mostly oxygen atoms) to produce nitrogen oxides. In our experiments we have condensed such reacting mixtures on the low-temperature (5.6 – 20 K) spectroscopic targets (salt windows or Pt-plated copper). For its subsequent

detection we have employed a number of spectroscopic techniques. We have observed in IR absorption and Raman spectroscopy many lines, mostly characteristic for nitrogen

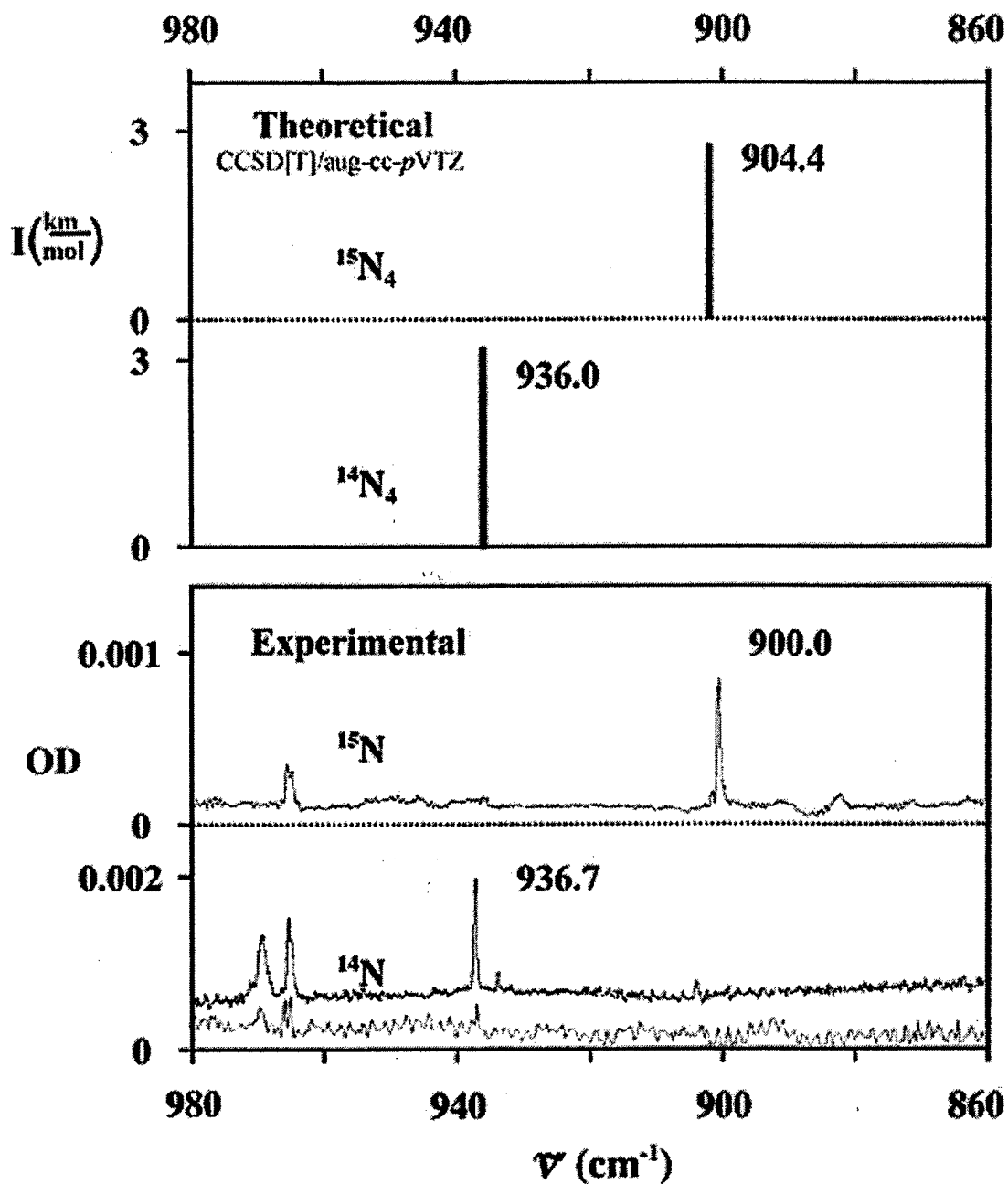


Figure 1. Observed IR absorption (lower set) from sample containing separately: $^{14}\text{N}_2$ (two separate experiments) and $^{15}\text{N}_2$ quenched plasma, and respective theoretical predictions (upper set). The peak at 969 cm^{-1} (bottom spectrum) belongs to NH_3 impurity and the unresolved doublet at 965 cm^{-1} (in both spectra) originates in O_4 .

oxides. In addition, we have detected absorption lines at energies that are highly compatible with signals predicted by high-level quantum mechanical calculations for tetrazete. In samples prepared with $^{14}\text{N}_2$ we observe a weak infrared transition at 936.7 cm^{-1} . It shifts to 900.0 cm^{-1} when $^{15}\text{N}_2$ is used. Both peaks do not correlate with any other features in the spectra and are best explained as originating from tetrahedral tetrazetes (N_4). Their positions are compatible with quantum chemical estimates for $^{14}\text{N}_4$, at 936.0 cm^{-1} and $^{15}\text{N}_4$, at 904.4 cm^{-1} . [ref. 1] Due to the high symmetry of N_4 only single IR absorption should be observable for a pure $^{14}\text{N}_4$ or $^{15}\text{N}_4$ isotopomers, making the convincing and unambiguous spectroscopic proof of their detection difficult on the basis of such observation alone. [ref. 1]

Therefore we designed and performed experiments with mixed $^{14}\text{N}_2$ and $^{15}\text{N}_2$. Now, without any change in electronic structure, the mass distribution dissymmetry

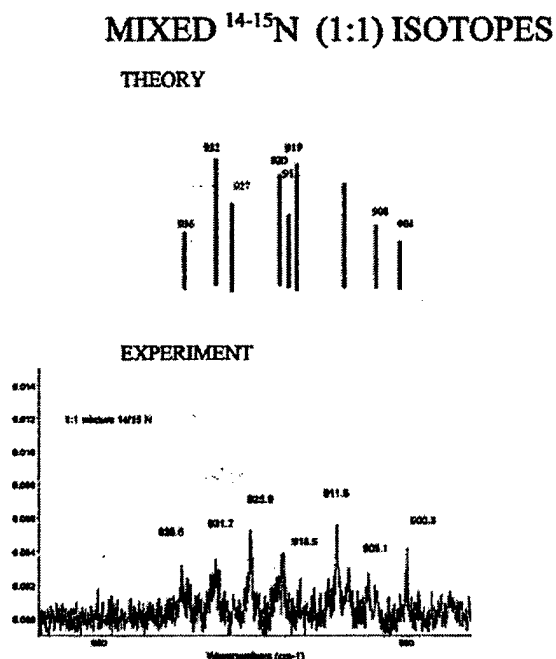


Figure 2. Calculated (top) and observed (bottom) fragment of the IR spectrum for 1:1 $^{14}\text{N}_2$ - $^{15}\text{N}_2$ microwave plasma quenched on a 10 K CsI window.

should lower the effective dipolar symmetry and activate several additional components in the IR spectrum, therefore making recognition and assignment much less ambiguous. We calculated the statistical weight factors for relative intensities in spectra of the mixed species [ref. 1]. The observed pattern reassembles well predictions, (Fig. 2) but we did not manage yet to reproduce this observation.

We have investigated broad range of varying experimental conditions of generation of nitrogen fragments using Fast Atom Bombardment (FAB), mostly of solid nitrogen substrate bombarded by N atoms but we have also looked at nitrogen matrices bombarded with Ar, Ne, Kr and Xe. In some experiments we have combined FAB with soft-vacuum uv-irradiations. Various charged and neutral species were

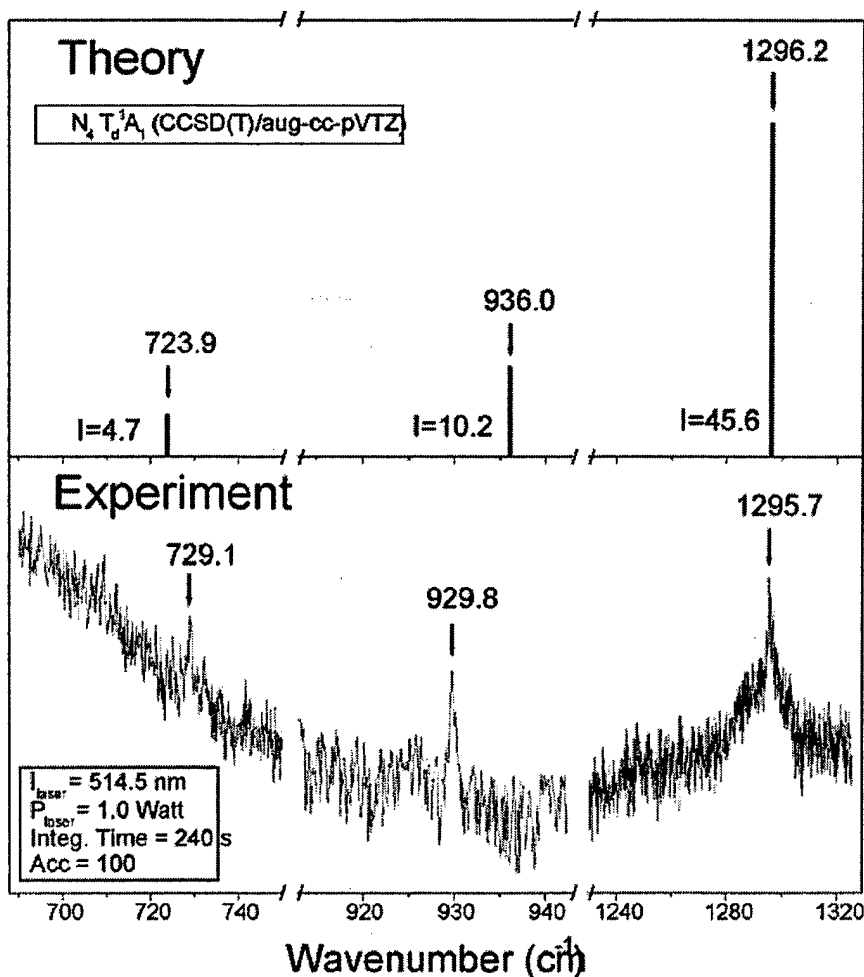


Figure 3. Predicted and observed Raman spectrum for N_4 .

generated and observed. Unfortunately, not even traces of the signals previously assigned to N_4 were detected. The by-product of these attempts: the detailed spectroscopy of all twelve possible isotopomers of N_2O (consisting of ^{14}N , ^{15}N , ^{16}O , ^{17}O , and ^{18}O atoms) has been published [Ref. 2; *J. Chem. Phys.* **2001**, *115*, 1757].

Finally, we have made numerous attempts, especially during the past two years, to record Raman spectra of the plasma reactions products. Although, some of them reassemble predicted pattern, they also suffer from low signal-to-noise ratio and low reproducibility. We were not able yet to obtain such spectra from samples prepared from pure $^{15}N_2$ or $^{14}N_2 - ^{15}N_2$ mixtures. Our extensive effort and attempts to employ Surface Enhanced Raman Spectroscopy (SERS) to increase detection sensitivity did not produce expected much stronger signals, but this work is still in progress, and is likely the most promising tool to provide eventually definitive conclusions.

Pentazole Anion, N_5^- Synthetic Effort

Our synthetic ("wet chemistry") effort concentrated on the N_5^- , which was to be generated by removing of a substituent (protective group) from a pentazole derivative. In this context, we studied the reactivity of 4-hydroxyphenylpentazole, and investigated the formation of alkyl pentazolecarboxylates. The former was subjected to ozonolysis, and our results [3] formed the basis for subsequent experimental observation of the N_5^- by other groups.

Our second strategy to generate the N_5^- involved the "2N+3N" condensation in which a linear pentazene chain containing a COOR group would spontaneously cyclize to form a substituted pentazole. Following this strategy, we investigated nucleophilic substitution reactions by the azide N_3^- anion at the electrophilic nitrogen center in azene $ROOC-N=N-L$, where L is a leaving group OMe [4] or $ArSO_2$ [3] or in hydrazine $E_2N-NE-Cl$ ($E=COOEt$) [5]. Unfortunately, the results showed that the addition-elimination mechanism does not operate in the azenes and no formation of a linear pentazene chain has been detected.

II. PATENT AND FISCAL REPORT

There was no intellectual property developed in this project. All our findings were published in peer-reviewed journals and presented at conferences:

1. Zheng, J.-P.; Blake, D. M.; Waluk, J.; Spanget-Larsen, J.; Radziszewski, J. G. "Tetrazaete (N_4). Can It Be Prepared and Observed?" *Chem. Phys. Lett.* **2000**, 328, 227-233.
2. Andrzej Lapinski, Jens Spanget-Larsen, Jacek Waluk, and J. George Radziszewski, "Vibrations of Nitrous Oxide: Matrix-Isolation FTIR Spectroscopy of Twelve N_2O Isotopomers" *J. Chem. Phys.* **2001**, 115, 1757.
3. Benin, V.; Kaszynski P.; Radziszewski, J. G. "Arylpentazoles Revisited: Experimental and Theoretical Studies of 4-Hydroxyphenylpentazole and 4-Oxophenylpentazole Anion" *J. Org. Chem.* **2002**, 67, 1354-1358.
4. Benin, V.; Kaszynski P.; Radziszewski, J. G. "Ambident Ethyl N-nitrosocarbamate Anion: Experimental and Computational Studies of Alkylation and Thermal Stability" *J. Am. Chem. Soc.* **2002**, 124, 14115-14126.
5. Benin, V.; Kaszynski P.; Radziszewski, J. G. "N-Chloro-N, N', N'-tris(ethoxycarbonyl)hydrazine and N,N-Dichloro-N',N'-bis(ethoxycarbonyl)hydrazine: Synthesis, Stability and Reactions with Nucleophiles", *Tetrahedron*, **2002**, 58, 2085-2090.
6. Benin, V.; Kaszynski P.; Radziszewski, J. G.; Young V. G. Jr. "Michael substitution in 4-toluenesulfonylazocarboxylate" *in preparation*.
7. J. George Radziszewski, Jun-Ping Zheng, Daniel M. Blake, Andrzej ,apinski, Jens Spanget-Larsen, Jacek Waluk "Novel HEDM: Tetrazaete (N_4). Can It Be Prepared and Observed?" 26th *International Symposium on Free Radicals*, Assisi, Italy, September **2001**.

FINANCIAL, STAFFING, and PROJECT MANAGEMENT

The grant was awarded as a one year funding with option for agency to extend it for additional year. Towards the end of second year we have requested and received a 6 - months "NO-cost" extension. While we were able to save some money on specialized equipment (instead of purchases as originally planned we have used the loaned equipment) we had to spent more funds on personnel than originally intended. With the prior approval of funding agency we have re-directed some funds initially planed to cover consulting and special fees for laboratory usage (these were waived).

All the awarded funds were expended and accounting of the expended funds was provided by the PI as the regular Project Status Reports and are summary is provided now by the Colorado School of Mines Accounting Office, as required by the terms of the contract.