

# Precise measurement of $\text{N}_2^+$ vibrational transition frequency

- toward the test of variation in  $m_p/m_e$

NICT

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We discuss the attainable accuracies of vibrational transition frequency of  $\text{N}_2^+$  molecular ion

$\text{N}_2^+$  molecular ion:

produced in a **selected state** by REMPI (photo-ionization)  
sympathetically cooled with laser cooled ion

with  $I = 0$

$(v, N) = (0, 0) - (1, 2)$  attainable accuracy  $10^{-14}$

(measured in Basel with the accuracy of  $1.8 \times 10^{-7}$ )

$(0, 2) - (1, 2)$  attainable accuracy  $10^{-16}$

$(0, 0) - (1, 0)$  attainable accuracy  $10^{-17}$

with  $I = 1, 2$  significant Zeeman shift

$v$ : vibrational state       $N$ : rotational state       $I$ : nuclear spin

# Why precise measurement of molecular transition is useful?

test of variation in  $m_p/m_e$        $f \propto (m_p/m_e)^\lambda$   
 $\lambda$ : sensitivity parameter

molecular **vibrational** transition:  $\lambda \sim -0.5$

molecular **rotational** transition :  $\lambda \sim -1$

**nuclear motion**

Reference candidate:  $^1S_0 - ^3P_0$  transition of  $^{87}\text{Sr}$  atom or  $^{27}\text{Al}^+$  ion  
small dependence for  $\alpha$  and  $m_p/m_e$   
accuracies of the order of  $10^{-18}$

# Current upper limit of variation in $m_p/m_e$

$$|\Delta(m_p/m_e)/(m_p/m_e)| < 10^{-16}/\text{yr}$$

comparison between quasar (10 billion light years) and on earth

Cs hyperfine transition and Yb<sup>+</sup> S-D, S-F transitions

## Required measurement uncertainty

$$|[\delta f / f]| < 10^{-16} \times \lambda$$

low  $|[\delta f / f]|$  or high  $\lambda$ ?

Transitions with  $\lambda \gg 1$  are generally sensitive also to the Stark and Zeeman perturbation

# My previous proposals

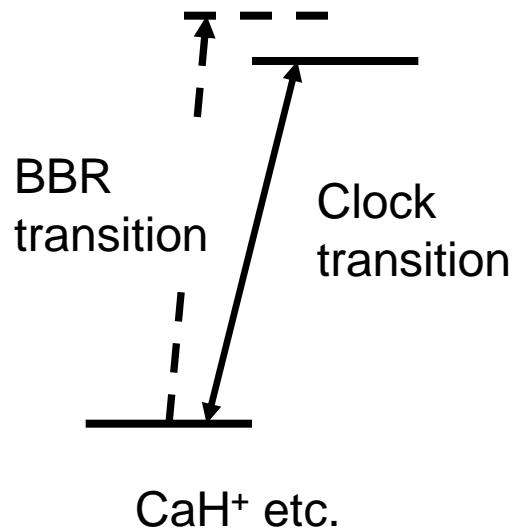
$X^1\Sigma(v,N) = (0,0) \rightarrow (1,0)$  transition of  $\text{CaH}^+$ ,  $\text{YbH}^+$

frequency : 40 – 50 THz

attainable accuracy  $10^{-16}$

Stark shift is large  $\rightarrow$  string crystal in a linear trap is required

**Blackbody radiation induced transitions disturb measurement** (cryogenic chamber required)



$^{14}\text{N}_2^+$  molecular ion in  $X^2\Sigma_g$  state

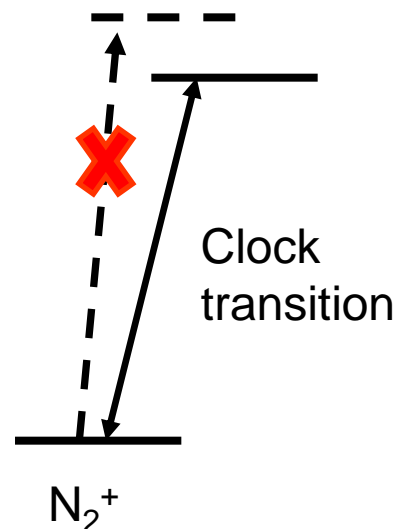
$I = 0, 2$   $N$ : even numbers (with  $^{15}\text{N}_2^+$  only  $I = 0$ )

$I = 1$   $N$ : odd numbers

There is **NO Electric Dipole** coupling between different states in the electronically ground state

**No transition is induced by blackbody radiation**

**Cryogenic chamber is not required**



# Stark shift

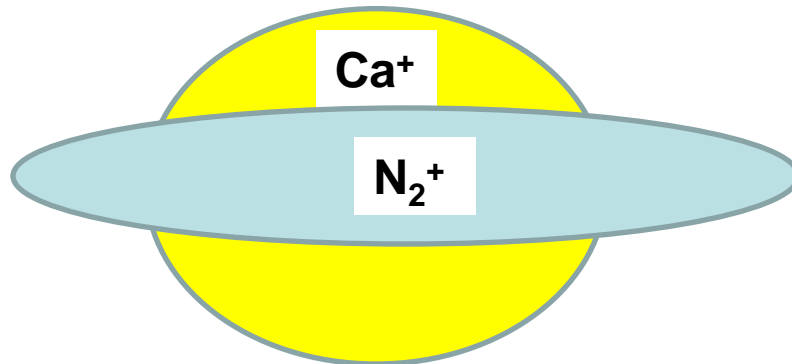
induced only by the coupling with electronically excited states

Stark shift at each state  $\rightarrow$  order of  $0.4 \text{ mHz}/(\text{V/cm})^2$

shift in the vibrational transition freq.  $< 4 \text{ }\mu\text{Hz}/(\text{V/cm})^2$

(diagonal coupling  $\rightarrow$  cancellation of shifts in upper and lower states)

**Measurement with a string crystal is not required**



can be measured with  
many molecular ions

# Zeeman shift

Magnetic field can cause Zeeman shift by the interaction with

Electron spin **S** ( $= 1/2$ ) :  $\mu_B g_S = 1.4 \text{ MHz/G}$

no dependence on the vibrational state

Nuclear spin **I** :  $\mu_B g_I = 300 \text{ Hz/G}$  for  $^{14}\text{N}_2^+$

about 0.1ppm difference with  $\Delta v = 1$

Molecular rotation **N** :  $\mu_B g_N = -49 \text{ Hz/G}$  for  $^{14}\text{N}_2^+$  in  $v = 0$

1% difference with  $\Delta v = 1$

Zeeman shift of the **order of 1 MHz** is induced by the magnetic field of **1 G** (because of **S**), and it is generally **non-linear**

**Exception 1:** Transition between **stretched states**  
(effect of **S** in both states are cancelled)

$$(F = S + I + N, M_F = \pm F)$$

with these case the Zeeman shift is **strictly linear**

$$\sim \Delta N \times 49 \text{ Hz/G}$$

$$N_u = N_d \neq 0 \sim N \times 0.5 \text{ Hz/G} \quad (\text{difference of } g_N)$$

$$N_u = N_d = 0 \sim I \times 30 \text{ } \mu\text{Hz/G} \quad (\text{difference of } g_I)$$

$$(\text{zero for } N_u = N_d = I = 0)$$

This discussion is valid only for molecules with  $^1\Sigma$  and  $^2\Sigma$   
(spin-spin interaction mixes different electron spin states with  $^3\Sigma$ )



## Exception 2: $\Delta N = \Delta J = \Delta F = \Delta M_F = 0$ transition

$$J = S + N, F = J + I$$

when  $I = 0$ ,  $|J, M_J\rangle$  states are given by the coupling of  $|M_S, M_N\rangle$  states

$$|J, M_J\rangle = a_1 |M_S = 1/2, M_N = M_J - 1/2\rangle + a_2 |M_S = -1/2, M_N = M_J + 1/2\rangle$$

Linear Zeeman coefficient at each states

$$C_Z = \underbrace{\mu_B g_S (|a_1|^2 - |a_2|^2)/2}_{\text{electron spin}} + \underbrace{\mu_B g_N [|a_1|^2 (M_J - 1/2) + |a_2|^2 (M_J + 1/2)]}_{\text{molecular rotation}}$$

$I = 0$  ( $J$ : good quantum number)

$a_{1,2}$ : no dependence on the vibrational states  $\Delta(|a_1|^2 - |a_2|^2) = 0$

Zeeman shift in Q transition

$$\Delta C_Z = \mu_B \Delta g_N [|a_1|^2 (M_J - 1/2) + |a_2|^2 (M_J + 1/2)] \quad N \times 0.5 \text{ Hz/G}$$

$I = 1, 2$  ( $J$ : not good quantum number)  $a_{1,2}$  has slight dependence on  $v$

Zeeman shift in Q transition

$$\Delta C_Z = \mu_B g_S \Delta(|a_1|^2 - |a_2|^2)/2 \quad \text{a few kHz/G}$$

electron spin effect NOT cancelled

# Experiment in Basel(Nat. Phys. **10**, 820(2014))

Measurement with Quantum Cascade Laser

$\text{N}_2^+$  ( $\nu, N$ )=(0,0)  $\rightarrow$  (1,2) transition  $\Delta N = \Delta J = \Delta F = 2$

$I = 0$  ( $\nu, N, J, M_J$ )=(0,0,1/2, $\pm 1/2$ )  $\rightarrow$  (1,2,5/2,  $\pm 5/2$ )

for  $M_J = 1/2 \rightarrow 5/2$  -100 Hz/G  $M_J = -1/2 \rightarrow -5/2$  100 Hz/G

(strict linear and cancelled averaging two transitions)

Attainable accuracy  $10^{-14}$  limited by electronic quadrupole shift

( $N = 0$  is automatically stretched state)

$I = 2$  (difficult to prepare in a stretched state)

observed spectrums

$(\nu, N, J, F)$ =(0,0,1/2,5/2)  $\rightarrow$  (1,2,5/2,9/2)

=(0,0,1/2,3/2)  $\rightarrow$  (1,2,5/2,7/2)

Zeeman shift induced by magnetic field of 1 G is larger than 0.1 MHz

**$(\nu, N)=(0,2) \rightarrow (1,2)$  transition with  $I = 0$  ( $F = J$ )**

$$\Delta N = \Delta J = \Delta M_J = 0 \quad J = 3/2 \text{ or } 5/2$$

Stark, Zeeman, and Electric quadrupole shifts at upper and lower states are **cancelled more than 99 %**

**much higher accuracy is attainable than  $N = 0 \rightarrow 2$  transition**  
 $J = 3/2$

$$(\nu, N, J) = (0, 2, 3/2) \rightarrow (1, 2, 3/2)$$

$$\Delta M_J = 0 \quad M_J = \pm 1/2, \pm 3/2$$

Average of these 4 transition frequencies are free from

linear Zeeman	$M_J = +3/2$	+0.9 Hz/G	$M_J = +1/2$	+0.3 Hz/G
	$M_J = -1/2$	-0.3 Hz/G	$M_J = -3/2$	-0.9 Hz/G

electric quadrupole shift ( $< 0.1$  Hz)

**Actually we observe one overlapped spectrum free from these shifts**

$$\text{Quadratic Zeeman shift} \quad M_J = \pm 3/2 \quad -20 \text{ Hz/G}^2 \quad M_J = \pm 1/2 \quad -30 \text{ Hz/G}^2$$

**With magnetic field lower than 0.03 G, accuracy of  $5 \times 10^{-16}$**

$$J = 5/2$$

$$(\nu, N, J) = (0, 2, 5/2) \rightarrow (1, 2, 5/2)$$

$$\Delta M_J = 0 \quad M_J = \pm 1/2, \pm 3/2, \pm 5/2$$

Average of these 6 transition frequencies are free from

linear Zeeman  $M_J = \pm 5/2 \quad \pm 1.0 \text{ Hz/G}$

$$M_J = \pm 3/2 \quad \pm 0.6 \text{ Hz/G}$$

$$M_J = \pm 1/2 \quad \pm 0.2 \text{ Hz/G}$$

electric quadrupole shift ( $< 0.1 \text{ Hz}$ )

Actually we observe one overlapped spectrum free from these shifts

Quadratic Zeeman shift  $M_J = \pm 3/2 \quad +20 \text{ Hz/G}^2 \quad M_J = \pm 1/2 \quad +30 \text{ Hz/G}^2$

Averaging  $(\nu, N, J) = (0, 2, 3/2) \rightarrow (1, 2, 3/2)$

$$(0, 2, 5/2) \rightarrow (1, 2, 5/2)$$

also the quadratic Zeeman shift is cancelled

Accuracy of  $10^{-16}$  can be obtained

**$\Delta N = \Delta J = \Delta F = \Delta M_F = 0$  transitions of molecular ions with  $I = 1, 2$**

$I = 1$  (odd rotational states)

$I = 2$  (even rotational states)

**J-mixing** makes the linear Zeeman shift large    **a few kHz/G**

**Narrow hyperfine splitting** makes the quadratic Zeeman shift large    **a few 100 Hz/G<sup>2</sup>**

**Complicated energy structure** makes the preparation in a selective quantum state difficult

**It seems difficult to measure with the uncertainty lower than  $10^{-12}$**

# $(\nu, N)=(0,0)-(1,0)$ transition with $I = 0$

$\text{N}_2^+$   $(\nu, N)=(0,0) \rightarrow (1,0)$  65 THz

$I = 0$

$(\nu, N, J, M_J)=(0,0,1/2, \pm 1/2) \rightarrow (1,0,1/2, \pm 1/2)$

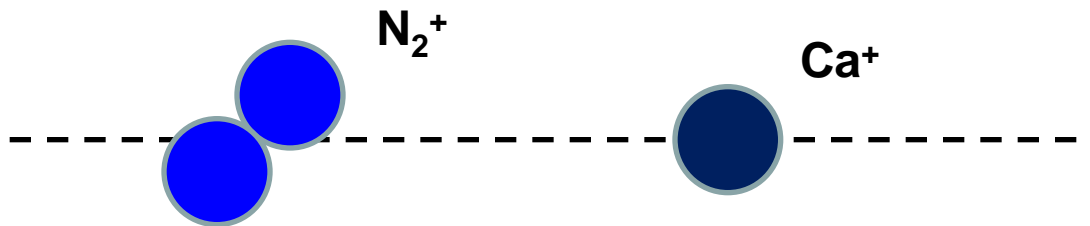
For a single transition frequency

**Zeeman shift is zero**

**Electric quadrupole shift is also zero**

Also the measurement with a **single molecular ion** in a string crystal is possible (**quantum logic detection**)

**Attainable accuracy  $10^{-17}$**



Also quadratic Doppler shift is smaller

# Q(0) transition should be observed by Raman transition

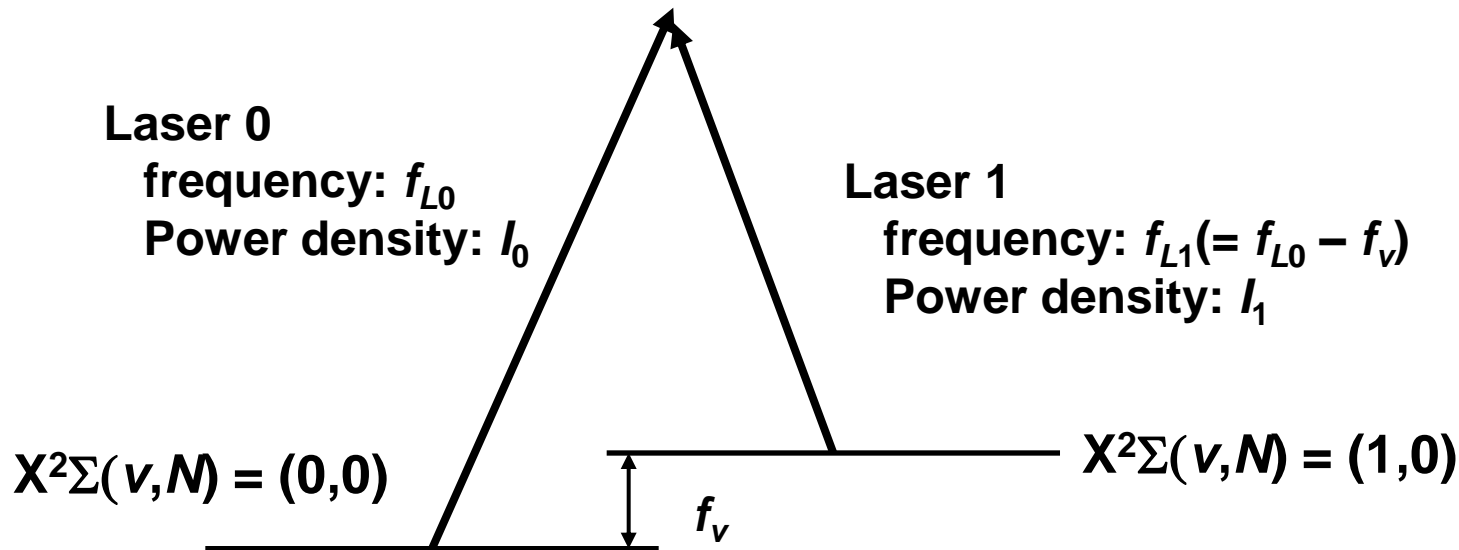
Stark is eliminated (  $I_0 = I_1$  : intensity should be stabilized)

	Frequencies	$I_{0,1}$ (Rabi freq. 1 Hz)	One laser shift
$\nu = 0 \rightarrow 1$	429.1 THz + 363.9 THz	3 W/cm <sup>2</sup>	$10^{-14}$
	541.6 THz + 476.4 THz	3 W/cm <sup>2</sup>	$2 \cdot 10^{-15}$

One intense laser with magic wavelength + another weak laser

Stark shift

$\nu = 0 \rightarrow 1$	<b>453.9</b> THz (3 kW/cm <sup>2</sup> ) + <b>388.7</b> THz (6 mW/cm <sup>2</sup> )	$10^{-17}$
	+ <b>519.1</b> THz (4.2 mW/cm <sup>2</sup> )	$10^{-18}$



## Comparison with other molecular ions

	$^{14}\text{N}_2^+$	$^{40}\text{CaH}^+$	$\text{HD}^+$
Natural linewidth (Hz)	$< 0.1$	5.5	0.14
DC Stark shift ( $/(V/\text{cm})^2$ )	$8 \cdot 10^{-20}$	$-3 \cdot 10^{-15}$	$1.1 \cdot 10^{-17}$
BBR shift (300 K)	$4 \cdot 10^{-18}$	$-6 \cdot 10^{-16}$	$10^{-16}$

## Ca<sup>+</sup> cooling laser light shift

397 nm ( $/(W/\text{cm}^2)$ )	$4 \cdot 10^{-14}$	$7 \cdot 10^{-14}$
866 nm ( $/(W/\text{cm}^2)$ )	$-2 \cdot 10^{-15}$	$-2 \cdot 10^{-14}$

The Ca<sup>+</sup> cooling light shift can be eliminated taking the proper intensity ratio between 397 nm and 866 nm



# Conclusion

Precise measurement of  $\text{N}_2^+$  vibrational transition frequencies are useful to test the variation in the proton-to-electron mass ratio.

Attainable accuracies with  $I = 0$

$(v, N) = (0,0)-(1,2)$	$10^{-14}$	linear Zeeman	100 Hz/G
$= (0,2)-(1,2)$	$10^{-16}$	linear Zeeman	1 Hz/G
		quadratic Zeeman	20-30 Hz/G <sup>2</sup>
$= (0,0)-(1,0)$	$10^{-17}$	zero Zeeman shift	

With  $I = 1,2$

Linear Zeeman with Q-transition a few kHz/G

Quadratic Zeeman with Q-transition a few 100 Hz/G<sup>2</sup>

It is preferable to ionize molecules only in the  $I = 0$  state selectively  
best method : use  $^{15}\text{N}_2$

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Phys. Rev. A 92, 043423 (2015)

I appreciate a lot to be a member of FPUA, seeing that the precise measurement has an important role for all fields of physics

