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MEMORANDUM FOR PRR (Contractor/In-House Publication)

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FROM: PROI (TI) (STINFO)

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-TP-FY99-0114
Wilson and Christe (ERC) and Sheehy and Boatz, "Synthesis of Catenated Polynitrogen Compounds"

Presentation at HEDM Conference
Poster Session

(Public Release)

SYNTHESIS OF CATENATED POLY-NITROGEN COMPOUNDS

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PROGRAM OVERVIEW

- Completed
- SYNTHESIS OF NOVEL MONOPROPELLANTS CONSISTING OF HIGHLY ENDOOTHERMIC POLYINITROGEN ALLOTROPES
 - USE TECHNIQUES DEVELOPED IN SYNTHESIS OF OTHER ENERGETIC MATERIALS TO PURSUE CATENATED RATHER THAN POLYCYCLIC POLYINITROGEN

COMPOUNDS

RING CLOSURE REACTIONS FOR POLYCYCLIC COMPOUNDS ARE

UNKNOWN AND DIFFICULT TO ENVISION

IN CONTRAST, ONE CAN CONCEIVE OF REACTIONS THAT MIGHT LEAD TO CATENATED COMPOUNDS

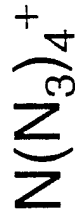
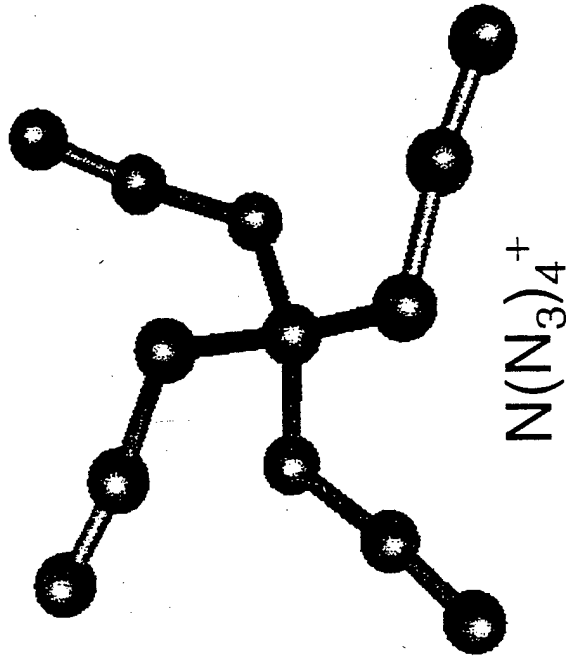
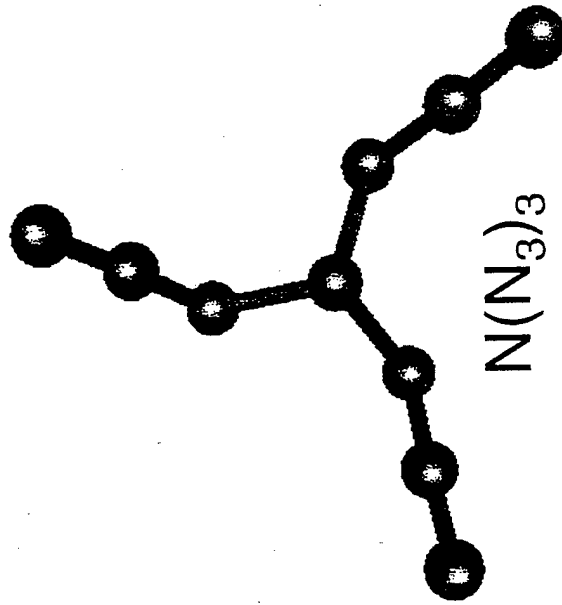
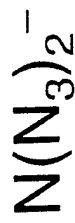
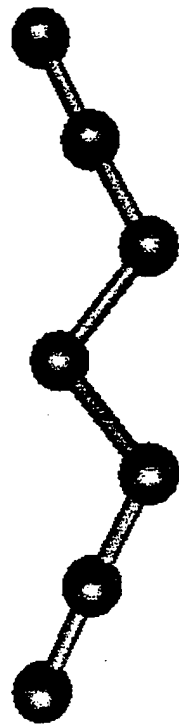
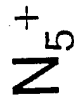
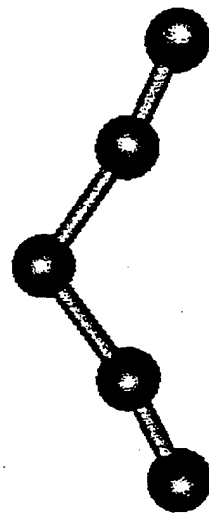
- USE THEORY AND CALCULATIONS TO GUIDE SYNTHESIS EFFORTS
- HIGH-RISK, HIGH-PAYOFF PROGRAM

PROPOSED COMPOUNDS ARE EXTREMELY ENERGETIC

STABILITY OF ENERGETIC MATERIALS TYPICALLY DECREASES WITH INCREASING ENDOTHERMICITY

CALCULATIONS ON CATENATED POLYINITROGEN SPECIES

- HAVE DEMONSTRATED THE FEASIBILITY OF



- AB INITIO CALCULATIONS SHOW THESE SPECIES TO BE VIBRATIONALLY STABLE

STATE OF THE ART IN HOMOLEPTIC CATENATED POLYNITROGEN COMPOUNDS

- ONLY TWO COMPOUNDS KNOWN WHICH CAN BE PREPARED "IN BULK"
N₂ LONG KNOWN, BUT FIRST ISOLATED IN PURE FORM ONLY IN
1772 INDEPENDENTLY BY

RUTHERFORD

SCHEELE

CAVENDISH

AZIDE, N₃⁻, DISCOVERED IN 1890 BY

CURTUIS

- THE ABSENCE OF ANY OTHER SUCH COMPOUND IS A TESTIMONY TO THE
PROBLEMS THAT CAN BE EXPECTED FOR THE SYNTHESIS OF NEW
POLYNITROGEN COMPOUNDS

SYNERGISM OF THEORY AND SYNTHESIS

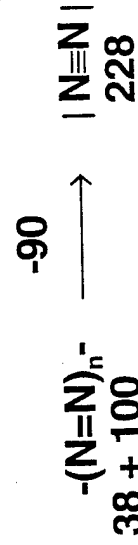
- **AFRL HAS EXCELLENT CAPABILITIES IN BOTH THEORY AND SYNTHESIS**
- **THANKS TO AFOSR PROGRAM**
- **QUANTUM-CHEMICAL CALCULATIONS ARE USED TO IDENTIFY PROMISING CANDIDATES AND HELP CHARACTERIZE NEW COMPOUNDS**
 - INFRARED SPECTRA, RAMAN SPECTRA, AND NMR CHEMICAL SHIFTS**
 - DECOMPOSITION PATHWAYS AND ENERGY BARRIERS**
 - THERMODYNAMIC PROPERTIES**
 - PROPELLANT SPECIFIC IMPULSE**
- **GENERAL APPROACH TO SYNTHESIS OF PROMISING CANDIDATES**
 - SYNTHESIZE COMPOUNDS ON A VERY SMALL SCALE**
 - IDENTIFY AND CHARACTERIZE THE NEW COMPOUNDS**
 - GET SENSITIVITY DATA AND PHYSICAL PROPERTIES**
 - SCALE UP THE SYNTHESIS OF VIABLE NEW MATERIALS**

PROBLEMS WITH SYNTHESIS OF POLYNITROGEN HEDM

- ALL THE ENERGY MUST COME FROM ENDOTHERMICITY WHICH MAKES POLYNITROGEN HEDM EXTREMELY DANGEROUS
- BASIS FOR HIGH ENERGY CONTENT ARE THE LARGE DIFFERENCES IN BOND

ENERGIES FOR N-N BONDS

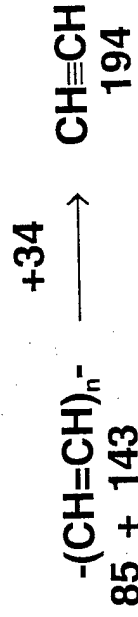
N-N	38 kcal/mol
N=N	100 kcal/mol
N≡N	228 kcal/mol



EXCEPTIONS: N₂, O₂

STABLE MONOMERS
UNSTABLE POLYMERS

C-C	85 kcal/mol
C=C	143 kcal/mol
C≡C	194 kcal/mol



NORMAL CASE:

STABLE POLYMERS
UNSTABLE MONOMERS

GENERAL CONCEPT FOR POLYINITROGEN HEDM SYNTHESIS

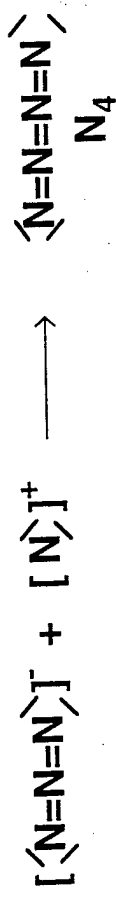
- ALL POLYINITROGEN COMPOUNDS ARE UNSTABLE WITH RESPECT TO N₂
- ACTIVATION ENERGY BARRIER TOWARD N₂ ELIMINATION IS DETERMINED BY THE WEAKEST BOND IN POLYINITROGEN COMPOUND
- THE BARRIER AND METASTABILITY OF POLYINITROGEN COMPOUNDS MUST BE INCREASED BY SUITABLE RESONANCE STRUCTURES



- DOUBLE BOND CHARACTER OF N-N BONDS IN AZIDE ION EXPLAINS ITS EXCEPTIONAL STABILITY
- HOW CAN THIS STABILIZATION EFFECT BE TAKEN ADVANTAGE OF?

EXPANSION OF THE AZIDE STRUCTURE

- ADDITION OF $[N]^{+}$ UNITS TO N_3^{-}



- HOWEVER, THEORETICAL CALCULATIONS SHOW THAT $D_{\infty h} N_4$ IS NOT STABLE



NEIGHBORING CHARGES OF EQUAL SIGN MUST BE AVOIDED

- NO PLAUSIBLE RESONANCE STRUCTURES CAN BE WRITTEN FOR N_4 WHICH RETAIN DOUBLE BOND CHARACTER WHILE AVOIDING NEIGHBORING CHARGES OF EQUAL SIGN

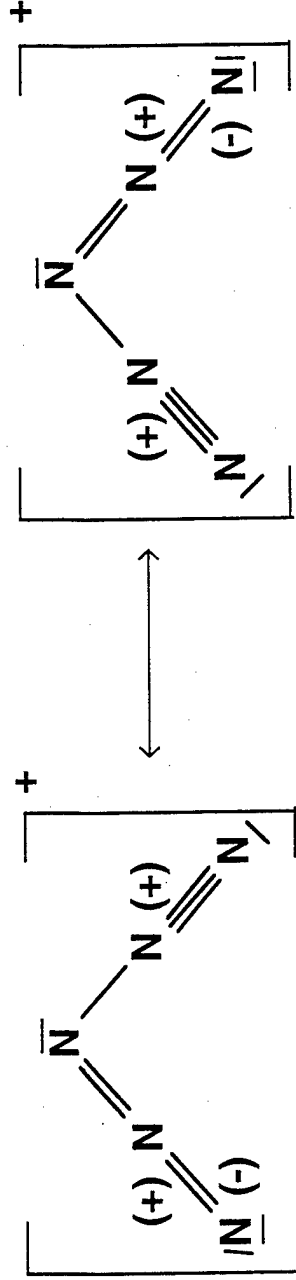
EXPANSION OF THE AZIDE STRUCTURE TO N₅⁺

- THE SAME PROBLEM EXISTS FOR N₅⁺ WITH NEIGHBORING POSITIVE CHARGES



- RESONANCE STRUCTURES, HOWEVER, CAN BE WRITTEN WHICH AVOID THIS

PROBLEM

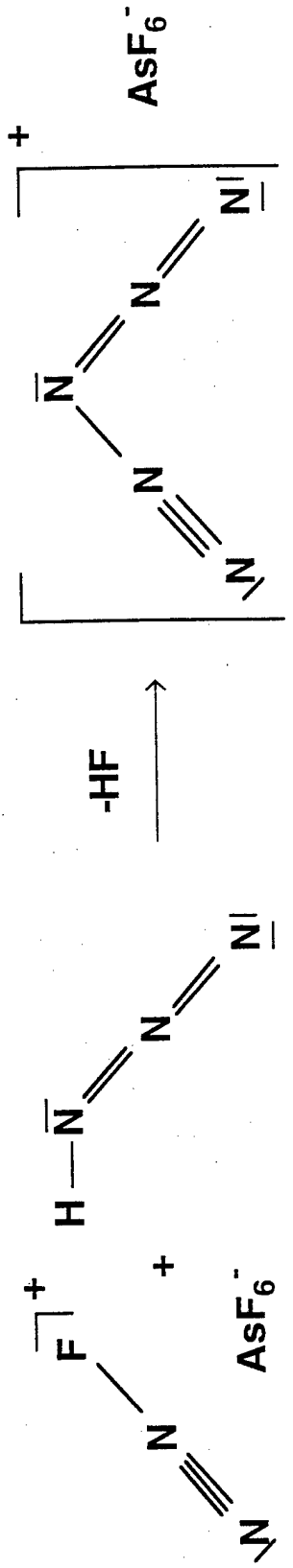


- AB INITIO CALCULATIONS (CCSD(T) AND B3LYP) CONFIRM THE STABILITY OF THIS

C_{2v} STRUCTURE

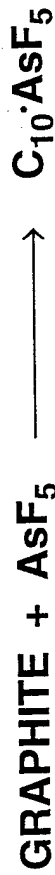
SELECTION OF SUITABLE STARTING MATERIALS FOR N_5^+ SYNTHESIS

- REQUIREMENTS
 - STARTING FRAGMENTS MUST HAVE ALREADY BUILT IN WEAKENED BONDS
 - MUST HAVE A FORMAL POSITIVE CHARGE (IP OF $N_2 = 359$ kcal/mol)
 - COUPLING REACTION MUST BE EXOTHERMIC
 - CHOICE OF SUITABLE SOLVENT (HEAT SINK, STABILIZATION, SAFETY)
- IDEAL CANDIDATE SYSTEM



SYNTHESIS OF $N_2F^+MF_6^-$ (M = As, Sb) STARTING MATERIAL

- KNOWN SYNTHESIS



- ATTEMPTS TO SIMPLIFY $N_2F^+MF_6^-$ SYNTHESIS WERE UNSUCCESSFUL



(VARYING TEMPERATURES AND PRESSURES)

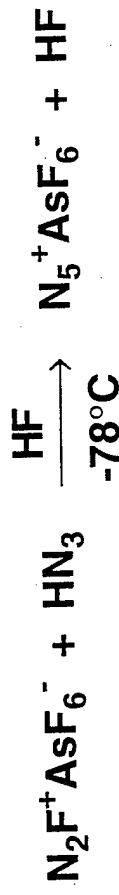
(METHOD COMPARABLE TO SUCCESSFUL SYNTHESIS OF $\text{NF}_4^+\text{SbF}_6^-$)



(250°C AND 150 ATM PRESSURE)

ACTUAL SYNTHESIS OF $N_5^+ AsF_6^-$

- SYSTEM WORKED AS PLANNED



HIGH YIELD

ONLY OTHER BYPRODUCT 20-40% $H_2N_3^+AsF_6^-$

2 MMOL (0.5 G) SCALE

- PROPERTIES OF $N_5^+AsF_6^-$

WHITE SOLID WHICH IS SPARINGLY SOLUBLE IN HF

MARGINALLY STABLE AT 22°C

HIGHLY ENERGETIC, REACTS VIOLENTLY WITH WATER AND ORGANICS

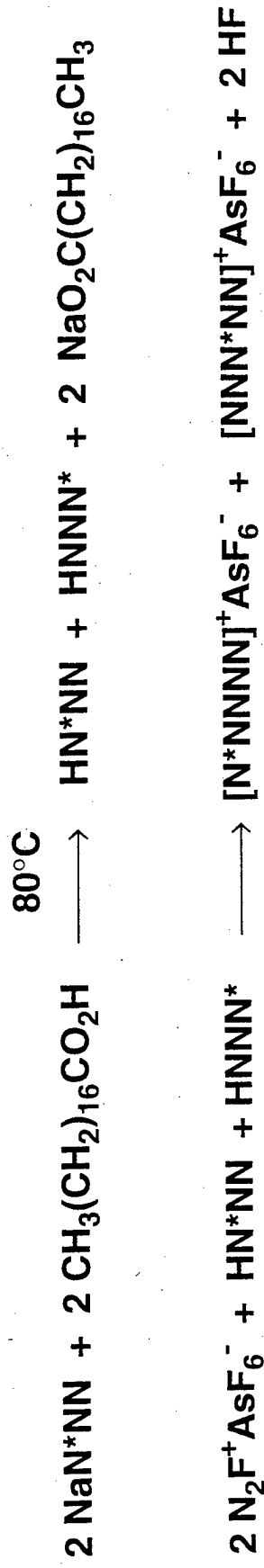
CALCULATED $\Delta H_f^\circ N_5^+(g) = 353 \text{ kcal/mol}$

POWERFUL OXIDIZER

1st I.P. OF $O_2 = 288 \text{ kcal/mol}$

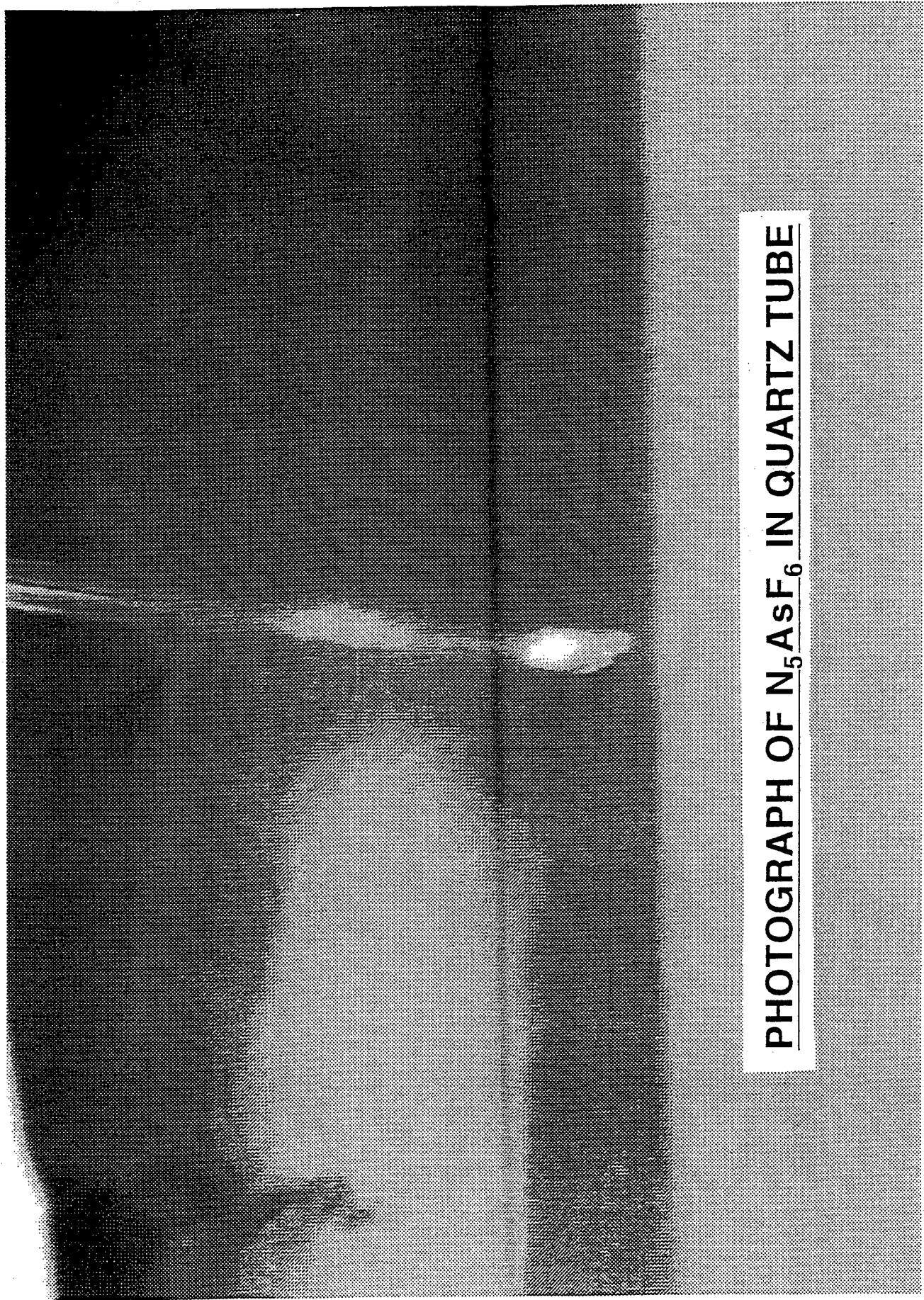
1st I.P. OF $N_2 = 359 \text{ kcal/mol}$

SYNTHESIS OF ^{15}N LABELED $\text{N}_5^+ \text{AsF}_6^-$



^{15}N LABELED N_5AsF_6 NEEDED FOR POSITIVE IDENTIFICATION OF

N_5^+ BY SPECTROSCOPIC METHODS

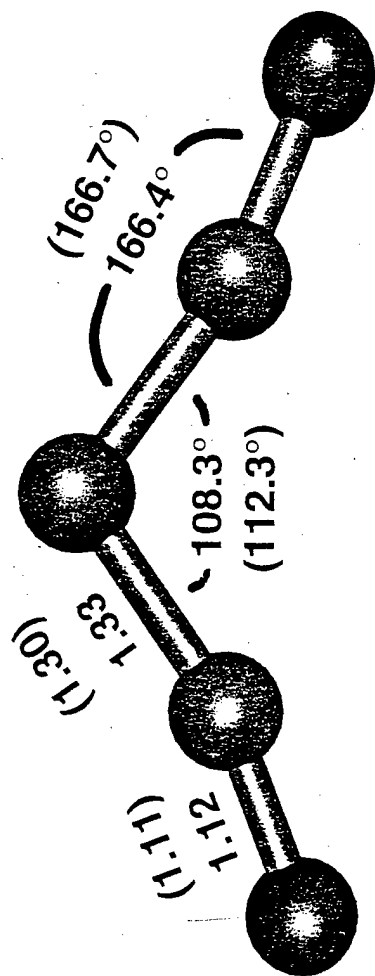


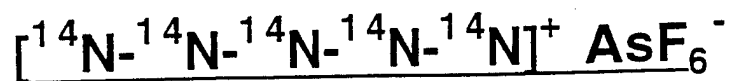
PHOTOGRAPH OF N₅AsF₆ IN QUARTZ TUBE

CHARACTERIZATION OF $N_5^+AsF_6^-$

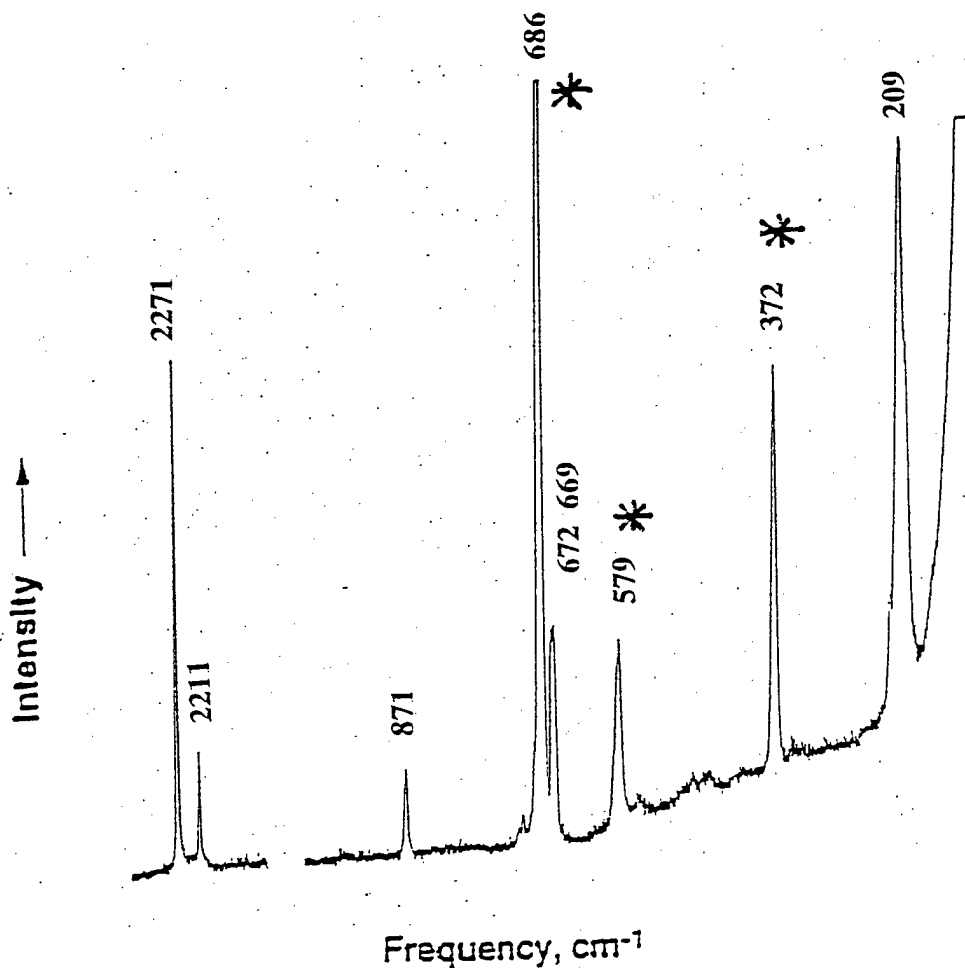
- ^{14}N AND ^{15}N NMR SPECTRA
- LOW-TEMPERATURE RAMAN AND INFRARED SPECTRA OF NORMAL AND ISOTOPICALLY LABELED N_5^+
- NORMAL COORDINATE ANALYSIS
- MASS SPECTROSCOPY
- THEORETICAL CALCULATIONS
 - OPTIMIZED GEOMETRY
 - VIBRATIONAL SPECTRA
 - ISOTOPIC SHIFTS
 - NMR SHIFTS
 - HEAT OF FORMATION

OPTIMIZED GEOMETRIES FOR N_5^+ CCSD(T) (B3LYP) VALUES



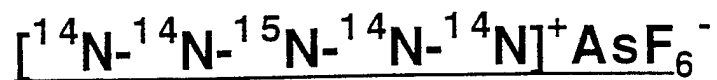
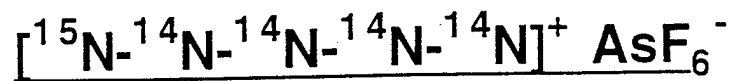


LOW-TEMPERATURE RAMAN SPECTRUM

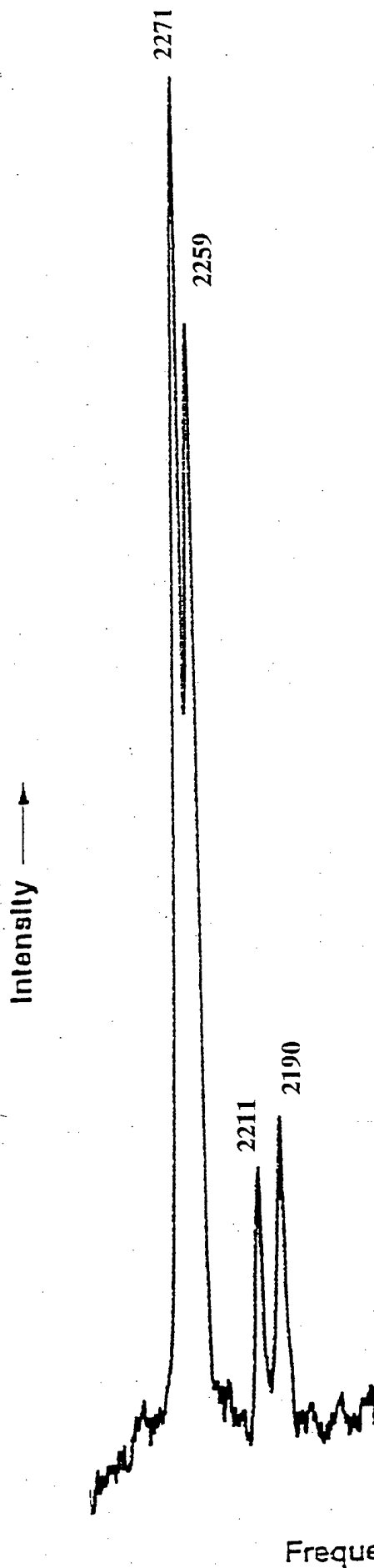


* = AsF_6^-

N_5^+	OBSD (cm^{-1})	CCSD(T) (cm^{-1})	B3LYP (cm^{-1})
ν_1 (A1)	2271	2229	2336
ν_7 (B2)	2211	2175	2282
ν_2 (A1)	871	818	850
ν_4 (A1)	209	181	193

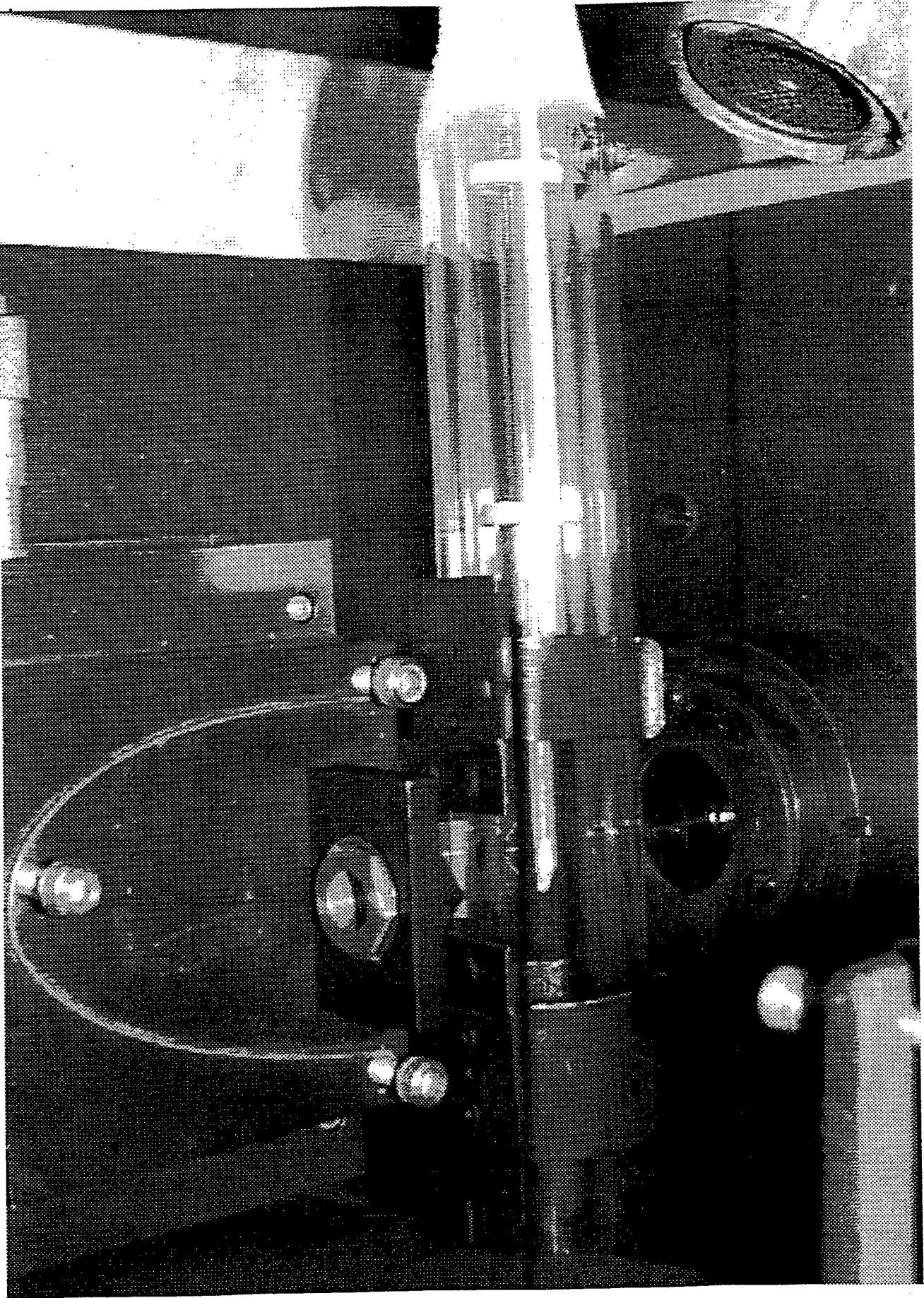


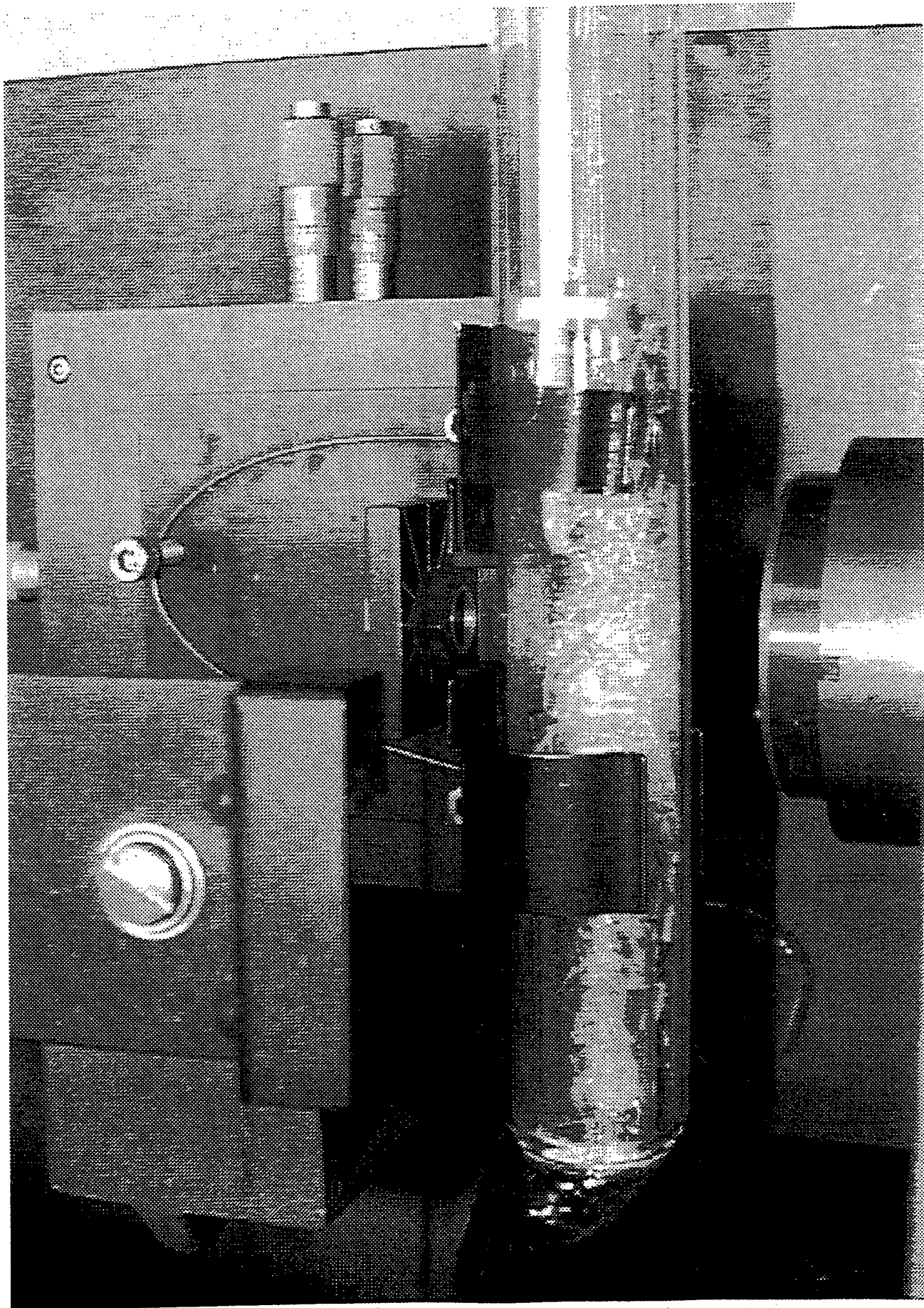
LOW-TEMPERATURE RAMAN SPECTRUM



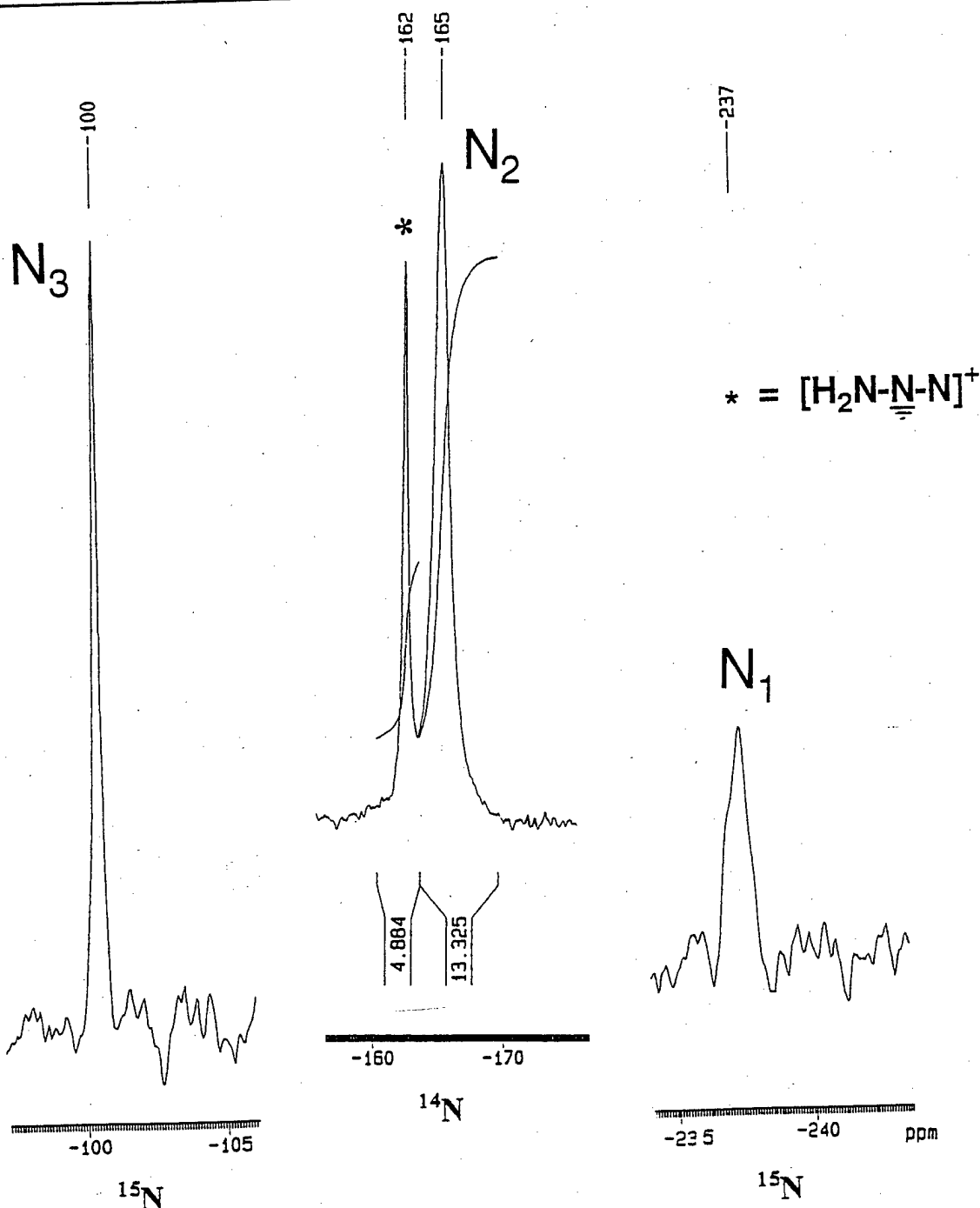
14N-15N SHIFTS (cm⁻¹)

	OBSD	CALCD
ν ₁	12	11.8
ν ₇	21	21.4
ν ₂	14	14.1





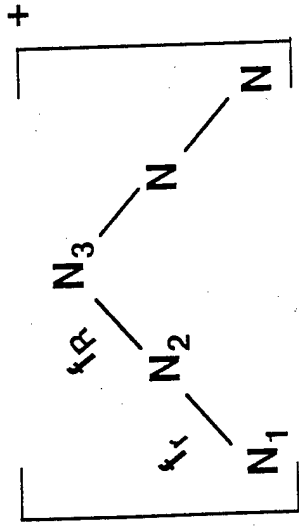
NITROGEN NMR SPECTRA OF



NMR SHIFTS (ppm)	OBSD	CALCD
N_1	-237.3	-235
N_2	-165.3	-166
N_3	-100.4	-95

FORCE FIELD ANALYSIS FOR N_5^+

- TWO MOST IMPORTANT FORCE CONSTANTS



$$f_r = 20.08 \text{ mdyn/\AA}$$

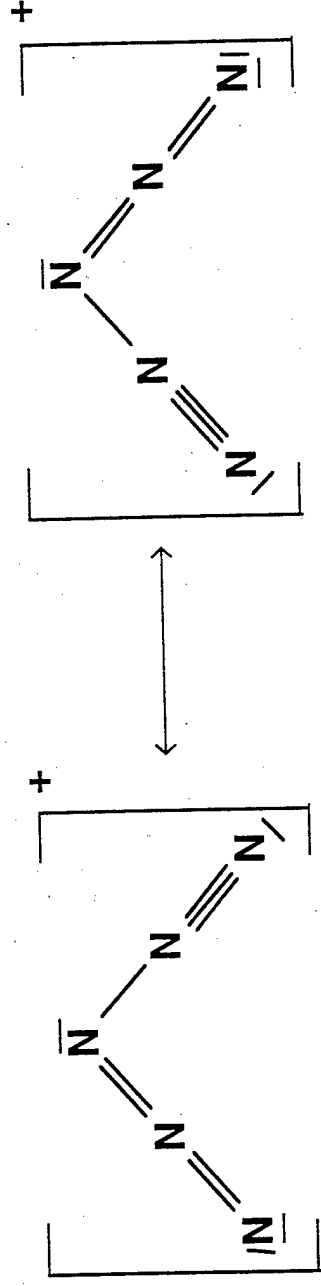
$$f_R = 6.59 \text{ mdyn/\AA}$$

- TYPICAL FORCE CONSTANT VALUES FOR N-N

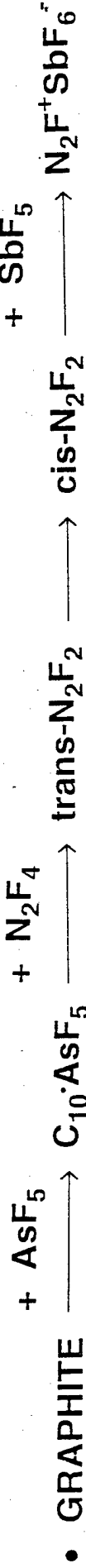
3.6 mdyn/\AA
10.2 mdyn/\AA
22.4 mdyn/\AA

SINGLE BONDS
DOUBLE BONDS
TRIPLE BONDS

- THUS N(2)-N(3) HAS BOND ORDER OF ~ 1.5 AND IS RESONANCE STABILIZED AT THE EXPENSE OF N(1)-N(2)



WHAT NEXT?



(X10)

SCALE UP

METATHESIS



STABILITY TESTS
SAFETY TESTS

COMPATIBILITY
TEST

MAKE A BETTER POLY-N CATION
 $\text{N}(\text{N}_3)_4^+$, XeN_3^+ , etc.

MAKE A LARGER POLY-N ANION
 $\text{N}(\text{N}_3)_2^-$, etc.

CHARACTERIZATION
SAFETY DATA

SCALE UP

PROCESS IMPROVEMENT

TESTING

PRODUCTION

ESTIMATED ENERGY CONTENT OF $N_5^+N_3^-$

- HEAT OF FORMATION OF $N_5^+N_3^-$

$$\Delta H_f^{298} N_5^+ = 351 \text{ kcal/mol} \quad (\text{THIS WORK})$$

$$\Delta H_f^{298} N_3^- = 43.2 \text{ kcal/mol} \quad (\text{NBS TABLES})$$

$$U_L N_5^+N_3^- \sim 130 \pm 20 \text{ kcal/mol} \quad (\text{ESTIMATE})$$

$$\Delta H_f^{298} N_5^+N_3^- (s) = 351 + 43 - 130 = 264 \pm 25 \text{ kcal/mol}$$

- ENERGY DENSITY OF $N_5^+N_3^- (s) = 2.36 \text{ kcal/g}$

- COMPARISON OF ENERGY DENSITIES (kcal/g)

O_3	$C(N_3)_3^+N(NO_2)_2^-$	HN_3	$N_5^+N_3^-$	H_2/O_2
0.71	1.42	1.63	2.36	3.21

SUMMARY

- THE FEASIBILITY OF POLYNITROGEN BASED HEDM COMPOUNDS HAS BEEN DEMONSTRATED BY THE SUCCESSFUL BULK SYNTHESIS OF N_5^+
- THE $N_5^+AsF_6^-$ SALT IS OF SURPRISING STABILITY AND WAS UNAMBIGUOUSLY IDENTIFIED BY VIBRATIONAL AND NMR SPECTROSCOPY OF UNLABELED AND ^{15}N LABELED N_5^+ AND THEORETICAL CALCULATIONS
- THE N_5^+ CATION IS THE FIRST NEW CATENATED HOMOLEPTIC POLYNITROGEN COMPOUND PREPARED IN BULK IN OVER 100 YEARS AND ONLY THE THIRD KNOWN COMPOUND OF THIS TYPE BESIDES ELEMENTAL NITROGEN AND AZIDE
- THEORETICAL CALCULATIONS PLAYED A CRUCIAL ROLE IN THE SUCCESSFUL IDENTIFICATION OF N_5^+ AND DEMONSTRATE THE POWERFUL SYNERGISM OF THEORY AND SYNTHESIS

ACKNOWLEDGEMENT

- DR. MARIO FAJARDO (MASS SPECTRA)
- DR. JOHN STANTON (NMR SHIFT CALCULATIONS)
- MR. ALAN KERSHAW (NITROGEN NMR SPECTRA)

Table 1. Observed and Calculated Nitrogen NMR Data for N_5^+

	chemical shifts, ^a ppm				
	observed ^b	calculated, ^c CCSD(T)/QZP			
	¹⁵ N	¹⁴ N	N ₁	N ₂	N ₃
$[^{15}N_1 - ^{14}N_2 - ^{14}N_3 - ^{14}N_{2'} - ^{14}N_{1'}]^+$	-237.3	-165.3 ^d	-235	-166	-95
$[^{14}N_1 - ^{14}N_2 - ^{15}N_3 - ^{14}N_{2'} - ^{14}N_{1'}]^+$	-100.4				

alignment

(a) Chemical shifts are given relative to neat CH_3NO_2 as external standard. (b) The spectra were recorded hydrogen-coupled at $-63^\circ C$ in anhydrous HF solution which was acidified with AsF_5 . (c) An empirical correction of -20 ppm was applied to all calculated values, based on a comparison between the calculated and observed shifts of a number of closely related molecules and ions. (d) The other two resonances are badly exchange broadened and were not detected in the ^{14}N spectrum.

Table 2. Low-temperature Raman and Infrared Spectra of Solid $^{14}\text{N}_5^+ \text{AsF}_6^-$ and Their Assignments Compared to the Calculated Harmonic Frequencies of Free Gaseous N_5^+

observed freq, cm^{-1} (rel intens)		assignt (point group)		calcd freq ^d , (intens) ^b	
Raman	IR	$^{14}\text{N}_5^+(\text{C}_{2v})$	$\text{AsF}_6^-(\text{O}_h)$	B3LYP	CCSD(T)
-130°C	-196°C				
2271 [44]	2270 m	$\nu_1(\text{A}_1)$		2336 (22)	2229 (13) [215] ^c
2211 [8]	2210 s	$\nu_7(\text{B}_2)$		2282 (147)	2175 (105) [42]
	1088 s	$\nu_8(\text{B}_2)$		1167 (141)	1032 (138) [2]
871 [7]	872 w	$\nu_2(\text{A}_1)$		850 (4)	818 (0.5) [5]
	704 vs		$\nu_3(\text{F}_{1u})$		
686 [100]	680 sh		$\nu_1(\text{A}_{1g})$		
672 [17]		$\nu_3(\text{A}_1)$	or part of $\nu_1(\text{A}_{1g})$	678 (1)	644 (2) [1]
669 [18]			$\nu_1(\text{A}_{1g})$ or $\nu_3(\text{F}_{1u})$		
579 [16]	575 w		$\nu_2(\text{E}_g)$		
		$\nu_5(\text{A}_2)$		502 (0)	475 (0) [1]
	420 sh	$\nu_6(\text{B}_1)$		424 (7)	405 (6) [0]
		$\nu_9(\text{B}_2)$		436 (0.6)	399 (1) [0.5]
	394 vs		$\nu_4(\text{F}_{1u})$		
372 [32]	380 sh		$\nu_5(\text{F}_{2g})$		
	360 sh				
209 [44]		$\nu_4(\text{A}_1)$		193 (0.5)	181 (0.3) [6]
127 [55]		lattice vibration			

(a) Using a 6-311 + G(2d) basis set. (b) IR intensities in km/mol ; Ra intensities in $\text{\AA}^4/\text{amu}$. (c) The Ra intensities were calculated at the RHF level.

Table 4. Results from the Normal Coordinate Analysis^a of N₅⁺

approx mode description in point group C _{2v}	frequency, cm ⁻¹		symmetry force constants ^b , CCSDT (B3LYP)						potential energy distribution ^a , %			
	obsd	CCSD(T)(B3LYP) ^c	F ₁₁	F ₂₂	F ₃₃	F ₄₄	F ₅₅	F ₆₆	F ₇₇	F ₈₈	F ₉₉	
A ₁ v ₁ in phase terminal stretches	2270	2229 (2336)	F ₁₁ 19.573(21.314)									93(1) + 6(2)
v ₂ sym central stretch	872	818 (850)	F ₂₂ 0.702(-843)	5.546(6.952)								62(2) + 23(3) + 13(4) + 2(1)
v ₃ central bending		644 (678)	F ₃₃ 0.085(-4137)	1.377(1.535)	1.540(1.427)							39(3) + 33(2) + 23(4) + 5(1)
v ₄ in phase terminal bends	209	181 (193)	F ₄₄ 0.167(171)	0.204(0.312)	0.120(0.108)	0.373(-425)						64(4) + 37(3) - 1(2)
A ₂ v ₅ torsion		475 (502)	F ₅₅ 0.0266(0.0281)									100(5)
B ₁ v ₆ torsion		405 (424)	F ₆₆ 0.0236(0.0246)									100(6)
B ₂ v ₇ out of phase term stretch	2210	2175 (2282)	F ₇₇ 19.491(21.272)									96(7) + 4(8)
v ₈ asym central stretch	1088	1032 (1167)	F ₈₈ 1.197(1.359)	4.780(5.927)								95(8) + 4(7)
v ₉ out of phase terminal bends		399 (436)	F ₉₉ 0.200(195)	0.085(0.159)	0.358(423)							99(9) + 1(8)

(a) The following symmetry coordinates were used for [N₁-N₂-N₃-N₂-N₁]⁺: S₁=v(1-2)+v(1'-2'); S₂=v(2-3)+v(2'-3); S₃=δ(2-3-2'); S₄=δ(1-2-3)+δ(1'-2'-3); S₅=τ(1-2-3-2)-τ(2-3-2)-τ(2-3-2)-τ(2-3-2)-τ(2-3-2)-τ(2-3-2); S₆=τ(1-2-3)-v(1-2)-v(1'-2'); S₇=v(2-3)-v(2'-3); S₈=δ(1-2-3)-δ(1'-2'-3); S₉=δ(1-2-3)-δ(1'-2'-3). (b) The two most important internal force constants, estimated from the calculated symmetry force constants and the observed frequencies are f₍₁₋₂₎=20.08 mdyn/Å and f₍₂₋₃₎=6.59 mdyn/Å. Stretching constants in mdyn/Å, deformation constants in mdyn/Å², and stretch-bend interaction constants in mdyn/rad.