ROTATIONAL SPECTRA OF THE MOLECULAR IONS H_2NCO^+ AND NCO^-

Valerio Lattanzi
Carl A. Gottlieb
Patrick Thaddeus
Michael C. McCarthy

Harvard-Smithsonian Center for Astrophysics
School of Engineering & Applied Sciences, Harvard University

Sven Thorwirth

I. Physikalisches Institut Universität zu Köln
Max-Planck-Institut für Radioastronomie

The H, N, C, O system

✓ 4 main elements in the ISM; > 90 % molecules detected

✓ HNCO observed in over 60 galactic sources and 9 external galaxies

✓ Discovery of isomerization

(Liebig & Gay-Lussac, Ann. Chim. Phys. 1824)

✓ Cyanic acid and fulminic acid recently observed in interstellar gas

(Brünken et al., ApJ 2009; Marcelino et al., ApJ 2009)

The NCO^- anion

✓ Closed-shell $^1\Sigma$ ground state with a very large electron affinity (EA = 3.6 eV)

✓ *(Bradforth et al., 1992)*

✓ Several studies on the solid state properties of cyanate ion

(Sherman & Wilkinson, 1973)

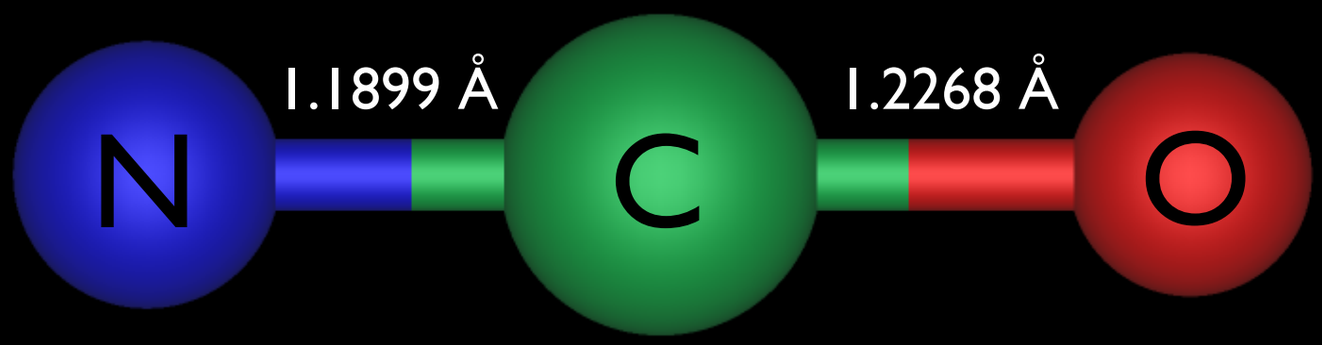
✓ IR laser spectroscopy work derived ground state rotational constant and CD quartic term; from CC study dipole moment of μ = 1.5 D

(Gruebele et al., 1987; Pak et al., 1997)

✓ No-detection search for NCO^- in dark cloud, L134N by Morisawa et al.

(Morisawa et al., 2005)

✓ New CCSD(T)/aug-cc-pwCV5Z calculations for nitrogen quadrupole coupling constant (eQq)



Protonated isocyanic acid, H_2NCO^+ & $HNCOH^+$

- ✓ Isocyanic acid large proton affinity (7.49 eV)
- ✓ C_{2v} isomer more stable form by ~ 18 kcal/mol

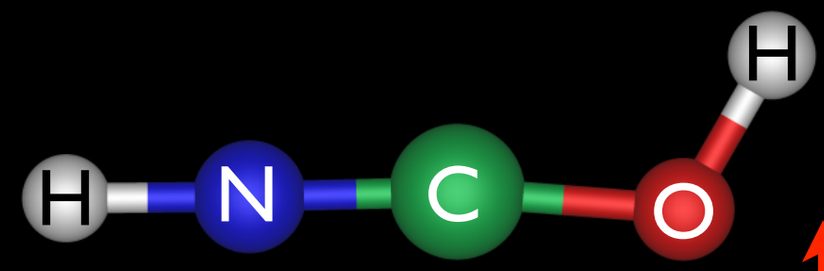
(Green, 1981)

- ✓ In the gas phase protonation sequence is:

$H_3^+ + HNCO \rightarrow H_2 + H_2NCO^+$

(Hudson, 2005)

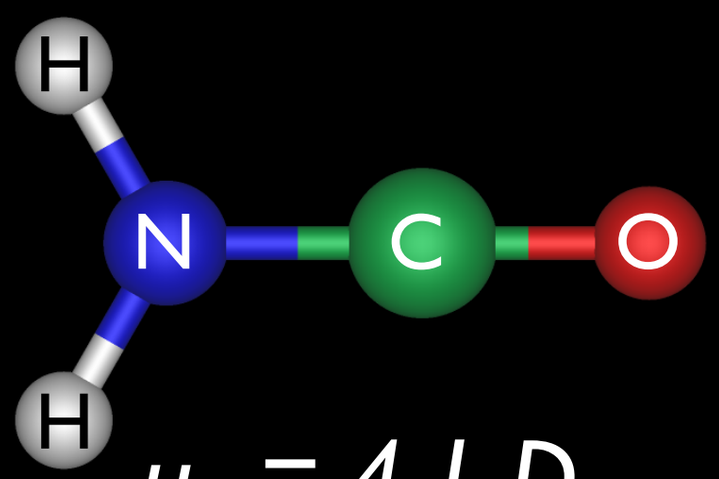
- ✓ No lab/astro data
- ✓ New calculations:
  - ✓ *H_2NCO^+*:
    CCSD(T)/cc-pwCV5Z - CCSD(T)/cc-pVQZ
  - ✓ *$HNCOH^+$*:
    CCSD(T)/cc-pwCVQZ - CCSD(T)/cc-pVTZ



$\mu_a = 1.3$ D

$\mu_b = 1.7$ D

18 kcal/mol



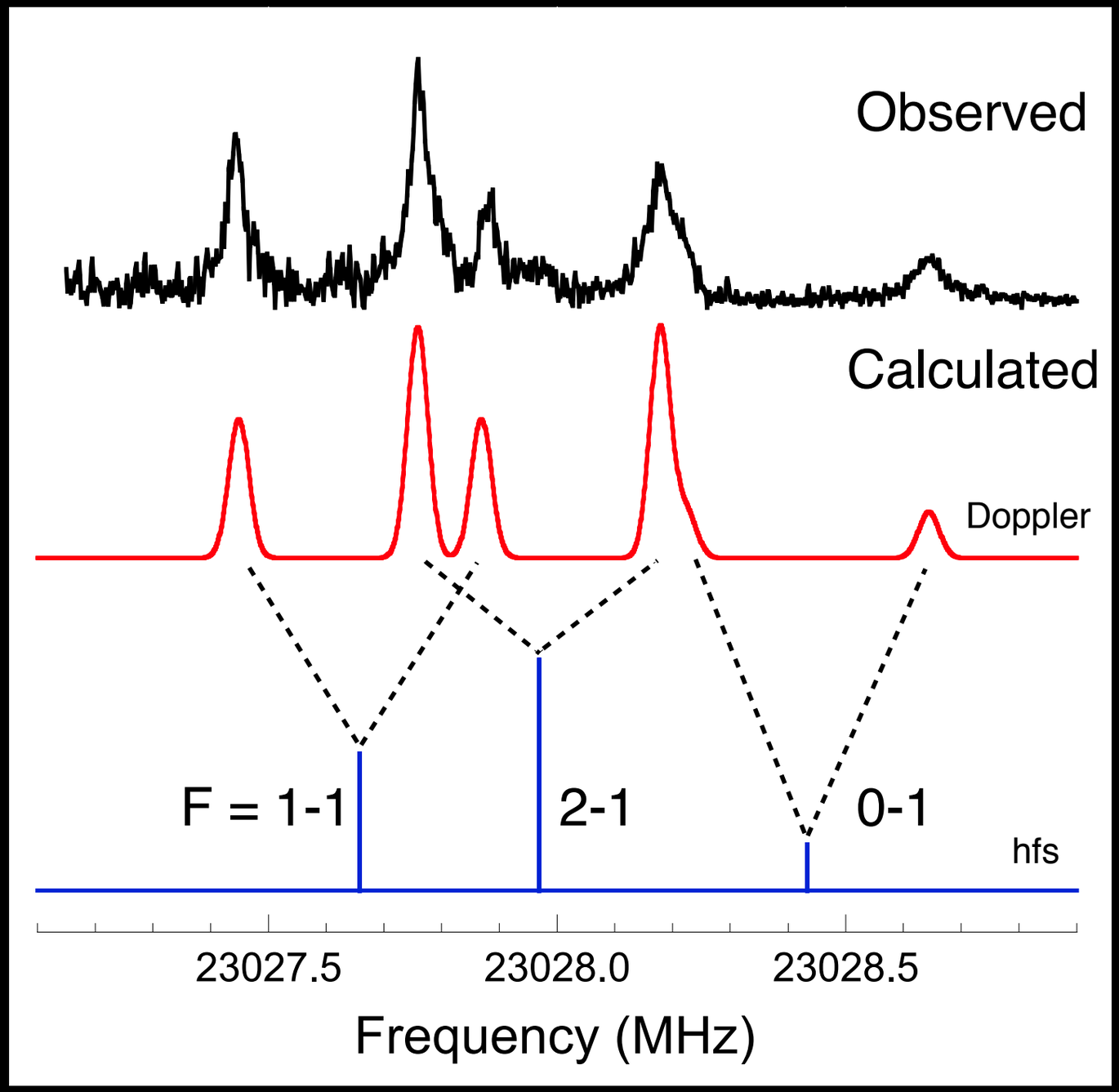
$\mu_a = 4.1$ D

Experimental setup - FTMW

- ✓ Detection of the fundamental rotational transition by FTMW spectroscopy
  - ✓ 5 - 42 GHz
  - ✓ 6 Hz pulsed nozzle to inject the supersonic molecular beam (~ Mach 2)
- ✓ T_{rot} ~ 1-3 K
- ✓ Synthesized isocyanic acid from KOCN + H_3PO_4
- ✓ DC discharge of HNCO heavily diluted in a H_2 buffer

J = 1 - 0

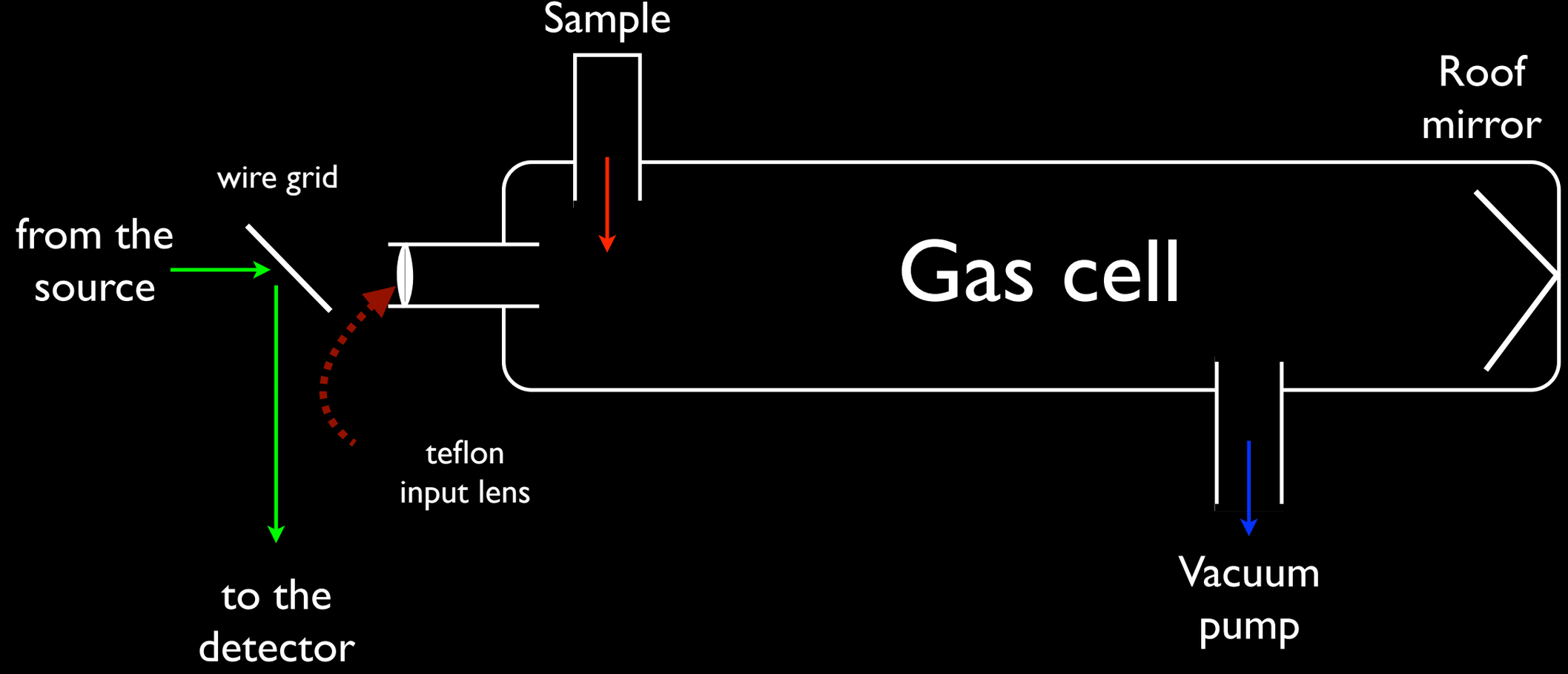
- ✓ 4 consecutive scans
- ✓ 15 minutes each
- ✓ 2σ from IR rotational constant
- ✓ expected 3:5:1 hyperfine ratio



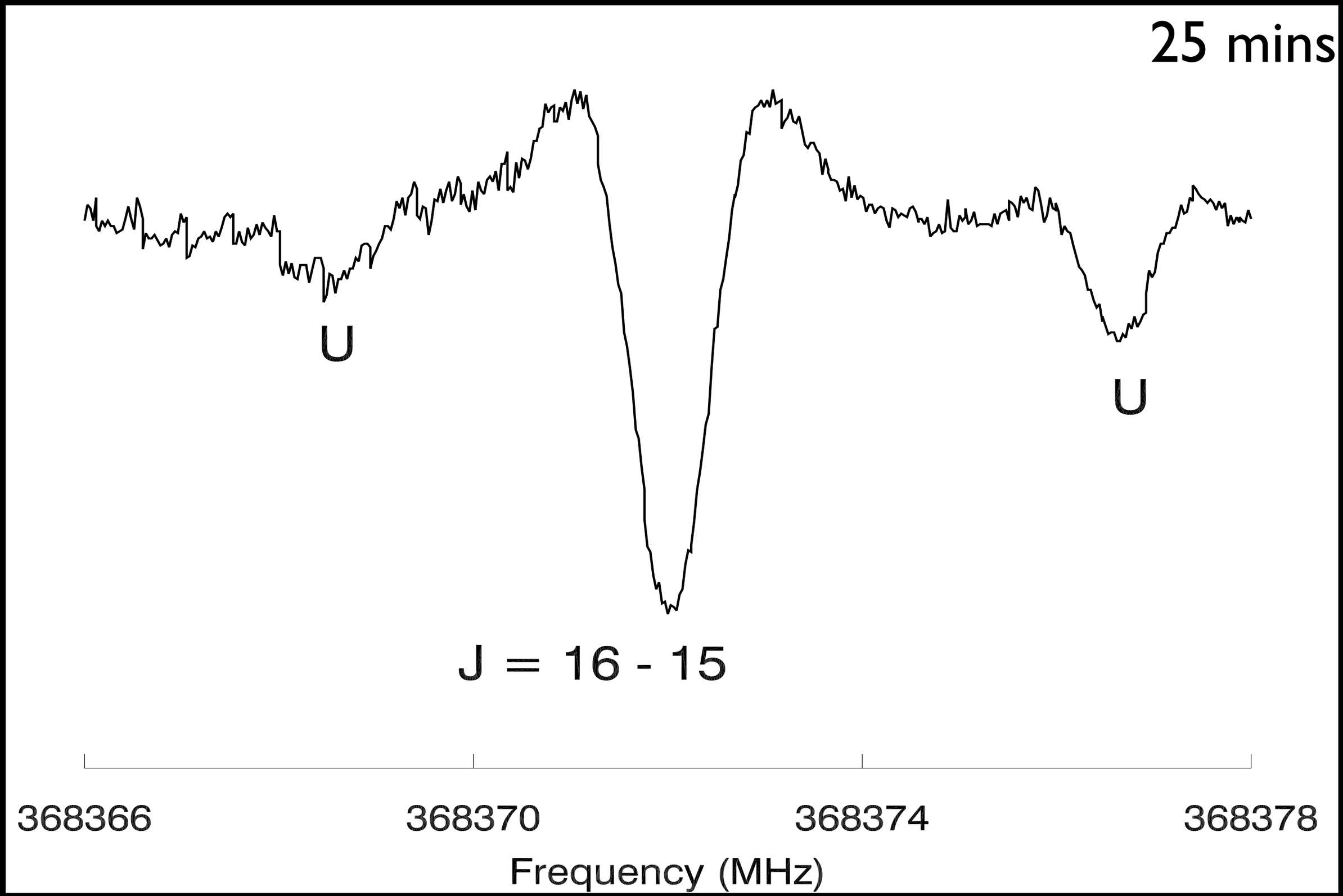
Lattanzi et al., ApJ in press

Experimental setup - mm-wave

- ✓ Mixture of H_2O and $(CN)_2$ in an argon buffer, in a room temperature cell
- ✓ 6 lines detected with this conditions in the 161 - 368 GHz range



MM-wave spectrum



NCO^- : freqs & consts

Transition		Frequency	$O-C$
$J'-J$	$F'-F$	(MHz)	(kHz)
$1-0$	$1-1$	23027.659(2)	1
	$2-1$	23027.969(2)	0
	$0-1$	23028.432(2)	0
$7-6$		161189.304(20)	9
$8-7$		184214.146(20)	3
$9-8$		207238.157(20)	29
$10-9$		230261.101(20)	-21
$13-12$		299323.109(20)	7
$16-15$		368372.276(20)	-5

Constant	This work	IR	Theoretical
B	11513.96789(50)	11516.3(13)	11507
$10^3 D$	4.5588(16)	4.62(33)	
eQq	$-1.0307(37)$		-1.00

Lattanzi et al., ApJ in press

H_2NCO^+ & $HNCOH^+$

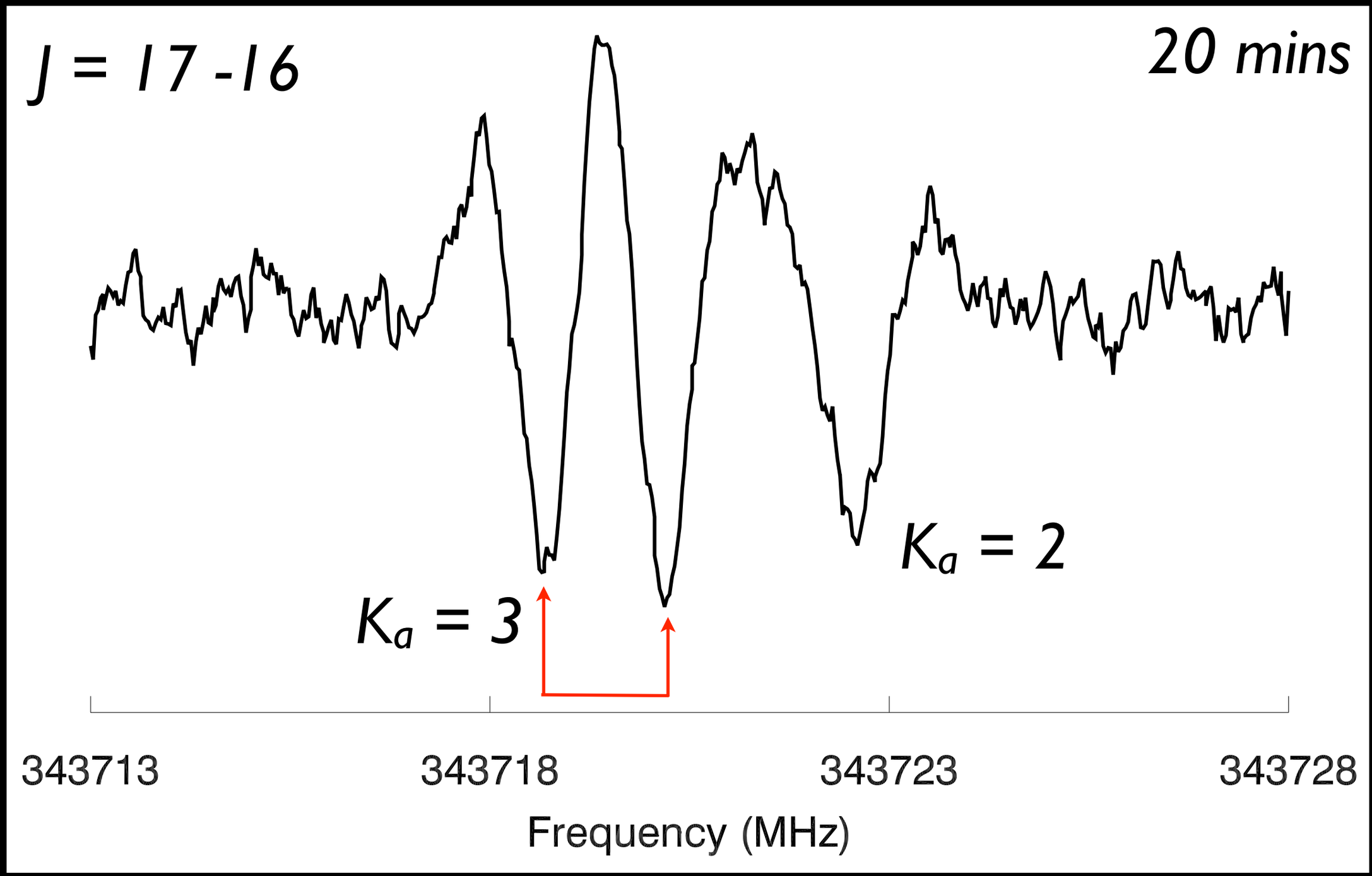
- ✓ Under the same experimental conditions, search with FTMW for protonated isocyanic acid
- ✓ Fundamental rotational transition of H_2NCO^+ found at 0.02% from the predicted value!!
- ✓ Soon observed the J(2 - 1) $K_a = 0$ and $K_a = 1$ lower
- ✓ All the transitions with the expected hyperfine structure
- ✓ First two $K_a = 0$ rotational transitions of the higher energy isomer (18 kcal/mol) $HNCOH^+$

mm spectrum of H_2NCO^+

- ✓ After the MW detection, mm-wave search
- ✓ Better condition using the *HNCO* synthesized sample in a -50 °C cell
- ✓ A total of 18 mm-wave transitions detected
- ✓ Up to K_a = 3

Constant (MHz)	Laboratory	Theoretical
A	319339(33)	319690.8
B	10278.6785(19)	10280.3
C	9948.9010(14)	9951.8
D_{JK}	0.381397(85)	0.386
$10^3 D_J$	3.0604(12)	2.96
$10^3 D_K$	25.3	25.3
$10^6 d_1$	−108.8(16)	−96.6
$10^6 d_2$	−41.4(13)	−26.2
χ_{aa}(N)	3.6263(56)	3.205
χ_{bb}(N)	1.369(14)	0.932

mm spectrum of H_2NCO^+



Conclusion

✓ *B* and *D* for the anion three orders of magnitude improvement

✓ The entire rotational spectrum can now be calculated well into the THz region to 1 km s^{-1}

✓ Two new molecular ions detected for the first time

✓ mm-wave spectrum of H_2NCO^+ good for radioastronomical search

✓ Isomer interstellar chemistry

✓ mm-wave search for $HNCOH^+$ in progress

Acknowledgments

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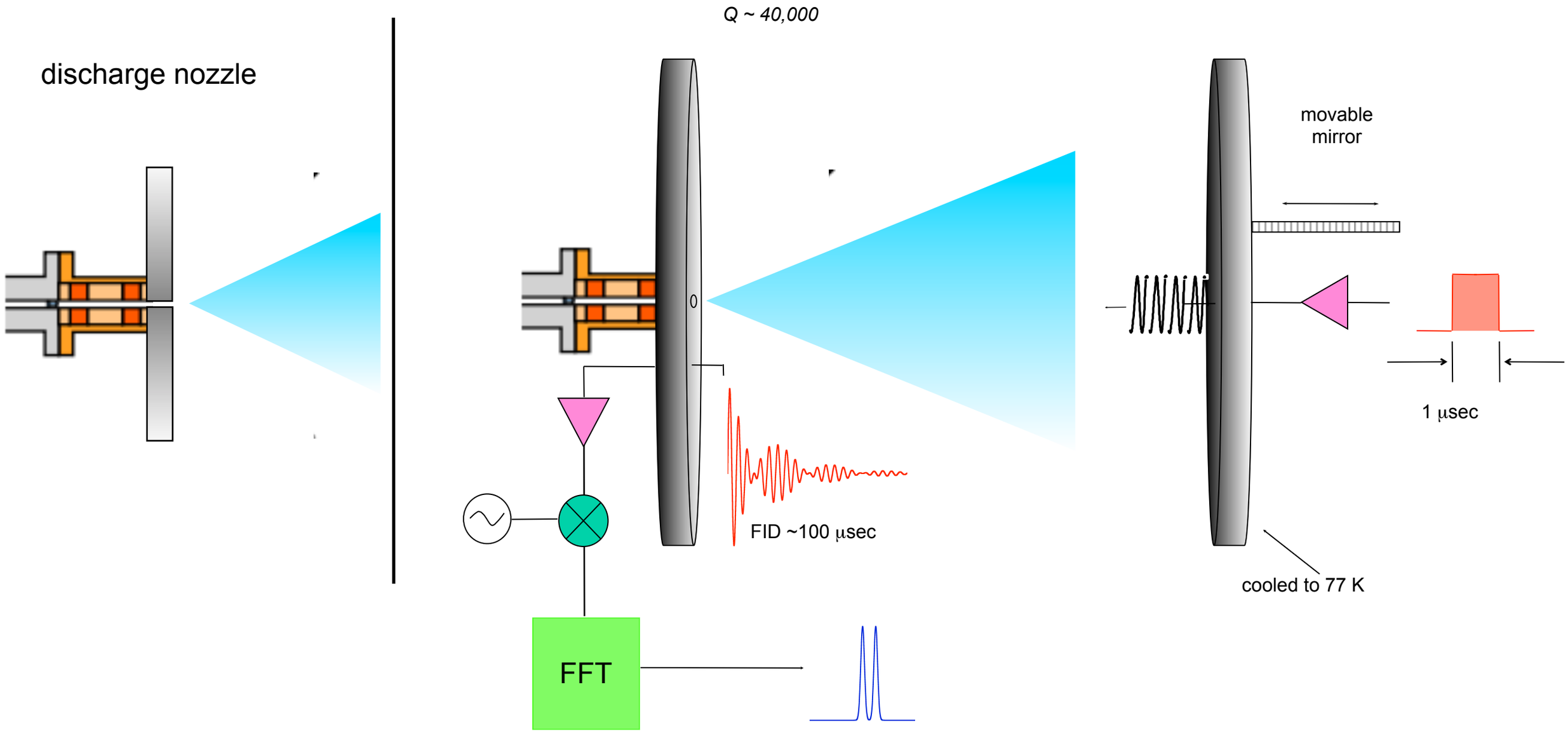
FTM spectrometer



credit M. C. McCarthy