PHYSICAL REVIEW A **92**, 043423 (2015)

$N_2{}^+$ quadrupole transitions with small Zeeman shift

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(Received 31 August 2015; published 30 October 2015)

The vibrational transition frequencies of a $N_2{}^+$ molecular ion are advantageous for precise measurement because the Stark shift is much smaller than that of heteronuclear diatomic molecules. The ${}^{14}N_2{}^+$ S(0) transition has been observed by a group in Basel. For most transitions, the Zeeman shift limits the attainable accuracy. This paper reports the quadrupole transitions (observed with simpler apparatus than that required for the Raman transition) for which the Zeeman shift is less than 100 Hz at a magnetic field of 1 G. Q(N) transitions (N: even) of the molecular ion with $I = 0$ are advantageous for measurement within an uncertainty of 10^{-16}. The transition frequencies of molecular ions with $I \neq 0$ are difficult to measure within an uncertainty of 10^{-12} because J-mixing makes the linear Zeeman coefficient in the Q transitions large and narrow hyperfine splitting makes the quadratic Zeeman coefficient large.

DOI: 10.1103/PhysRevA.92.043423 PACS number(s): 32.60.+i, 06.20.Dk, 33.20.Ea

I. INTRODUCTION

The precise measurement of molecular vibrational transitions is useful for investigating the variation in the proton-to-electron mass ratio. The vibrational transition frequency of SF_6 has been measured in a thermal beam with an uncertainty of 10^{-14} [1]. The first- and second-order Doppler effects are significant in measurement using molecules in a free space at room temperature, and measurement with cold trapped molecules is required to obtain higher accuracy. The measurement of the vibrational transition frequencies of molecules such as ^{40}Ca ^{6}Li, ^{88}Sr ^{6}Li [2], and ^{174}Yb ^{6}Li [3,4] has been proposed. These molecules can be potentially generated in large numbers from cold atoms through photoassociation or Feshbach resonances and may be trapped in optical traps. Collision shifts are suppressed by trapping the molecules in three-dimensional optical lattices and the ac Stark shift can be eliminated by setting the trap laser wavelength to the magic wavelength. The frequency uncertainty can potentially be lower than 10^{-16} in this method; however, the generation and trapping of the above molecules has not yet been demonstrated.

The transition frequencies of molecular ions can also potentially be measured with high accuracy, because molecular ions can be easily trapped and cooled through sympathetic laser cooling simultaneously with trapped atomic ions. The electric field at the node of a linear trap is zero, therefore, the transition frequency of molecular ions in a string crystal (localized on the node) is free from the Stark shift. On the other hand, the Stark shift becomes significant as the distribution of molecular ions is broadened in the radial direction. Therefore, the measurement should be performed with a limited number of molecular ions, and the preparation of molecular ions in a selected quantum state is required. XH^+ (X: even isotopes of the group II elements) molecular ions [5–7] can be probed with a single molecular ion in a string crystal because the molecular ion can be pumped to the vibrational-rotational ground state, where there is no hyperfine splitting [8]. The overtone-vibrational transition of a ${}^{40}CaH^+$ molecular ion has been observed by Khanyile *et al.* [9]. The attainable uncertainty for the ${}^{40}CaH^+$ vibrational frequency was estimated to be on the order of 10^{-16}. However, owing to the large permanent electric dipole moment of these molecular ions (3–5 D), the internal states are constantly reshuffled through the interaction with black-body radiation. To mitigate the effect of black-body radiation, a cryogenic environment is required. For a HD^+ molecular ion [10–12], the permanent dipole moment (10^{-3} D) is much smaller than that of XH^+ molecular ions and the interaction with black-body radiation is much weaker. However, the hyperfine structure is complicated and the measurement should be performed with many molecular ions, whose distribution is broadened in all directions. Therefore, the Stark shift is significant.

Homonuclear diatomic molecular ions in the Σ state are advantageous for precise measurement for the following reasons. There are only even or odd (depending on the nuclear spin) rotational states and there is no electronic dipole ($E1$) transition between different vibrational-rotational states in the electronic ground state. Therefore, black-body radiation cannot induce any undesirable transitions and a cryogenic chamber is not required. The Stark shift, induced only by the coupling with electronically excited states, is two orders smaller than that for the HD^+ molecular ion. Therefore, the Stark shift can also be lower than 10^{-16} when the distribution of the molecular ions is broadened in the radial direction by a few μm. Pumping to a selected quantum state using the $E1$ spontaneous emission transition [8] is not applicable for homonuclear molecular ions, but this problem is solved by the state-selective production of the molecular ion by resonance-enhanced multiphoton ionization (REMPI) [13,14]. Measurement with a $H_2{}^+$ molecular ion has been studied [15]. The problem with the $H_2{}^+$ molecular ion is the quadratic Doppler shift, which is 7×10^{-17} assuming a kinetic energy of 1 mK. Considering the mass ratio between $H_2{}^+$ and Be^+ (the lightest ion that can be laser cooled) ions, the sympathetic cooling efficiency of the $H_2{}^+$ molecular ion cannot be particularly high, although this problem can be mitigated by sideband cooling.

We have shown that the $Q(0)$ transition frequency of a $N_2{}^+$ molecular ion can be measured within an uncertainty of 10^{-17} because the Zeeman and electric quadrupole shifts

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are zero [16]. The quadratic Doppler shift is smaller than that of $H_2{}^+$ and HD^+ molecular ions by the ratio of their masses. The $Q(0)$ transition is one-photon forbidden, and the spectrum should be observed via the Raman transition using two lasers with frequencies at which the Stark shift is eliminated [16,17]. Quadrupole transitions can be observed with simpler experimental apparatus than that required for the Raman transition, although the attainable accuracy is mainly limited by the Zeeman shift. Germann *et al.* observed the $S(0)$ transition of a $^{14}N_2{}^+$ molecular ion [18]. This paper lists the quadrupole transitions of $^{14}N_2{}^+$ and $^{15}N_2{}^+$ molecular ions for which the Zeeman shift induced by a magnetic field of 1 G is less than 100 Hz. The $^{14}N^{15}N^+$ molecular ion is not discussed in this paper because it is a heteronuclear molecular ion having a complicated hyperfine structure and a Stark shift two orders larger than that of $^{14}N_2{}^+$ and $^{15}N_2{}^+$.

We employ the following notation throughout this paper: v is the vibrational quantum number, N describes the nuclear rotation of the molecule, S denotes the electronic spin of the molecule, and I is the total nuclear spin of the molecule. J is the quantum number of the spin rotation coupling ($J = S + N$) and F is the hyperfine quantum number ($F = J + I$). $M_X (X = S,I,N,J,F)$ is the component of X parallel to the magnetic field. ^{14}N (^{15}N) atoms have a nuclear spin of 1 (1/2) and thus the possible total numbers of nuclear spins of the $^{14}N_2{}^+$ ($^{15}N_2{}^+$) molecular ion are $I = 0,1,2$ ($I = 0,1$). Owing to the symmetry of the nuclear spin wave function, the possible rotational states are severely limited. In the $^2\Sigma_g$ electronic ground state only even rotational levels are possible for $I = 0,2$ ($I = 0$) for the $^{14}N_2{}^+$ ($^{15}N_2{}^+$) molecular ion. For both isotopes with $I = 1$, only odd rotational states can exist.

II. ZEEMAN SHIFT

In general, the energy eigenstates of $N_2{}^+$ molecular ions with nuclear spin I in the $X\,^2\Sigma_g$ state can be described by the wave function $\Psi(v,N,J,F,M_F)$, which can be expressed as

$$\Psi(v,N,J,F,M_F) = \Sigma a_m \psi_m(v,N,M_S,M_N,M_I), \tag{1}$$

where ψ_m is the wave function with deterministic values of $(M_S,M_N,M_I) = [M_S(m),M_N(m),M_I(m)]$ satisfying $M_F = M_S(m) + M_N(m) + M_I(m)$. The Zeeman energy shift induced by a magnetic field B is given by

$$\begin{aligned} E_Z(\Psi) &= h\mu_B B[g_S(\Psi)\langle M_S(\Psi)\rangle + g_N(\Psi)\langle M_N(\Psi)\rangle \\ &\quad + g_I(\Psi)\langle M_I(\Psi)\rangle]\,, \\ \langle M_{S,N,I}\rangle &= \Sigma |a_m|^2 M_{S,N,I}(m) \end{aligned} \tag{2}$$

with the Bohr magneton μ_B(=1.3996 MHz/G) and the g factors $g_{S,N,I}$. Table I lists the values of $\mu_B g_{S,N,I}$, where values of g_N were estimated by the same method as used by Karr *et al.* for the $H_2{}^+$ molecular ion [19]. While g_S is independent of the vibrational state, the values of g_N in the $v = 0$ and 1 states are different by an amount on the order of 1%. Also g_I is dependent on v because of the magnetic shielding effect of the surrounding electrons, but its difference between the $v = 0$ and 1 states is on the order of 0.1 ppm [20].

TABLE I. Values of Zeeman coefficients of electron spin ($\mu_B g_S$), nuclear spin ($\mu_B g_I$), and molecular rotation ($\mu_B g_N$). The dependence on the vibrational state v is only significant for $\mu_B g_N$.

	$^{14}N_2{}^+$ (Hz/G)	$^{15}N_2{}^+$ (Hz/G)
$\mu_B g_S$	2.8025×10^6	2.8025×10^6
$\mu_B g_I$	307.92	429.69
$\mu_B g_N(v = 0)$	−50.107	−46.748
$\mu_B g_N(v = 1)$	−49.547	−46.328

In general, a_m depends on B and the Zeeman shift is not linear. For a low magnetic field,

$$\langle M_{S,N,I}(\Psi)\rangle = \langle M_{S,N,I}(\Psi)\rangle_{B=0} + \left[\frac{d\langle M_{S,N,I}(\Psi)\rangle}{dB}\right]_{B=0} B, \tag{3}$$

and the Zeeman shift can be approximated by

$$\begin{aligned} E_Z(\Psi)/h &= [C_S(\Psi) + C_N(\Psi) + C_I(\Psi)]B \\ &\quad + [D_S(\Psi) + D_N(\Psi) + D_I(\Psi)]B^2, \\ C_{S,N,I}(\Psi) &= \mu_B g_{S,N,I}(\Psi)\langle M_{S,N,I}(\Psi)\rangle_{B=0} \\ D_{S,N,I}(\Psi) &= \frac{\mu_B g_{S,N,I}(\Psi)}{2}\left[\frac{d\langle M_{S,N,I}(\Psi)\rangle}{dB}\right]_{B=0}. \end{aligned} \tag{4}$$

The Zeeman shift of the transition frequency between the states Ψ_u and Ψ_l is

$$\Delta f_Z = \frac{E_Z(\Psi_u) - E_Z(\Psi_l)}{h}. \tag{5}$$

Mainly because of the electron spin, there is a Zeeman shift of order 1 MHz/G in most of the $N_2{}^+$ transition frequencies. However, the Zeeman shift is much smaller when $\langle M_S(\Psi_u)\rangle_{B=0} = \langle M_S(\Psi_l)\rangle_{B=0}$ because g_S is independent of the molecular quantum state and $[C_S(\Psi_u) - C_S(\Psi_l)] = 0$. This condition is satisfied in the following cases.

For the stretched states ($F = S + N + I, M_F = \pm F$) in the $X^2\Sigma$ state, $\langle M_{S,N,I}\rangle$ are all determined to be $\pm S, \pm N, \pm I$, and E_Z is strictly given by ($D_{S,N,I} = 0$)

$$E_Z(\Psi)/h = \pm\mu_B B[g_S S + g_N(\Psi)N + g_I(\Psi)I], \tag{6}$$

and the Zeeman shift of the $[v_l, N_l, (I + N_l + 1/2), \pm(I + N_l + 1/2)] \rightarrow [v_u, N_u, (I + N_u + 1/2), \pm(I + N_u + 1/2)]$ transition frequency is given by

$$\Delta f_Z = \pm\mu_B B\{g_N(v_u)N_u - g_N(v_l)N_l + I[g_I(v_u) - g_I(v_l)]\}. \tag{7}$$

Actually, $|g_I(v_u) - g_I(v_l)| \ll |g_N(v_u) - g_N(v_l)|$ and Δf_Z is

$$\begin{aligned} &N_u \neq N_l : \Delta f_Z \approx \mu_B g_N(v_u)(N_u - N_l) \\ &N_u = N_l \neq 0 : \Delta f_Z \approx \mu_B N_l[g_N(v_u) - g_N(v_l)] \\ &N_u = N_l = 0 : \Delta f_Z \approx \mu_B I[g_I(v_u) - g_I(v_l)]. \end{aligned}$$

This discussion is not valid for molecules with $S \geqslant 1$ (for example, a NH molecule in the $^3\Sigma$ state) because the spin-spin interaction causes the stretched state $(N,M_S,M_N) = (N,S,N)$ to mix with the $(N+2,S,N)$, $(N+2,S-1,N+1)$, and $(N+2,S-2,N+2)$ states [21].

Next we consider the $\Delta N = \Delta J = \Delta F = \Delta M_F = 0$ vibrational transition. For the molecular ion with $I = 0$, J is a good quantum number and a_m in Eq. (1) is exactly obtained using the ladder operators. Therefore, $\langle M_{S,N,I}(\Psi)\rangle_{B=0}$ is independent of the vibrational state and the linear Zeeman coefficient is given only by the difference in g_N [for the $Q(0)$ transition, g_I]. The quadratic Zeeman shift exists but it is relatively small, as shown below. $D_{S,N,I}$ is inversely proportional to the hyperfine splitting f_{hf} and the difference between $D_{S,N,I}$ in the $v = 0$ and 1 states mainly originates from the difference f_{hf} between the $v = 0$ and 1 states, which is on the order of 1% [20]. The effect of the electron spin is dominant for the quadratic Zeeman shift, and the Zeeman shift in the transition frequency is approximately given by

$$\Delta f_Z = C_N(v_u,N,J,F,M_F)\left[1 - \frac{g_N(v_l)}{g_N(v_u)}\right]B + D_S(v_u,N,J,F,M_F)\left[1 - \frac{f_{hf}(v_u)}{f_{hf}(v_l)}\right]B^2. \tag{8}$$

When $I \neq 0$, there is a mixture between the J and $J \pm 1$ states with the same N and F quantum numbers (J mixture). When $S = 1/2$, $\Psi(v,N,J,F,M_F)$ is actually given by

$$\begin{aligned}
&\Psi(v,N,N+1/2,F,M_F)\\
&\quad = \cos\theta \cdot \Psi_0(v,N,N+1/2,F,M_F)\\
&\qquad + \sin\theta \cdot \Psi_0(v,N,N-1/2,F,M_F)\\
&\Psi(v,N,N-1/2,F,M_F)\\
&\quad = \sin\theta \cdot \Psi_0(v,N,N+1/2,F,M_F)\\
&\qquad - \cos\theta \cdot \Psi_0(v,N,N-1/2,F,M_F),
\end{aligned} \tag{9}$$

where Ψ_0 denotes the wave function with a_m obtained using ladder operators. The value of θ is slightly dependent on the vibrational state because the spin-rotation splitting is dependent on the vibrational state. Considering that the difference between the hyperfine splitting in the $v = 0$ and 1 states is on the order of 1%, the differences in θ and $\langle M_S(\Psi)\rangle_{B=0}$ are also expected to be of the same order. Therefore, the linear Zeeman coefficients with the $\Delta N = \Delta J = \Delta F = \Delta M_F = 0$ vibrational transitions are expected to be a few kHz/G. Equation (8) is valid for the transition between $F = S + N + I$ states, where there is no J mixing.

III. ELECTRIC QUADRUPOLE SHIFT

For states with an electric quadrupole moment, the interaction with an electric field gradient can lead to a significant shift of the transition frequency. An example is the electric quadrupole shift of $S \rightarrow D$ transitions of alkali-metal-like ions [22]. Electric quadrupole shifts also exist for molecular ions in the $N \neq 0$ states. For the HD$^+$ molecular ion, the electric quadrupole coefficients of different rovibrational transitions have been estimated to be 10–150 mHz/(V/mm^2) [23], which is one order smaller than those for $S \rightarrow D$ transitions of alkalilike ions. The quadrupole shift in the $N_2{}^+$ transition frequencies is expected to has the same order as that of HD$^+$ because the atomic radii (0.53 A and 0.56 A for H and N atoms, respectively) and the bond lengths of both molecular ions (1.05 A and 1.1 A for HD$^+$ and $N_2{}^+$, respectively) are almost the same. Therefore, the electric quadrupole shift is expected to be less than 1 Hz. The cancellation of this shift at upper and lower states is significant for the $\Delta N = \Delta J = \Delta F = \Delta M_F = 0$ vibrational transition, and the actual shift is expected to be less than 0.1 Hz.

TABLE II. Mass and the $v = 0-1$ transition frequency (f_v) for $^{14}N_2{}^+$ and $^{15}N_2{}^+$ molecular ions. The rotational constants (B_v and D_v) and spin-rotation coupling constants (γ_v) are also listed for the $v = 1$ and 0 states (for $^{15}N_2{}^+$, only for $v = 1$) [24–26]. The rotational energy is given by $B_v N(N+1) - D_v N^2(N+1)^2$.

	$^{14}N_2{}^+$	$^{15}N_2{}^+$
mass (a.u.)	28	30
f_v (THz)	65.2	63.0
B_1 (GHz)	57.05	53.30
B_0 (GHz)	57.63	
D_1 (kHz)	179	159
D_0 (kHz)	178	
γ_1 (MHz)	276.9	258.6
γ_0 (MHz)	280.2	

The electric quadrupole shift is eliminated by averaging the electric quadrupole shifts over all M_F (see Sec. V) because it is proportional to $3M_F^2 - F(F+1)$ [22]. When $F = 0$ or $1/2$, the electric quadrupole shift is always zero; therefore, the $Q(0)$ transition frequency of the $N_2{}^+$ molecular ion with $I = 0$ is free from this shift [16].

IV. SHIFT IN THE *S*(0) TRANSITION FREQUENCY

The mass, the $v = 0 - 1$ transition frequency, the rotational constants, and the spin-rotation coupling constants of $^{14}N_2{}^+$ and $^{15}N_2{}^+$ molecular ions are listed in Table II.

Germann *et al.* observed the $^{14}N_2{}^+$ $(v,N) = (0,0) \rightarrow (1,2)$ transition frequency in a Coulomb crystal and measured the following transition frequencies, which satisfy $\Delta N = \Delta J = \Delta F$ [18]:

$I = 0$, $(v,N,J,F) = (0,0,1/2,1/2) \rightarrow (1,2,5/2,5/2)$ 65,539.831(12) GHz

$I = 2$, $(v,N,J,F) = (0,0,1/2,5/2) \rightarrow (1,2,5/2,9/2)$ 65,539.815(12) GHz

$I = 2$, $(v,N,J,F) = (0,0,1/2,3/2) \rightarrow (1,2,5/2,7/2)$ 65,540.039(12) GHz.

Currently the spectrum linewidth is 19 MHz and the frequency uncertainty is expected to be reduced by the frequency stabilization of the probe laser (quantum cascade laser). Transitions that do not satisfy $\Delta N = \Delta J = \Delta F$ are also possible because of the J mixing but the transition rate is lower by a factor of $\sin^2\theta$ [θ appears in Eq. (9)].

We first consider the molecular ion with $I = 0$. There is no hyperfine splitting in the $(v,N) = (0,0)$ state. In the $(v,N) = (1,2)$ state, there is spin-rotation splitting of 692 MHz ($^{14}N_2{}^+$) [24] and 646 MHz ($^{15}N_2{}^+$) [25]. Table III shows the linear and quadratic Zeeman coefficients in the (v,N,J,M_J) states.

For the $(v,N,J,M_J) = (0,0,1/2,\pm 1/2) \rightarrow (1,2,5/2,\pm 5/2)$ transition, the Zeeman shift is strictly linear with coefficients of ∓ 99.2 Hz/G ($^{14}N_2{}^+$) and ∓ 92.6 Hz/G ($^{15}N_2{}^+$), respectively. The average of the $M_J = \pm 1/2 \rightarrow \pm 5/2$ transition frequencies is free from the Zeeman shift. The attained accuracy is expected to be on the order of 10^{-14}, which is limited by the electric quadrupole shift.

TABLE III. Linear and quadratic Zeeman coefficients of ${}^{14}\mathrm{N}_2{}^+$ and ${}^{15}\mathrm{N}_2{}^+$ molecular ions in the $I = 0$ $X^2\Sigma(v,N,J,M_J)$ states.

			${}^{14}\mathrm{N}_2{}^+$		${}^{15}\mathrm{N}_2{}^+$	
v	N	(J,M_J)	linear (MHz/G)	quadratic (kHz/G^2)	linear (MHz/G)	quadratic (kHz/G^2)
0	0	(1/2,1/2)	1.4016	0	1.4016	0
1	2	(5/2,5/2)	1.4015	0	1.4015	0
		(5/2,3/2)	0.8410	1.811	0.8410	1.941
		(5/2,1/2)	0.2803	2.717	0.2803	2.912
		(3/2,3/2)	−0.8409	−1.811	−0.8409	−1.941
		(3/2,1/2)	−0.2803	−2.717	−0.2803	−2.912

For the $M_J = \pm 1/2 \to \pm 3/2$ and $\pm 1/2 \to \pm 1/2$ transition frequencies, the linear Zeeman coefficients are much larger than that for the $\pm 1/2 \to \pm 5/2$ transition. Although the linear Zeeman shift can be eliminated by averaging the $\pm M_J'' \to \pm M_J'$ transition frequencies, the transition spectrum for a large linear Zeeman coefficient is broadened by the fluctuation of the magnetic field. There is also a quadratic Zeeman shift. To reduce the quadratic Zeeman shift to less than 1 Hz, the magnetic field should be maintained at less than 0.01 G. By averaging the $(v,N,J) = (0,0,1/2) \to (0,2,5/2)$ and $(0,0,1/2) \to (0,2,3/2)$ transition frequencies, the quadratic Zeeman shift is also eliminated. However, this method appears to be difficult because the $(0,0,1/2) \to (0,2,3/2)$ transition is weak.

Next we consider the ${}^{14}\mathrm{N}_2{}^+$ molecular ion with $I = 2$, whose hyperfine structure is shown in Table IV. Table V shows the linear and quadratic Zeeman coefficients in several (v,N,J,F,M_F) states.

TABLE IV. Hyperfine structure of ${}^{14}\mathrm{N}_2{}^+$ molecular ion with $I = 2$, which is shown as the transition frequency from the lowest hyperfine state f_{hf} [24].

(v,N)	(J,F)	f_{hf} (MHz)
(0,0)	(1/2,3/2)	0
	(1/2,5/2)	274
(1,2)	(3/2,7/2)	0
	(3/2,5/2)	21.9
	(3/2,3/2)	59.6
	(3/2,1/2)	85.4
	(5/2,1/2)	631.2
	(5/2,3/2)	669.6
	(5/2,5/2)	721.9
	(5/2,7/2)	777.9
	(5/2,9/2)	828.5

TABLE V. Linear and quadratic Zeeman coefficients of ${}^{14}\mathrm{N}_2{}^+$ molecular ion with $I = 2$ in several hyperfine substates. Values in the parentheses were values calculated ignoring the J-mixing effect.

(v,N)	(J,F,M_F)	linear (MHz/G)	quadratic (kHz/G^2)
(0,0)	(1/2,5/2,5/2)	1.40	0
	(1/2,5/2,3/2)	0.841	4.59
	(1/2,3/2,3/2)	−0.841	−4.59
(1,2)	(5/2,9/2,9/2)	1.40	0
	(5/2,7/2,7/2)	0.95(1.15)	−23.8
	(3/2,7/2,7/2)	−1.18(-0.84)	−1.59

The Zeeman shift is smallest for the $(v,N,J,F,M_F) = (0,0,1/2,5/2,\pm 5/2) \to (1,2,5/2,9/2,\pm 9/2)$ transition. The Zeeman shift is strictly linear with the coefficients of ∓ 99.2 Hz/G; therefore, the average of both transition frequencies is free from the Zeeman shift. Considering J as a good quantum number, the linear Zeeman coefficient of the $(v,N,J,F,M_F) = (0,0,1/2,3/2,\pm 3/2) \to (1,2,3/2,7/2,\pm 7/2)$ transition should also be the same value. However, the wave function $\Psi(1,2,3/2,7/2,\pm 7/2)$ is actually given by

$$\Psi(1,2,3/2,7/2,\pm 7/2) = 0.1800\Psi_0(1,2,5/2,7/2,\pm 7/2) - 0.9837\Psi_0(1,2,3/2,7/2,\pm 7/2). \tag{10}$$

As shown in Table V, the linear Zeeman shift in the $(v,N,J,F,M_F) = (1,2,3/2,7/2,\pm 7/2)$ state is different from the value calculated ignoring the J mixing by 30% and the linear Zeeman coefficient at the transition frequency is ∓ 0.34 MHz/G. The linear Zeeman coefficients at all other transition frequencies are larger than 0.1 MHz/G and measurement within an uncertainty of 10^{-10} appears to be difficult. A molecular ion with $I = 0$ appears to be more advantageous than one with $I = 2$ for measuring the transition frequencies with high accuracy.

V. SHIFT IN THE $Q(2)$ TRANSITION FREQUENCY

Generally, vibrational transition frequencies with $\Delta N = \Delta J = \Delta F = \Delta M_F = 0$ are more easily measured with high accuracy because of the cancellation of the Stark, Zeeman, and electric quadrupole shifts at upper and lower states (including the influence of J mixing). In this section, we discuss the $(v,N) = (0,2) \to (1,2)$ $\Delta J = \Delta F = \Delta M_F = 0$ transitions.

For the ${}^{14}\mathrm{N}_2{}^+$ molecular ion with $I = 0$, the spin-rotation splitting in the $(v,N) = (1,2)$ and $(0,2)$ states was measured to be 692 MHz [24] and 701 MHz [26], respectively. For the ${}^{15}\mathrm{N}_2{}^+$ molecular ion, the value in the $(v,N) = (1,2)$ state was measured to be 646 MHz [25] but the value in the (0,2) state has never been measured. Here we assume that the ratio of the hyperfine splitting in the $v = 0$ and 1 states is the same for ${}^{14}\mathrm{N}_2{}^+$ and ${}^{15}\mathrm{N}_2{}^+$; the hyperfine splitting in the (0,2) state was estimated to be 654 MHz. Table VI shows the linear and quadratic Zeeman shifts in the $(v,N,J) = (0,2,3/2) \to (1,2,3/2)$ and $(0,2,5/2) \to (1,2,5/2)$ transition frequencies with $\Delta M_J = 0$. The Zeeman shift is much smaller than the $S(0)$ transition. The linear Zeeman shift is canceled by averaging the $\pm M_J \to \pm M_J$ transition frequencies. The average of all M_J transition frequencies is also free from the electric quadrupole shift (order of ± 0.1 Hz at each state). Actually the difference among all M_J transition frequencies is less than 1 Hz at a magnetic field of 0.3 G, and we can only observe the overlapping spectra for both the $J = 3/2$ and $5/2$ transitions. These overlapping spectra are free from the linear Zeeman shift and electric quadrupole shift. When the magnetic field is kept lower than 0.03 G, the Zeeman shift in each

TABLE VI. Linear and quadratic Zeeman coefficients in the $Q(2)$ transition frequencies of $^{14}N_2{}^+$ and $^{15}N_2{}^+$ molecular ions with $I = 0$.

		$^{14}N_2{}^+$		$^{15}N_2{}^+$	
J	M_J	linear (Hz/G)	quadratic (Hz/G^2)	linear (Hz/G)	quadratic (Hz/G^2)
3/2	3/2	0.91	−21	0.85	−23
	1/2	0.30	−32	0.28	−34
5/2	5/2	1.0	0	0.96	0
	3/2	0.61	21	0.57	23
	1/2	0.21	32	0.19	35

TABLE VII. Hyperfine structure of $^{14}N_2{}^+$ in the $(v,N) = (1,1)$ state as the transition frequencies from the lowest state [24].

(J,F)	f_{hf} (MHz)
(1/2,3/2)	0
(1/2,1/2)	3.7
(3/2,1/2)	365.9
(3/2,3/2)	423.7
(3/2,5/2)	480.2

single transition frequency is lower than 0.03 Hz (uncertainty of 5×10^{-16}). By averaging the measured frequencies of the overlapping spectra of the $J = 3/2$ and $5/2$ transitions with a weight ratio of 2 : 3 (ratio of degeneracy), the quadratic Zeeman shift is also eliminated and an accuracy of 10^{-16} also appears to be attainable without a magnetic shield. This limit is given by the Stark shift induced by the probe laser (20 mW/cm^2, -4×10^{-17}) and the statistical uncertainty.

For the $^{14}N_2{}^+$ molecular ion with $I = 2$, the Zeeman shift is strictly linear for the $(v,N,J,F,M_F) = (0,2,5/2,9/2,\pm 9/2) \rightarrow (1,2,5/2,9/2,\pm 9/2)$ transition frequency with the coefficient ±1.0 Hz/G; therefore, the average of the $M_F = \pm 9/2 \rightarrow \pm 9/2$ transition frequencies is free from the Zeeman shift. For the $(v,N,J,F) = (0,2,5/2,9/2) \rightarrow (1,2,5/2,9/2)$ transitions with other M_F, the linear Zeeman coefficients are smaller. Other transition frequencies have linear Zeeman coefficients of a few kHz/G because of the J mixing (see Sec. II). After the stretched states, the quadratic Zeeman coefficient is smallest for the $(J,F,M_F) = (3/2,7/2,\pm 7/2)$ states, which are coupled with only the $J = 5/2$ states. The quadratic Zeeman coefficient at the $(v,N,J,F,M_F) = (0,2,3/2,7/2,\pm 7/2) \rightarrow (1,2,3/2,7/2,\pm 7/2)$ transition frequency is approximately -19 Hz/G^2. For other transitions, the quadratic Zeeman shift is induced by the coupling with the neighboring hyperfine components and its coefficients are larger than ±100 Hz/G^2.

For molecular ions with $I = 0$, the $Q(2)$ transition frequencies can be measured with an accuracy of 10^{-16} by taking the average of the $(v,N,J) = (0,2,3/2) \rightarrow (1,2,3/2)$ and $(0,2,5/2) \rightarrow (1,2,5/2)$ $\Delta M_J = 0$ transition frequencies. To exclude the overlap of the Zeeman-sensitive spectra of molecular ions with $I = 2$, it is preferable to ionize only N_2 molecules in the $N = 2, I = 0$ state. The $^{15}N_2$ molecule, which does not have the $I = 2$ state, is useful for this purpose. The discussion in this section is valid for all Q transitions with even rotational states.

VI. SHIFT IN THE Q(1) TRANSITION FREQUENCY

For both of the $^{14}N_2{}^+$ and $^{15}N_2{}^+$ isotopes, odd rotational states can exist only in the $I = 1$ state, where the J-mixing effect is significant. Table VII shows the hyperfine structure of the $^{14}N_2{}^+$ molecular ion in the $(v,N) = (1,1)$ state [24].

The Zeeman shift in the $(v,N,J,F,M_F) = (0,1,3/2,5/2,\pm 5/2) \rightarrow (1,1,3/2,5/2,\pm 5/2)$ transition frequencies is strictly linear with a coefficient of 0.5 Hz/G. The average of both transition frequencies is free from the Zeeman shift and the attainable accuracy is limited by the electric quadrupole shift to the order of 0.1 Hz. For other M_F transitions, the linear Zeeman coefficients are smaller, but there is also a quadratic Zeeman shift with a coefficient larger than 100 Hz/G^2. For other $\Delta N = \Delta J = \Delta F = \Delta M_F = 0$ transitions, the linear Zeeman coefficient is a few kHz/G because of the J mixing. It is actually difficult to selectively produce a molecular ion with the $(v,N,J,F,M_F) = (0,1,3/2,5/2,\pm 5/2)$ states; therefore, measurement of the $Q(1)$ transition frequency within an uncertainty of 10^{-12} appears to be difficult. The discussion in this section is valid for all Q transitions with odd rotational states.

VII. CONCLUSION

The precise measurement of molecular vibrational transitions is useful for investigating the variation in the proton-to-electron mass ratio. This paper discusses the Zeeman shift in the $v = 0 \rightarrow 1$ vibrational quadrupole transition frequencies of the $^{14}N_2{}^+$ and $^{15}N_2{}^+$ molecular ions. For S transitions, only the transition frequencies between stretched states can be measured within an accuracy of 10^{-14} (limited by the electric quadrupole shift). Measurement within an accuracy of 10^{-10} is difficult for other transitions because the Zeeman shift induced by a magnetic field of 1 G is larger than 0.1 MHz.

Q transitions are more easily measured with high accuracy because of the cancellation of the Zeeman, Stark, and electric quadrupole shifts at upper and lower states. For the $I = 0$ $Q(2)$ $\Delta J = \Delta F = \Delta M_F = 0$ transition, all spectra with different M_F overlap when the magnetic field is less than 1 G, and the observed spectra are free from the linear Zeeman shift and electric quadrupole shift. Also, the quadratic Zeeman shift is eliminated by averaging the $J = 3/2$ and $5/2$ transition frequencies with a weight ratio of degeneracy of 2 : 3 and an accuracy of 10^{-16} is attainable.

The transition frequencies of a molecular ion with $I \neq 0$ appear to be difficult to measure within an uncertainty of 10^{-12} because (i) the linear Zeeman coefficient is a few kHz/G for Q transitions because of J mixing, (ii) the quadratic Zeeman shift is large because of narrow hyperfine splitting, and (iii) the preparation of a molecular ion in a selected state is difficult because of the complicated energy structure. Therefore, the selective production of molecular ions with $I = 0$ appears to be be preferable to exclude the overlap of the spectra of $^{14}N_2$ molecular ions with $I = 2$. Measurement with $^{15}N_2{}^+$ appears to be useful because only $I = 0$ is possible for the even rotational states. When REMPI is performed with a high resolution, $^{14}N_2$ molecules with $I = 0$ can also be ionized selectively. The $Q(0)$ transition appears to be measurable with an accuracy of 10^{-17} because it is free from Zeeman and electric quadrupole shifts with a single transition, making measurement with a single molecular ion also possible [16]. With this method, the Stark shift induced by a trap electric field and the quadratic Doppler shift are smaller than those in the case of measurement with many molecular ions. However, the experimental apparatus is more complicated than for the observation of other transitions because the $Q(0)$ transition is one-photon forbidden and should be measured by the Raman transition with two lasers having frequencies at which the Stark shift is eliminated [16,17].

Measurement with the $N_2{}^+$ molecular ion is easier than with the $H_2{}^+$ molecular ion because the quadratic Doppler shift and the linear Zeeman coefficients in the $\Delta N = \Delta J = \Delta F = \Delta M_F = 0$ transition frequencies are inversely proportional to the nuclear mass. The $^{16}O_2{}^+$ molecular ion might also be a useful molecular ion for the precise measurement [27], because it is a homonuclear diatomic molecular ion with $I = 0$. The Zeeman shifts in the vibrational transition frequencies are expected to have the same order as for $Q(N)$ transitions of the $N_2{}^+$ molecular ion with $I = 0$ (N is even). The Stark shift is induced by the coupling between $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states (the energy gap is 5.91 THz), which appears to be larger than that for $N_2{}^+$ but much smaller than that for heteronuclear molecules.

ACKNOWLEDGMENTS

The author thanks S. Willitsch and J. P. Karr for useful discussions. This research was supported by a Grant-in-Aid for Scientific Research(B) (Grant No. 25287100) and a Grant-in-Aid for Exploratory Research (Grant No. 15K13545) from the Japan Society for the Promotion of Science (JSPS).

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