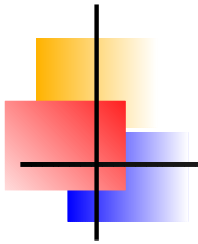

Electronic Structure & Spectroscopy of NH^+

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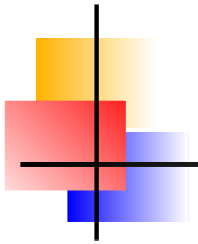
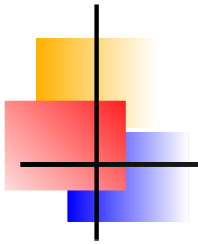


Outline

- Generalities of NH^+
- Details of calculations



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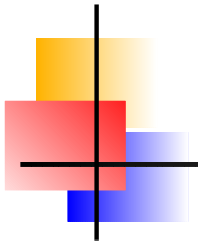
Results

- Doublets, quartets & sextets : an overview
- The five known electronic states
- Five new bound states



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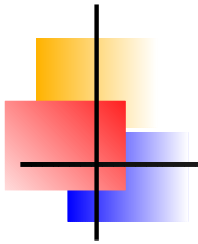
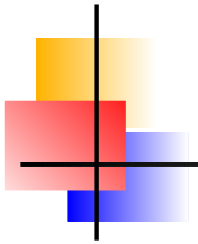
- Reactions forming NH^+ in space
- Spectroscopic data relevant in the search for NH^+
- Conclusions



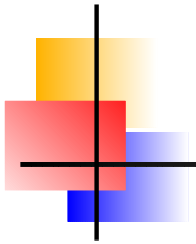
Generalities of NH^+

- Cation of the imidogen radical NH
- Both, free radical & ion
  $\Rightarrow$ extremely reactive
  $\Rightarrow$ very short lifetime
- Exists in flames & combustion plasmas
- Important in astrophysics
- Observed only in emission



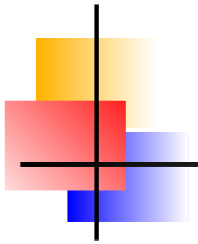
NH^+ *an elusive astrophysical species*

- Missing in the august 2004 NRAO list
  (125 observed intestellar & circumstellar molecules)
- *Snow* looked for the $C^2\Sigma^+ \rightarrow X^2\Pi$ UV line (2889 Å)
  could not observe it !
- We are not aware of searches for NH^+ in the visible



NH^+ an elusive astrophysical species

- NH^+ listed in the 1999 UMIST database for astrochemistry (modelling)
- Numerous possible precursors of NH^+ : NH_3, HNC, N_2H^+, $HCNH^+$, HC_3NH^+, NH_2, NH, ...
- Various mechanisms proposed for the formation of NH^+

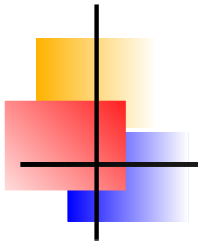


Postulated/observed diatomic cations

H_2^+	PH^+	O_2^+	CCl^+	PO^+
HeH^+	SH^+	CN^+	NS^+	SO^+
CH^+	HCl^+	CO^+	SiC^+	ClO^+
NH^+	C_2^+	NO^+	SiN^+	S_2^+
OH^+	N_2^+	CP^+	SiO^+	SiS^+
SiH^+		CS^+	PN^+	

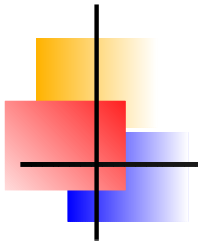
Only 3 species observed ! (out of 28)

$\Rightarrow$ more observational effort required !



Why NH^+ has not been observed in space ?

- Abundance of NH^+ most likely very low !
  $\Rightarrow$ awaiting for progress in detector sensitivity
- Absorption & emission lines obscured
  by those of more abundant species ?
- Signal below noise level ?
- Observations from above the Earth's atmosphere
  seem compulsory
- Not enough observational effort ?
  $\Rightarrow$ visible, IR, submilimeter, MW, radio



Details of the calculations

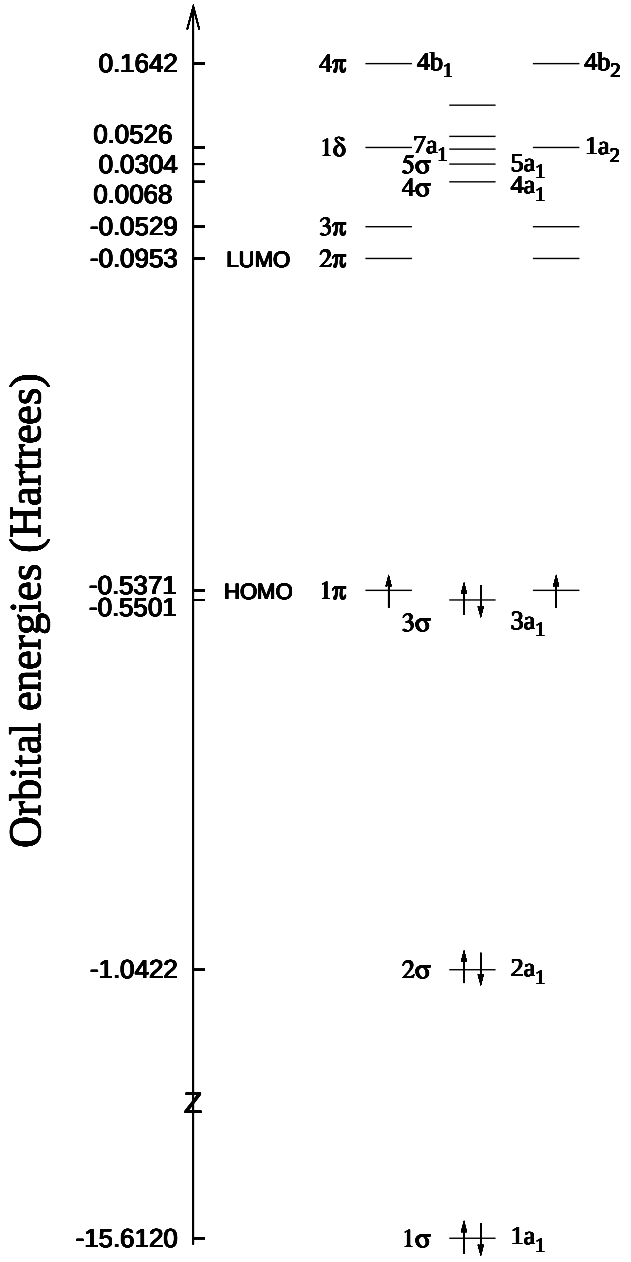
Electronic structure calculations

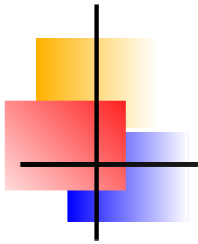
Ab initio SCF MRSD–CI

Bonn–Wuppertal package

Basis : DZ + POL + Ryd (3s,3p,3d,4s) + s,p bond

SCF MO diagram of NH





The first electronic states of NH^+

The ground state

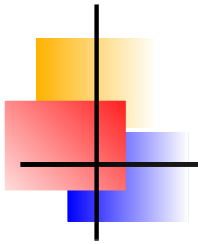
- $7e$
- One–open–shell
- $1\sigma^2 2\sigma^2 3\sigma^2 1\pi$

The first excited states

- $3\sigma \rightarrow 1\pi$
- Three–open–shell
- $1\sigma^2 2\sigma^2 3\sigma 1\pi^2$
- $\sigma\pi^2$

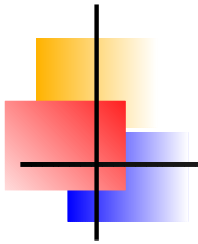
  $\Rightarrow {}^4\Sigma^-, {}^2\Sigma^-, {}^2\Delta, {}^2\Sigma^+$

Only states observed !



Surprising:

From the infinity number of electronic states of NH^+, only the states arising from the $3\sigma \rightarrow 1\pi$ excitation have been observed !



Calculated states of NH^+

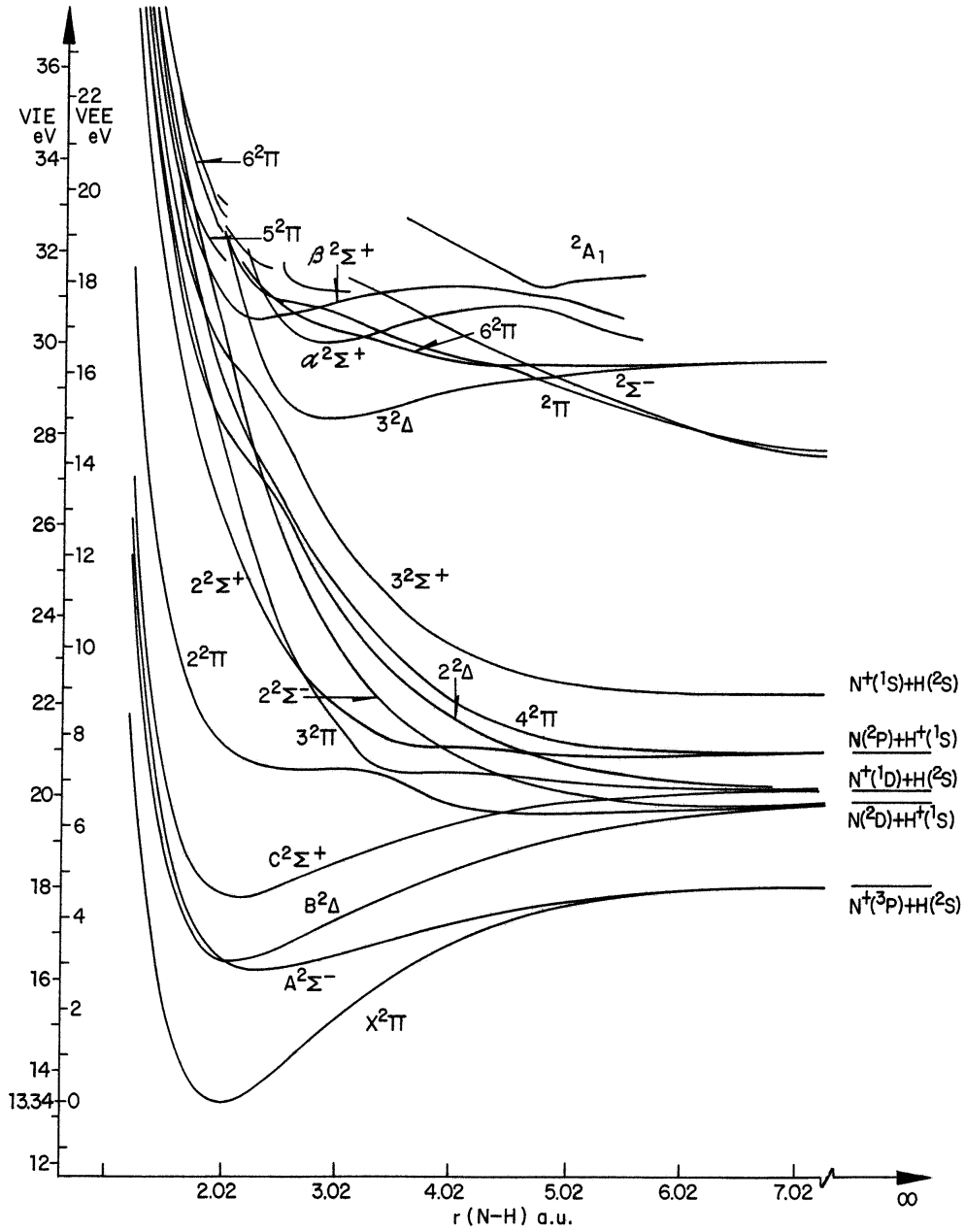
- 49 electronic states

  18 doblets

  22 quartets

  9 sextets

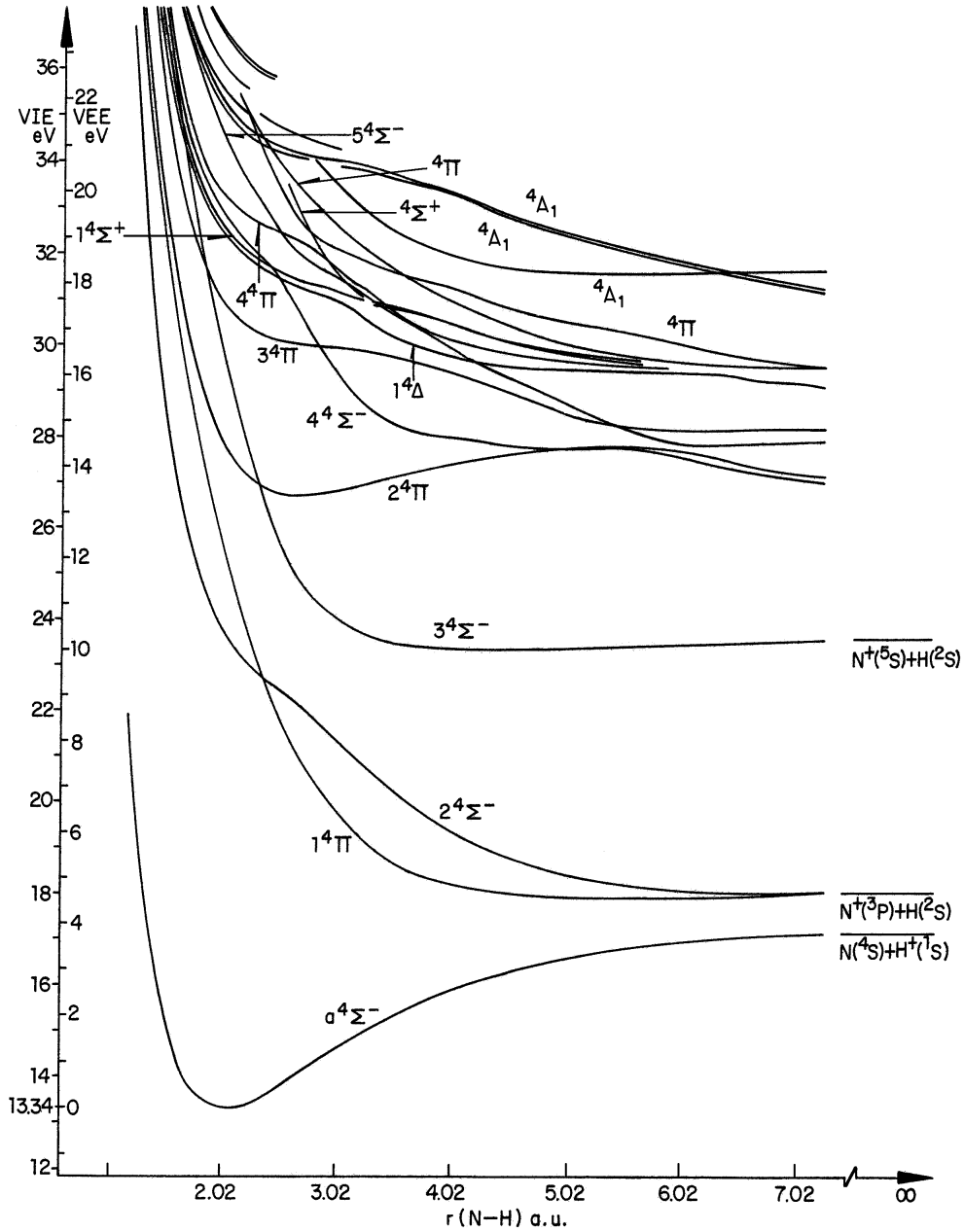
Doublet electronic states of NH^+



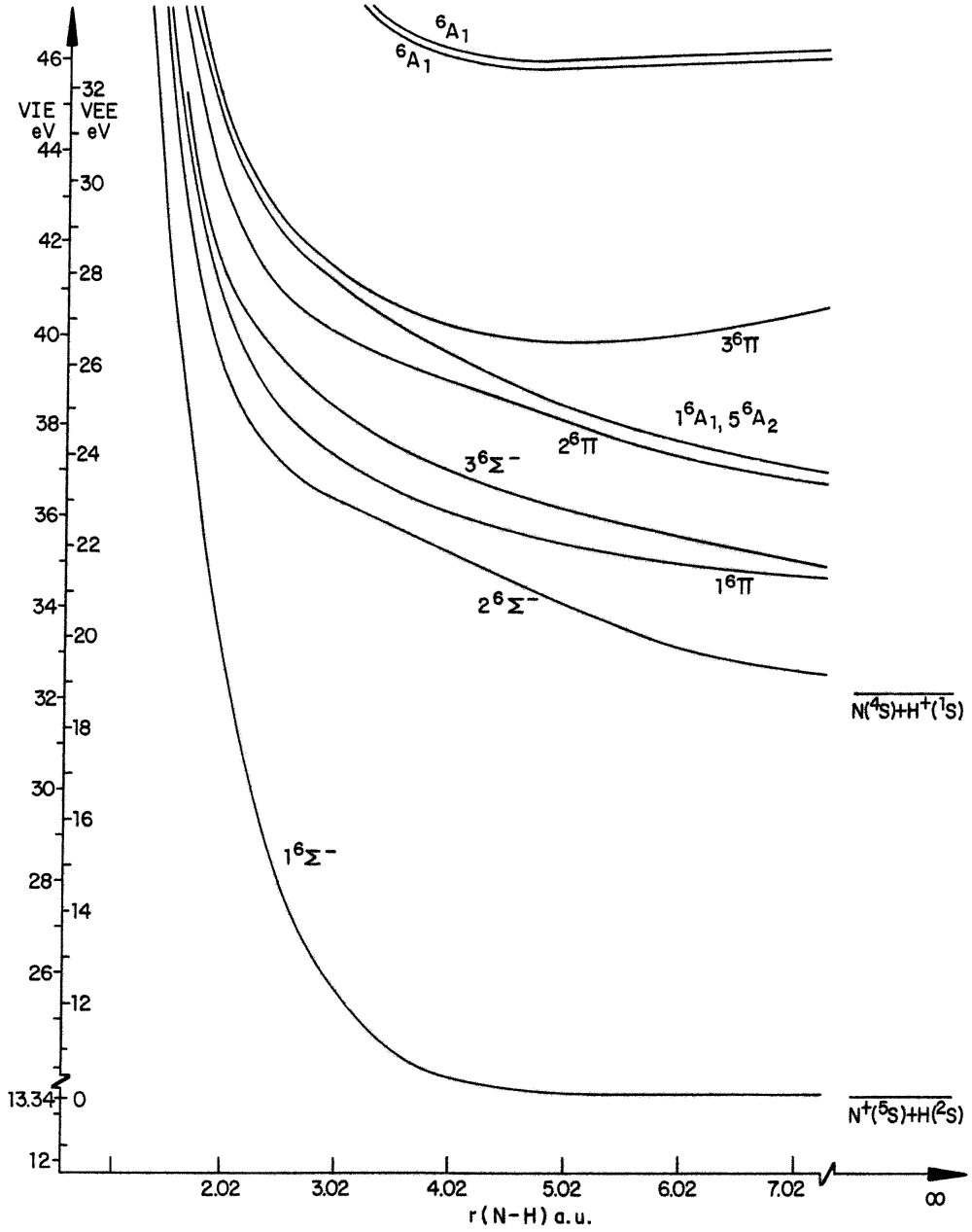
Attributes of the lowest doublet electronic states of NH^+ at $r_e(X^2\Pi)$

State	Character	Dominant/(chief) excitation	Configuration(s)
$^2\Sigma^+$ $(\alpha)^\dagger$	V	$3\sigma^2 \rightarrow 1\pi 10\sigma$	$0.19\ 2\sigma^2 1\pi_x^2 10\sigma + 0.19\ 2\sigma^2 1\pi_y^2 10\sigma$ $+0.07\ 2\sigma 3\sigma^2 1\pi_x^2 + 0.07\ 2\sigma 3\sigma^2 1\pi_y^2$
$4^2\Sigma^+$ $(\beta)^\dagger$	RV	$1\pi \rightarrow 9\sigma$	$0.28\ 2\sigma^2 3\sigma^2 9\sigma$ + $0.20\ 2\sigma^2 3\sigma^2 11\sigma$
$3^2\Delta^\dagger$	V	$3\sigma^2 \rightarrow 1\pi 10\sigma$	$0.20\ 2\sigma^2 1\pi_x^2 10\sigma + 0.19\ 2\sigma^2 1\pi_y^2 10\sigma$ $0.30\ 2\sigma^2 1\pi_x 1\pi_y 10\sigma + 0.22\ 2\sigma^2 3\sigma 1\pi_x 2\pi_y$
$3^2\Pi$	VR	$3\sigma \rightarrow 10\sigma$	$0.51\ 2\sigma^2 3\sigma 1\pi_x 10\sigma + 0.11\ 2\sigma^2 3\sigma 1\pi_x 9\sigma$
$2^2\Sigma^+$	VR	$1\pi \rightarrow 10\sigma$	$0.44\ 2\sigma^2 3\sigma^2 10\sigma + 0.10\ 2\sigma^2 3\sigma^2 9\sigma$
$2^2\Pi$	V	$3\sigma^2 \rightarrow 1\pi^2$	$0.91\ 2\sigma^2 1\pi_x 1\pi_y^2$
$1^2\Sigma^+$ (C)	V	$3\sigma \rightarrow 1\pi$	$0.45\ 2\sigma^2 3\sigma 1\pi_x^2 + 0.45\ 2\sigma^2 3\sigma 1\pi_y^2$
$1^2\Delta$ (B)	V	$3\sigma \rightarrow 1\pi$	$0.46\ 2\sigma^2 3\sigma 1\pi_x^2 + 0.46\ 2\sigma^2 3\sigma 1\pi_y^2$ $0.92\ 2\sigma^2 3\sigma 1\pi_x 1\pi_y$
$1^2\Sigma^-$ (A)	V	$3\sigma \rightarrow 1\pi$	$0.92\ 2\sigma^2 3\sigma 1\pi_x 1\pi_y$
$1^2\Pi$ (X)	V		$0.89\ 2\sigma^2 3\sigma^2 1\pi_x$

Quartet electronic states of NH^+

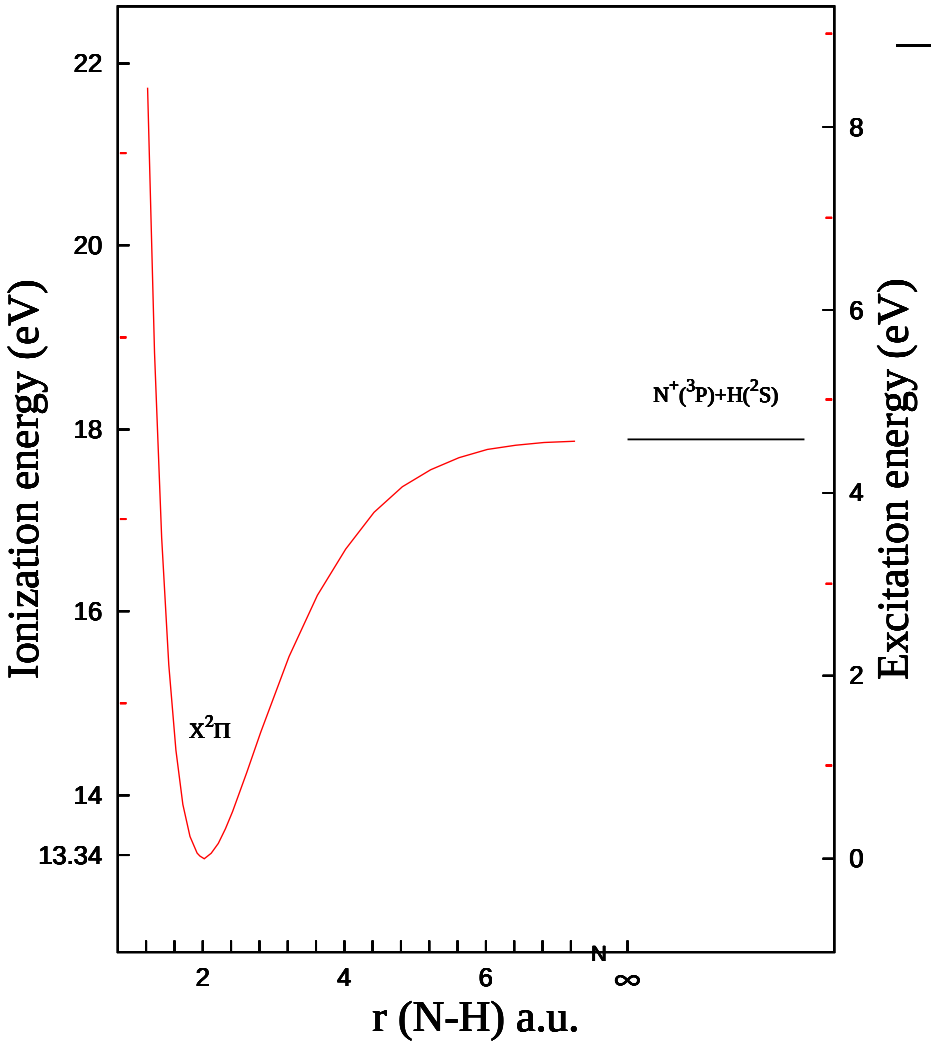


Sextet electronic states of NH^+



Observed electronic states of NH^+

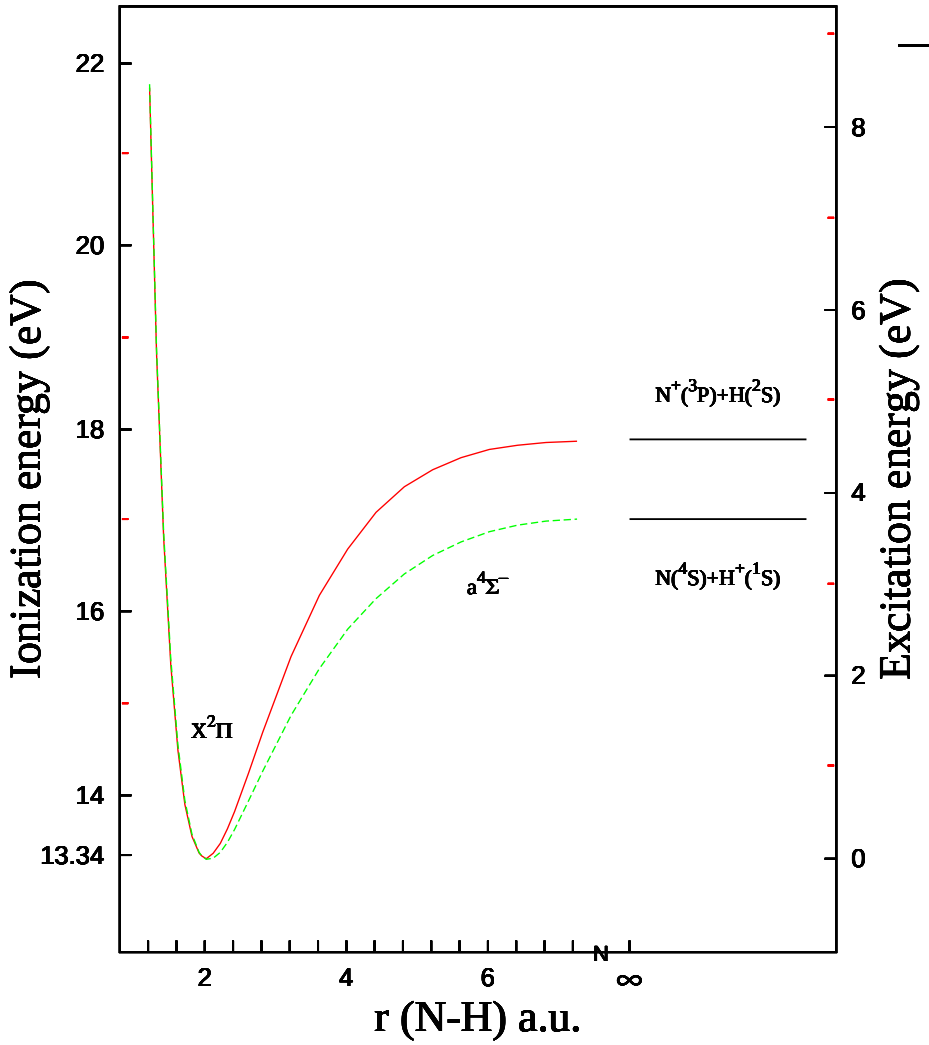
Molecular parameters of $X^2\Pi$



	T	E
r_e (Å)	1.067	1.0692
B_e (cm^{-1})	15.62	15.68
ω_e (cm^{-1})	3166	3047
D_e (eV)	$\geq$ 4.54	4.664
IP (eV)	13.34	13.476

Observed electronic states of NH^+

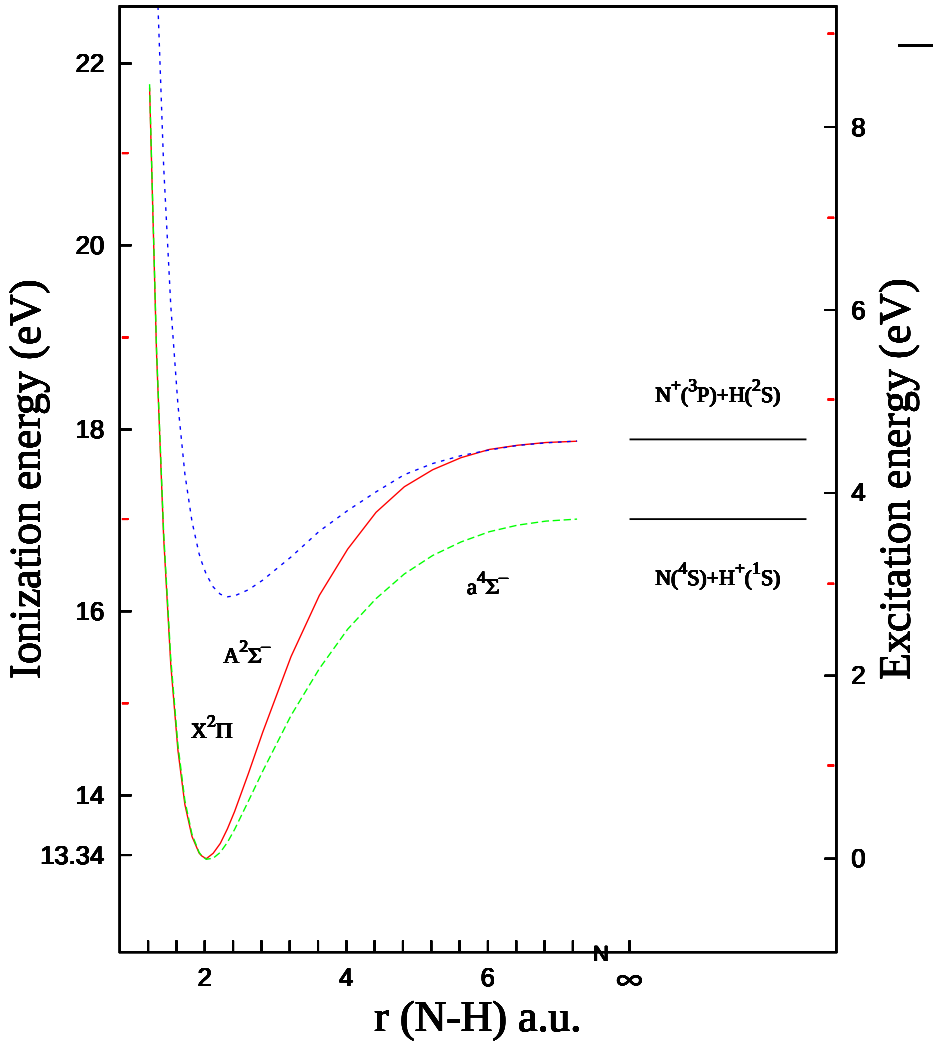
Molecular parameters of $a^4\Sigma^-$



	T	E
r_e (Å)	1.088	1.093
B_e (cm^{-1})	15.32	15.013
ω_e (cm^{-1})	2796	2672
D_e (eV)	3.72	3.664
T_e (eV)	−113	354
IP (eV)	13.29	—

Observed electronic states of NH^+

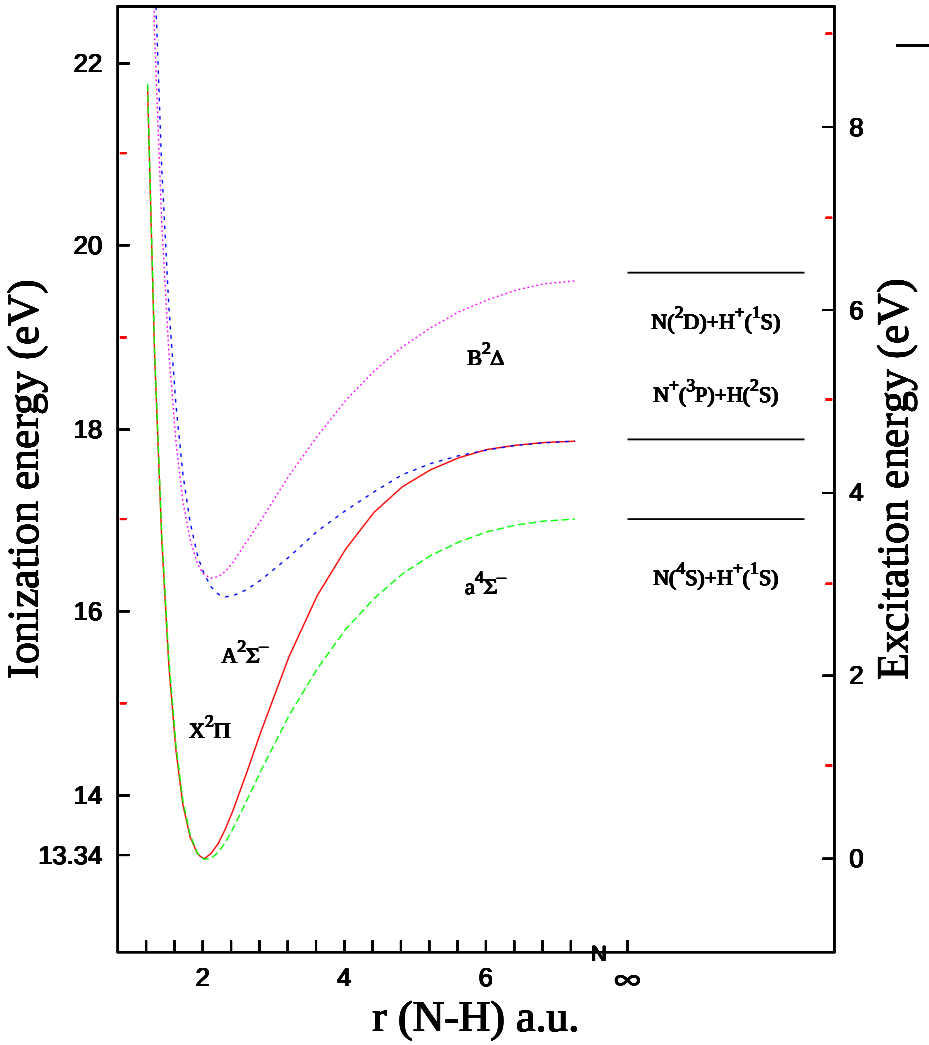
Molecular parameters of $A^2\Sigma^-$



	T	E
r_e (Å)	1.244	(1.2704)
B_e (cm^{-1})	11.71	(11.1105)
ω_e (cm^{-1})	1766	1706.9
D_e (eV)	$\geq$ 1.70	—
T_e (eV)	2.87	(2.67)
IP (eV)	16.18	16.16

Observed electronic states of NH^+

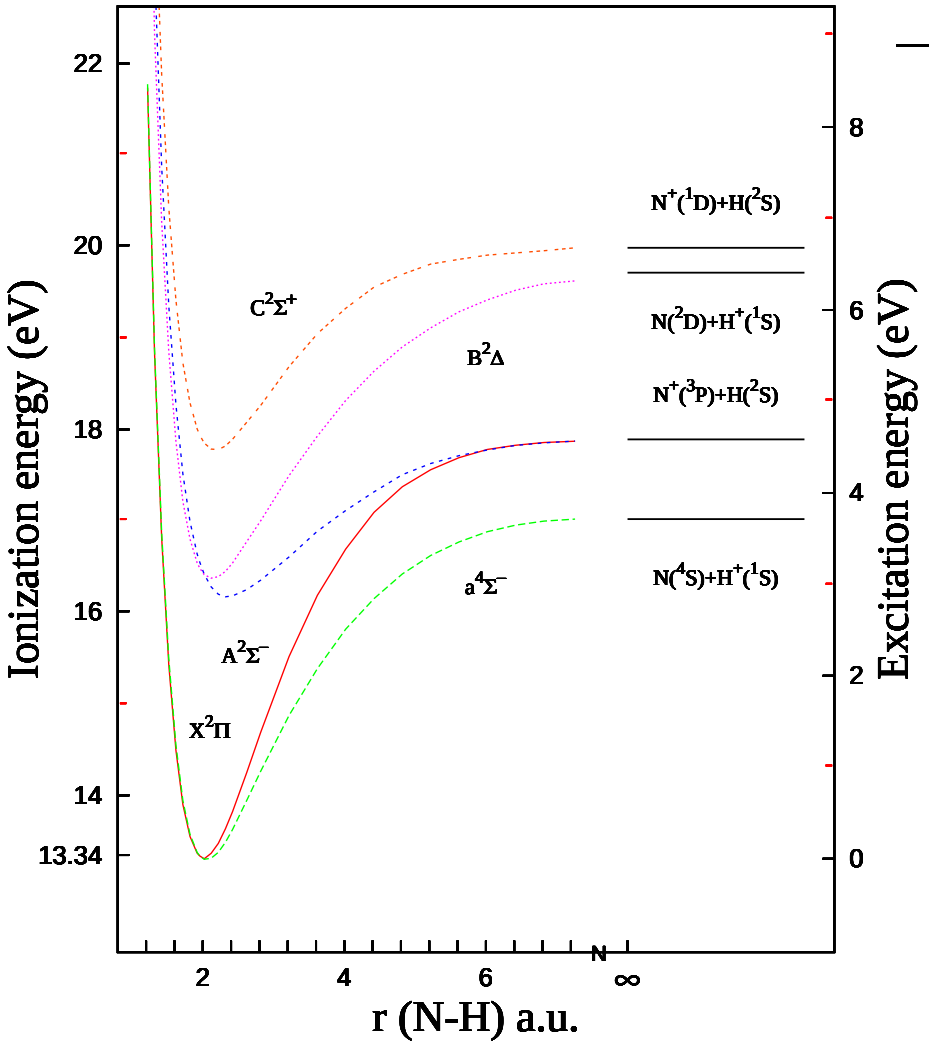
Molecular parameters of $B^2\Delta$



	T	E
r_e (Å)	1.130	(1.1519)
B_e (cm^{-1})	14.18	13.8
ω_e (cm^{-1})	2506	2371
D_e (eV)	$\geq$ 3.25	—-
T_e (eV)	3.06	(2.846)
IP (eV)	16.37	16.34

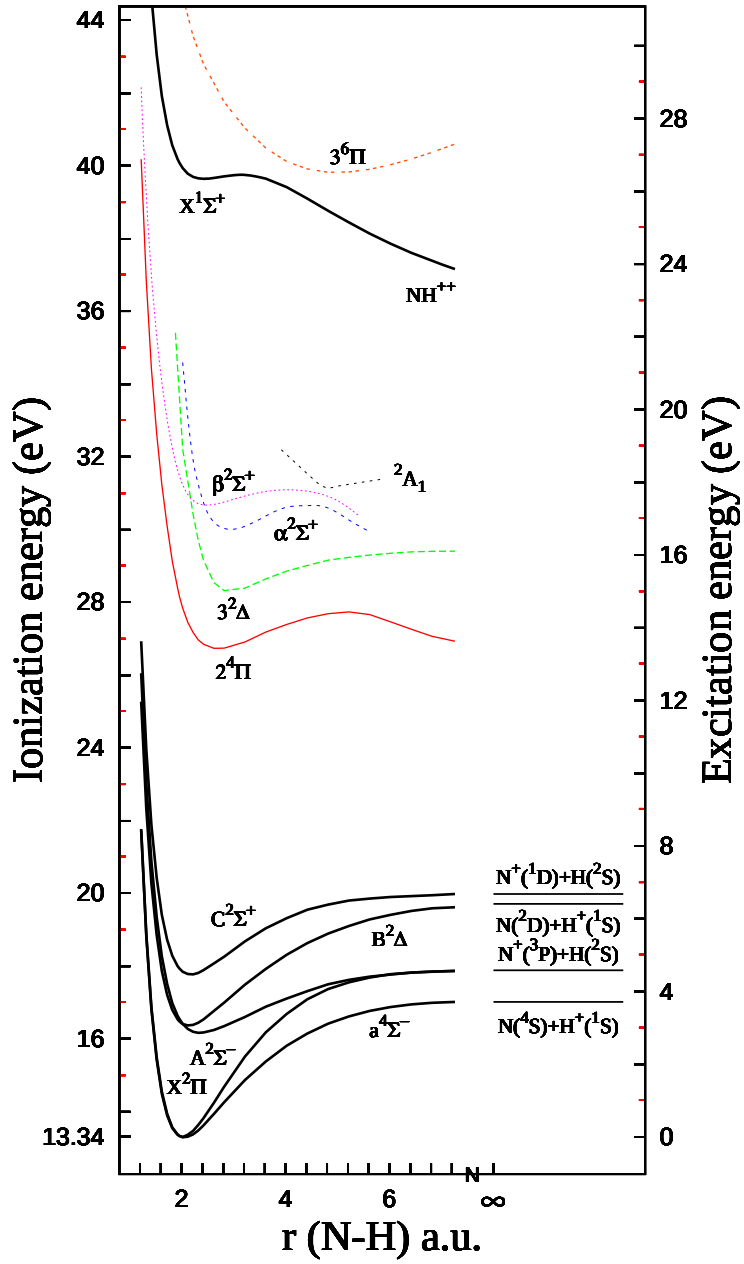
Observed electronic states of NH^+

Molecular parameters of $C^2\Sigma^+$



	T	E
r_e (Å)	1.150	1.164
B_e (cm^{-1})	13.70	13.231
ω_e (cm^{-1})	2373	2310
D_e (eV)	≥ 2.17	—-
T_e (eV)	4.46	4.28
IP (eV)	17.77	—-

New bound electronic states of NH^+



Spectroscopic properties of the new bound states of NH^+

Property	Unit	States				
		$2^4\Pi$	$3^2\Delta$	$\alpha^2\Sigma^+$	$\beta^2\Sigma^+$	$3^6\Pi$
r_e	Å	1.428	1.562	1.551	1.228	2.642
ω_e	cm^{-1}	1601	3038	1863	2970	742
B_e	cm^{-1}	8.85	8.17	7.53	12.02	2.59
D_e	eV	$\geq$1.0	$\geq$1.10	$\geq$1.05	$\geq$0.69	$\geq$0.78

Reactions that might be involved in the formation of NH^+ in space

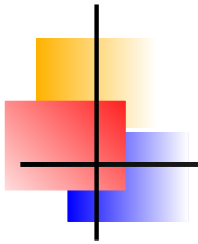
Reaction	Process	Region	Rate constant
NH+$h\nu$ $\rightarrow$NH$^+$+e	PI		1.00×10^{-11}
	PI, $\lambda < 919$ Å	C, ISM	
NH_3+$h\nu$$\rightarrow$NH$^+$+$H_2$+$e$	PI		6.9×10^{-9}
NH+γ $\rightarrow$NH$^+$+e	CRI		1.30×10^{-17}
H$^+$+NH$\rightarrow$NH$^+$+H	CT		2.10×10^{-9}
		LDC,MDC	1.0×10^{-9}
N$^+$+NH$\rightarrow$NH$^+$+N	CT	MDC,DMC	3.70×10^{-10}
O$^+$+NH$\rightarrow$NH$^+$+O	CT	MDC,DMC	3.60×10^{-10}
H_2^++NH$\rightarrow$NH$^+$+H_2	CT		7.60×10^{-10}
			$\sim 1 \times 10^{-9}$
N_2^++NH$\rightarrow$NH$^+$+N_2	CT		6.50×10^{-10}
CN$^+$+NH$\rightarrow$NH$^+$+CN	CT		6.50×10^{-10}
CO$^+$+NH$\rightarrow$NH$^+$+CO	CT		3.20×10^{-10}
OH$^+$+NH$\rightarrow$NH$^+$+OH	CT		3.60×10^{-10}

Reactions that might be involved in the formation of NH^+ in space

Reaction	Process	Region	Rate constant
$He^+ + HNC \rightarrow NH^+ + C + He$	IN		5.00×10^{-10}
$He^+ + NH_2 \rightarrow NH^+ + He + H$	IN		8.00×10^{-10}
$He^+ + NH_3 \rightarrow NH^+ + He + H_2$	IN		1.76×10^{-10}
	2.2×10^{-9}		
$N^+ + H_2 \rightarrow NH^+ + H$	IN		1.00×10^{-9}
		DMC	0.48×10^{-9}
$N^+ + HD \rightarrow NH^+, ND^+$	IN		
$N^+ + H_2O \rightarrow NH^+ + OH$	IN	C	
$N^+ + H_2S \rightarrow NH^+ + HS$	IN		5.70×10^{-11}
$N^+ + HCO \rightarrow NH^+ + CO$	IN		4.50×10^{-10}
		ISC	0.45×10^{-9}
$H_2^+ + N \rightarrow NH^+ + H$	IN		1.90×10^{-9}
$N^+(^3P) + H(^2S) \rightarrow NH^+(A^2\Sigma^-)$	RA	DMC	3×10^{-7}
$\rightarrow NH^+(X^2\Pi) + h\nu$			

Spectroscopic data relevant in the search for NH^+ in space

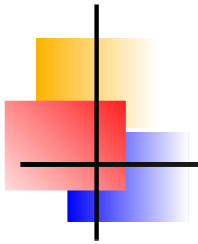
Spectral region	Upper state	Lower state	Transition	Transition energy
VUV	$2^4\Pi$	$a^4\Sigma^-$	$2^4\Pi \rightarrow a^4\Sigma^-$	979 Å
UV	$C^2\Sigma^+$	$X^2\Pi$	$C(v'=0) \rightarrow X(v''=0)$	2885 Å
			$C(v'=1) \rightarrow X(v''=0)$	2725 Å
			$C(v'=1) \rightarrow X(v''=1)$	2980 Å
Visible	$B^2\Delta$	$X^2\Pi$	$B(v'=0) \rightarrow X(v''=0)$	4348.5 Å
	$A^2\Sigma^-$	$X^2\Pi$	$A(v'=1) \rightarrow X(v''=0)$	4312.7 Å
			$A(v'=0) \rightarrow X(v''=0)$	4628.9 Å
			$A(v'=0) \rightarrow X(v''=1)$	5349.4 Å
IR	$X^2\Pi(v=1)$	$X^2\Pi(v=0)$	1–0	3.17 μm (3150 c
Far–IR	$a^4\Sigma^-$	$X^2\Pi(v''=0)$	$a(v'=0)$–$X(v''=0)$	T_0=354 cm^{-1}
				$T_v \sim 550$ cm^{-1}
Submil.	$X^2\Pi_{\frac{1}{2}}(v=0,J=\frac{3}{2})$	$X^2\Pi_{\frac{1}{2}}(v=0,J=\frac{1}{2})$	$J=\frac{3}{2} \leftarrow J=\frac{1}{2}$	1.019 GHz (34 c
Radio	$X^2\Pi_{\frac{1}{2}}$	$X^2\Pi_{\frac{1}{2}}$	$e \leftarrow f$	13.52GHz
(Λ–doub)	$(v=0,N=1,J=\frac{1}{2},e)$	$(v=0,N=1,J=\frac{1}{2},f)$		(0.451cm^{-1})



Conclusions

The present study represents a substantial contribution to the knowledge of the electronic structure of NH^+

- We calculated 49 electronic states. The majority reported for the first time
- Improved, more detailed potential energy curves
- Spectroscopic parameters of known bound electronic in good agreement with our theoretical values
- We found five new bound electronic states of NH^+
- Calculating many electronic states not a mere academic exercise
  $\Rightarrow$ novel, interesting spectroscopic information can be obtained



Conclusions

$\Rightarrow$ Challenge for experimentalists

- Detect the five new bound electronic states (r_e, ω_e, B_e, VEE)