



Precise Measurement of Transition Frequencies of Optically Trapped $^{40}\text{Ca}^{19}\text{F}$ Molecules

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The laser cooling and trapping of molecules have recently been achieved. In this paper, the possibility of precisely measuring the vibrational transition frequencies of optically trapped $^{40}\text{Ca}^{19}\text{F}$ molecules is discussed. The quadratic Stark shift induced by the trap laser is eliminated using the trap laser frequencies where the Stark energy shifts at upper and lower states are equal (magic frequencies). At one value of the magic frequency, molecules are trapped at the positions where the power density is minimum, therefore, the measurement is not sensitive to the detuning of the trap laser frequency from the magic frequency. Measurement with an uncertainty of 10^{-17} appears to be possible using the $(v, N, J, F, M) = (0, 0, 1/2, 1, \pm 1) \rightarrow (1, 0, 1/2, 1, \pm 1)$ transition frequency.

1. Introduction

The development of laser cooling has made a major contribution to many fields of physics, including the precise measurement of atomic transition frequencies. Several atomic transition frequencies have been measured with uncertainty on the order of 10^{-18} using ultracold neutral atoms and atomic ions.^{1–4} The precise measurement of molecular transition frequencies can strongly contribute to the development of physics through the detection of the electron electric dipole moment (eEDM),⁵ the measurement of the parity violation of chiral molecules,⁶ the search for the variation in the proton-to-electron mass ratio,⁷ and so forth. However, it has been difficult to obtain ultracold molecules, and molecular transition frequencies have never been measured with an uncertainty lower than 10^{-15} .

There have been several proposals for measuring the vibrational transition frequencies of molecular ions co-trapped with atomic ions, that can be laser cooled.^{8–11} A frequency uncertainty lower than 10^{-16} is expected for several vibrational transition frequencies of molecular ions, as already attained for several transition frequencies of atomic ions.^{3,4} However, note that measurements of the transition frequencies of ions are performed using small number of ions so that the Stark shift induced by the trap electric field is suppressed. By observing the fluorescence from a cycling transition (absorption of laser light and spontaneous emission transition), we can also monitor the transition using a single ion. The cycle transition does not exist for molecular ions and we cannot monitor the transition by this method. A quantum logical method, in which the information of the quantum state of an ion is transformed to the state of a co-trapped ion, has been developed to overcome this difficulty, and the $^{27}\text{Al}^+ \ ^1\text{S}_0\text{--}^3\text{P}_0$ transition has been monitored by this method.^{3,12,13} However, this method has only been successfully used at NIST (Boulder, U.S.A.).

Precise measurements of the $^1\text{S}_0\text{--}^3\text{P}_0$ transition frequencies of ^{87}Sr ,^{1,2} ^{171}Yb ,¹⁴ and ^{199}Hg ¹⁵ atoms have been performed using many atoms trapped by a standing wave of laser light. The trap laser frequency was chosen so that the quadratic Stark energy shifts at upper and lower states are equal and the quadratic Stark shift in the transition frequency is eliminated (magic frequency). It has been proposed that the same method can be used to precisely measure the vibrational

transition frequencies of $^{174}\text{Yb}^6\text{Li}$, $^{88}\text{Sr}^6\text{Li}$, and $^{40}\text{Ca}^6\text{Li}$ molecules (4–20 THz).^{16–18} However, the production of these molecules with ultralow kinetic energy has never been achieved. On the other hand, laser cooling has been successful for $^{88}\text{Sr}^{19}\text{F}$,¹⁹ $^{40}\text{Ca}^{19}\text{F}$,²⁰ and $^{174}\text{Yb}^{19}\text{F}$ ²¹ molecules. For $^{40}\text{Ca}^{19}\text{F}$ molecules, three-dimensional (3D) magneto optical trapping (MOT),^{20,22} magnetic traps,²³ and optical traps²⁴ have been obtained. The kinetic energy of a trapped molecule is $40 \mu\text{K}$,²⁴ which is expected to be reduced to μK order by sideband Raman cooling. The number of loaded molecules can be remarkably increased using a Zeeman slower.²⁵

In this paper, we discuss the possibility of precisely measuring $^{40}\text{Ca}^{19}\text{F}$ vibrational transition frequencies using molecules trapped by a standing wave of laser light. The collision shift is expected to be rather significant because the permanent dipole moment is as large as 3.07 D .²⁶ Molecular trapping in a 3D lattice is required to suppress the collision shift. Therefore, precise measurement is possible only for the transition frequencies whose Stark shift induced by the laser light is independent of the polarization. We propose the measurement of the $X^2\Sigma(v, N, J, F, M) = (0, 0, 1/2, 1, \pm 1) \rightarrow (1, 0, 1/2, 1, \pm 1)$ [Q(0, a)], $(0, 0, 1/2, 0, 0) \rightarrow (1, 0, 1/2, 0, 0)$ [Q(0, b)], and $(0, 1, 1/2, 0, 0) \rightarrow (1, 1, 1/2, 0, 0)$ [Q(1)] transition frequencies (17.472 THz ²⁷), where v and N are the quantum numbers of the vibrational and rotational states, respectively, $J = N + S$ ($S = 1/2$ is the electron spin), $F = J + I$ ($I = 1/2$ is the ^{19}F nuclear spin), and M is the component of F parallel to the magnetic field. The Q(0) transition frequency $f(0)$ is 144 MHz higher than the Q(1) transition frequency $f(1)$. The Stark shift induced by the laser light is independent of the polarization for these transition frequencies. For the $(N, J, F) = (1, 1/2, 1)$ state, the dependence on the polarization is not negligible because of the mixing with the $J = 3/2$ state.

2. CaF Molecular Lattice

Laser cooling is performed with a cooling laser that is quasi-resonant to the $X^2\Sigma(v, N) = (0, 1) \rightarrow A^2\Pi(v, J) = (0, 1/2)$ transition frequencies. Also repump lasers are irradiated to pump the molecules in the $v = 1, 2, 3$ states back to the cooling cycle. The cooling laser has four frequency components, which are quasi-resonant to the transitions from all (J, F) states. The frequency component

Table I. Trap laser frequency, where the $^{40}\text{Ca}^{19}\text{F}$ $(v, N) = (0, 0) - (1, 0)$ and $(0, 1) - (1, 1)$ transition frequencies are measured without the quadratic Stark shift f_{mag} , the position where the molecules are trapped, the power density required to obtain a potential depth of $10\ \mu\text{K}$ I_0 , the gradient of the Stark shift with respect to the detuning of the trap laser frequency dS/df , and the scattering rate γ are listed. A power density of I_0 is assumed for dS/df and γ . At magic frequency 2, molecules are trapped at the position where the power density is minimum, therefore, dS/df and γ are expected to be one order smaller than the values listed in this table.

	f_{mag} (THz)	Trap position	I_0 (kW/cm ²)	dS/df (/MHz)	γ (/s)
Magic frequency 1	470.5	antinode	7.2	1.2×10^{-16}	2.4
Magic frequency 2	498.3	node	1.1	2.2×10^{-16}	24

of the cooling laser that is resonant from the $X^2\Sigma(v, N, J, F) = (0, 1, 1/2, 0)$ state is turned off after the cooling. Then all trapped molecules are pumped to the $X^2\Sigma(0, 1, 1/2, 0)$ state.²³⁾ Measurement of the Q(1) transition frequency is possible in this situation. To measure the Q(0) transition frequency, the molecules are transformed to the $N = 0$ state by irradiating a π -pulse microwave.

Table I lists the magic frequency f_{mag} , the trap position (antinode or node), the power density required to obtain a potential depth of $10\ \mu\text{K}$ I_0 , the gradient of the Stark shift with respect to the detuning of the trap laser frequency dS/df , and the scattering rate γ . For dS/df and γ , a power density of I_0 was assumed. At magic frequency 2, molecules are trapped at the position where the power density is minimum, therefore dS/df and γ are expected to be one order smaller than the values shown in Table I when the trap potential depth is $10\ \mu\text{K}$. The difference in f_{mag} for the Q(0) and Q(1) transition frequencies is smaller than the estimation uncertainty (1 THz).

3. Stark and Zeeman Shift

The $\Delta N = \Delta J = \Delta F = \Delta M$ vibrational transition frequencies (where only v changes) are advantageous for precise measurement because the cancellation of the Stark and Zeeman shifts at the upper and lower states is significant. The DC Stark shift in Q(0) is $-0.38\ \text{Hz}/(\text{V}\cdot\text{cm})^2$ [$-2.2 \times 10^{-14}/(\text{V}\cdot\text{cm})^2$], which is two orders smaller than the Stark shifts at both states. For the Q(1) transition frequency, it is estimated to be on the order of $-1\ \text{mHz}/(\text{V}\cdot\text{cm})^2$ [$-5 \times 10^{-17}/(\text{V}\cdot\text{cm})^2$], because the DC Stark shift induced by the neighboring rotational states is zero for the $(J, F) = (1/2, 0)$ state. The Stark shift induced by blackbody radiation with a surrounding temperature of 300 K is $-64\ \text{mHz}$ (-3.2×10^{-15}) for both the Q(0) and Q(1) transition frequencies. The Zeeman shift in the Q(0, a) transition frequency is strictly linear with a coefficient of less than $\pm 0.1\ \text{mHz}/\text{G}$ ($\pm 5 \times 10^{-18}/\text{G}$) and it is perfectly eliminated by averaging the $M = \pm 1 \rightarrow \pm 1$ transition frequencies. The Zeeman shifts in the Q(0, b) and Q(1) transition frequencies are quadratic at magnetic fields lower than 10 G with coefficients of $-160\ \text{Hz}/\text{G}^2$ ($-9.1 \times 10^{-13}/\text{G}^2$) and $-210\ \text{Hz}/\text{G}^2$ ($-1.4 \times 10^{-12}/\text{G}^2$), respectively. The suppression of the magnetic field ($< 1\ \text{mG}$) is required to measure the Q(0, b) and Q(1) transition frequencies with an uncertainty lower than 10^{-17} .

The Q(0) and Q(1) transitions are one-photon forbidden and a two-photon transition is required. The transition can be observed via the Raman transition using with two cw laser

lights. When the power densities of two probe lasers are equal, the total Stark shift is eliminated by the combination of frequencies of 472.8 and 455.3 THz. The Rabi frequency of 1 Hz is obtained with a power density of $60\ \text{mW}/\text{cm}^2$ and the Stark shift induced by one laser light is $\pm 3.7 \times 10^{-15}$. When the fluctuation of the power ratio of the two probe lasers is less than 0.3%, the Stark shift is less than 10^{-17} . Using magic frequency 1 (trapped at the position where the light intensity is maximum), a Raman transition with a small Stark shift is also observed using a combination of an intense trap laser and weak probe laser with frequencies of $f_{\text{mag}} \pm f(0, 1)$.²⁸⁾ We can also observe the Raman transition using a frequency comb. The transition is observed by the contribution of many frequency components, when the repetition frequency f_{rep} corresponds to $f(0, 1)/n$ (n : integer). When the center of the frequency component distribution is close to f_{mag} , the cancellation between the Stark shifts induced by different frequency components is significant and the total Stark shift is on the order of 10^{-16} when a Rabi frequency of 1 Hz is obtained.

The $X^2\Sigma(v, N, J, F) = (0, 1, 1/2, 0) \rightarrow (1, 0, 1/2, 0)$ [P(1)] transition is an electric-dipole-allowed transition, whose Stark shift induced by laser light is independent of the polarization (measurement using a 3D lattice is possible). The P(1) transition frequency is 20.5 GHz lower than the Q(0, 1) transition frequency (17.452 THz). For this transition, the DC Stark shift is $38\ \text{Hz}/(\text{V}\cdot\text{cm})^2$ [$2.2 \times 10^{-12}/(\text{V}\cdot\text{cm})^2$] and the quadratic Zeeman shift is $5.4\ \text{kHz}/\text{G}^2$ ($3.1 \times 10^{-11}/\text{G}^2$). Therefore, the P(1) transition frequency is much less advantageous for precise measurement than the Q transition frequencies. However, this transition is advantageous for the non-destructive observation of the phase shift with a high signal-to-noise ratio.²⁹⁾

4. Conclusion

In this paper, we discussed the possibility of precisely measuring the $^{40}\text{Ca}^{19}\text{F}$ $X^2\Sigma(v, N, J, F) = (0, 0, 1/2, 1) \rightarrow (1, 0, 1/2, 1)$ (Q(0, a)), $(0, 0, 1/2, 0) \rightarrow (1, 0, 1/2, 0)$ (Q(0, b)), and $(0, 1, 1/2, 0) \rightarrow (1, 1, 1/2, 0)$ (Q(1)) transition frequencies. The Stark shift induced by the laser light is independent of the polarization; therefore, the quadratic Stark shift is eliminated by tuning the trap laser frequency to the magic frequencies for all the molecules trapped in a 3D lattice. Two values of the magic frequency were estimated. At one value of the magic frequency, molecules are trapped at the locations where the power density is minimum. The Q(0, a) transition frequency appears to be more advantageous for measurement with uncertainty lower than 10^{-17} because the Zeeman shift is strictly linear with a coefficient of less than $\pm 5 \times 10^{-18}/\text{G}$. This method also appears to be applicable to $^{88}\text{Sr}^{19}\text{F}$ and $^{174}\text{Yb}^{19}\text{F}$ molecules, for which laser cooling has been successful.

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