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Energy Flow Between Trapped Ions in Laser Cooling Fluorescence Mass Analysis Experiment

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Abstract: Two ultra cool different ions are considered as a unique quantum mechanical system in a harmonic trap. The properties of the system are investigated as a model of laser Cooling fluorescence mass analysis. The energy flow between the sample molecular ion and the atomic probe ion through the Coulomb interaction is analyzed as a process of Ferni resonant interaction of different states of the system. Using first order perturbation theory the translational energy efficiency between laser cooling atomic ion and the sample molecular ion is given, accordingly, signal strength distribution of mass spectra relative to mass number of sample molecular ions is discussed.

Keywords: Fluorescence Mass Analysis; Energy Flow; Trapped Ions

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1. Introduction

Besides the concentrated research area of Bose-Einstein condensation [1,2] and frequency standard [3,4] concerning application of laser cooling technique, it has been demonstrated to be possible to develop the single atomic and molecular ion detection method at ultra low temperature [5,6]. This method will be applicable in the area of high sensitive detection of chemical substance and in the study of chemical reaction dynamics. However, the main problem that hinders the application of this technique is the mass measurable range. Up to date, the mass measurable range is only about 1.5 times of the mass of laser cooled atomic ion, which has been demonstrated in the experiment of laser cooled Mg^{+} ion by Baba and Waki [5]. The measurable range is considered related to the efficiency of energy transfer between the sample molecular ion and laser cooled atomic ion. From a classical point of view, the kinetic energy transfer efficiency is dependent on the ratio of masses of two collision partners if an elastic collision is assumed. Thus, only a low transfer efficiency and then a weak signal of mass spectra will be obtained for those sample ions which have large mass difference relative to the laser cooled atomic ion. The signal strength of its mass spectra decreases with increasing the mass of the sample ion.

It is well known that the classical elastic collision model of ion interaction is a good approximation only in the case of high energy (relative to the kinetic energy of laser cooled ions). In other word, the de Broglie wave length of ions must be small enough comparing to their size [7] so that the wave property of particles can be neglected. In the experiment that trapped ions are cooled to a temperature of milli Kelvin order, the de Broglie wave length is estimated to be 10 nm for Mg^{+}, which is about two orders larger than its size. This result indicated that the classical elastic collision model is not suitable for analyzing the process of ion interaction in the ultra low temperature system. It was demonstrated by the experiment of sideband laser cooling [8] that a full quantum mechanical description of laser cooled and trapped ions should be employed. Therefore, investigations of the quantum mechanical model that describes the behavior of trapped ions at ultra low temperature become significant and necessary. A quantum theory of ions in a RF trap has also been developed by Brown [9] In the present paper, the two ultra cool different ions are considered as a unique quantum mechanical system in a harmonic trap. We investigate the properties of the system in order to understand the basic dynamic processes in laser cooling fluorescence mass analysis. The energy flow between the sample molecular ion and the atomic probe ion through the Coulomb interaction is analyzed as a process of Fermi resonant interaction of different states of the system. Using first order perturbation theory the translational energy transfer efficiency between laser cooled atomic ion and molecular sample ion is given, accordingly signal strength distribution of mass spectra relative to mass number of sample molecular ions is discussed.

Finally, we discuss the expansion of dynamic region of measurement.

2. Quantum Mechanical Model

The principle of laser cooling fluorescence mass analysis can be simply described as the detection of decay of fluorescence strength of laser cooled atomic ion, which is dependent on its temperature affected through the Coulomb interaction by the sample ions that are heated by an external electric field. The sample ions and the atomic ions are trapped in an ion trap at the same time, by the laser cooling of atomic ions and the sympathetic cooling effect [10-14], both the atomic probe ion and the sample ion in trap are

cooled to several hundreds milli Kelvin. At the low temperature state of the on gas, the fluorescence strength of laser cooled ion will decrease if we scan the frequency of heating electric field to a value at which the sample ions resonantly absorb energy from the electric field to vibrate in trap. Around this frequency, we will observe a sharp peak of fluorescence strength decay of laser cooled atomic ion, which becomes the mass analysis signal.

For simplicity, we consider a pure harmonic potential trap in which two ions exist, whose masses are m_1 and m_2 respectively. We assume that the ion with mass m_1 is an atomic ion called as probe ion which can be laser-cooled directly. The ion with mass m_2 is a sample ion with an unknown mass. For a certain trap potential, the ions with masses m1 and m2 will have different resonant vibrational frequency if m_1 is not equal to m_2. For a one-dimensional system, the state of the two ion system can be expressed by the wave function

$$\Psi = \Psi(x_1, x_2) \tag{2.1}$$

where x_1 and x_2 are coordinates of the probe ion and the sample ion, respectively. Here, the two ions are recognized as one system that has two vibrational modes. The vibrational frequencies are ω_1 and ω_2 for the vibration of probe ion and the sample ion. If we neglect the Coulomb interaction of ions, the energy of the system can be taken and expressed simply as

$$E_{mn} = (m + 1/2)\hbar\omega_1 + (n + 1/2)\hbar\omega_2 \tag{2.2}$$

where m and n are integers that represent the vibrational quantum numbers of the probe ion and the sample ion. During the measurement of the mass spectra, sample ion is excited to a higher vibrational level at first by the external electric field. We have

$$\Psi_{mn} \Longrightarrow \Psi_{mn'} \tag{2.3}$$

where n' is the new quantum number of the sample ion, where n' > n. Because of the Coulomb interaction of ions, the system will change its state to a new one after a certain time. The quantum number of the probe ion will increase to an integer a. The quantum number of the sample ion will decrease to an integer b, satisfying a>m and b<. n'. This process can be expressed as

$$\Psi_{mn'} \Longrightarrow \Psi_{ab} \tag{2.4}$$

Now, we discuss the probability of that the energy transfer process happens after a resonant excitation of the sample ion by the external electric field.

The Hamiltonian of the two-ion system in a trap can be written as

$$\hat{H} = \hat{P}_1^2/2m_1 + \hat{P}_2^2/2m_2 + V_1(trap) + V_2(trap) + V(1/r) \tag{2.5}$$

where V_1(trap) and V_2(trap) are the trap potential of ion m_1 and m_2, respectively. Here we assume a pure harmonic potential generated by an ideal trap as an approximation of RF trap. The V(1/r) in Eq. (2.5) represents the potential energy of the Coulomb interaction of the two ions. If the potential V(1/r) is small enough relative to the trap potential to be neglected, the motion of the two ions will be independent with vibration frequencies ω_1 and ω_2. The wave function of the system can be simply expressed as,

$$\Psi = \Psi_1(x_1)\Psi_2(x_2) \tag{2.6}$$

where $\Psi_1(x_1)$ and $\Psi_2(x_2)$ are the wave functions of the ion m_1 and the ion m_2 in a harmonic wave independently. The system will keep its state if the external electric field disappears. That is because the interaction between ions is not considered and the so called sympathetic cooling and sympathetic heating effect does not occur. However, for a real system, when we consider the Coulomb interaction, the wave function has a more complicated form that can be expressed by a linear combination of the harmonic eigenfunctions

$$\Psi = \sum_{ij} \beta_{ij} \Psi_{i1}(x_1)\Psi_{j2}(x_2) \tag{2.7}$$

where β_{ij} are coefficients. The Hamiltonian of the system is rewritten as

$$\hat{H} = \hat{H}_0 + \hat{H}' \tag{2.8}$$

where $\hat{H}_0$ is the part of the harmonic potential coming from trap, and $\hat{H}'$ represents the Coulomb interaction of ions. For simplicity, it can be written as

$$\hat{H} = {}^{1}/_{r} \tag{2.9}$$

For any two states of the system, both of the wave functions describe motion of two ions vibrating in trap. When the Coulomb interaction between ions can be considered as a perturbation, similar to the interaction of vibrational energy levels in a polyatomic molecule, the interaction between different states of the system can be regarded as Fermi resonance interaction. According to first-order perturbation theory, wavefunction of the system will be a linear combination of the unperturbed wavefunctions [15]

$$\Psi = \alpha\Psi_{mn'} + \beta\Psi_{ab} \tag{2.10}$$

With

$$\alpha = \left[\left(\frac{\sqrt{4W^2+\delta^2}+\delta}{2\sqrt{4W^2+\delta^2}}\right)\right]^{1/2} \tag{2.11}$$

and

$$\beta = \left[\left(\frac{\sqrt{4W^2+\delta^2}-\delta}{2\sqrt{4W^2+\delta^2}}\right)\right]^{1/2} \tag{2.12}$$

where α and β are two coefficients. The squares of α and β represent possibility of the system being in the related states. The δ in Eqs. (2.11) and (2.12) represents the difference of the two perturbed states and W represents the Coulomb interaction strength coming from the following integration,

$$W = \int \Psi_{mn'} \hat{H}' \Psi_{ab} dx \tag{2.13}$$

3. Energy Flow Process and Mass Spectra Signal Strength

The mass spectra signal comes from the decay of fluorescence strength of laser cooled atomic ions when they are heated through the Coulomb interaction by the sample ions. The strength of signal is dependent on the efficiency of the heating process, which is proportional to the square of coefficient β. We can find from the expression of α and β that for a non zero value of interaction term W, when δ is zero, which means the same energy levels of the two states, we have maximum value of β which is ${}^{1}/_{\sqrt{2}}$. In this case, we have the maximum mixture of the two unperturbed wave functions and maximum efficiency for state transformation described in equation (2.4). These phenomena can also be comprehended as the most energy flow between the two ions.

3.1. One Quantum Number Excitation of Sample ion

One quantum number excitation of vibration state of the sample ion in ion trap by an external electric field is the basic process in the measurement of mass spectra, since this process always has larger possibility than that of the overtone excitation. In this case, the vibration energy of the sample ion increases $\hbar\omega_2$. Due to the Coulomb interaction, this part of the energy will be transferred to the atomic ion. The probability of this transformation is the square of coefficient β that is dependent on energy difference δ. The vibration frequency of the sample ion ω_2 can be rewritten as

$$\omega_2 = \in \omega_1 + \sigma\omega_1 \tag{3.1}$$

where $\in$ is an integer and $0 \le \sigma < 1$. In the case of $\in \neq 0$, the nearest state of the system relative to $\Psi_{mn'}$ is $\Psi_{(m+\in)n}$. This corresponds to the case where the mass of the sample ion is smaller than the mass of the atomic probe ion. The probability of system transferring to this new state is the square of β with the energy difference

$$\delta = \sigma\omega_1 \tag{3.2}$$

As discussed above, when $\delta = 0$, we have the maximum value of β, i.e., the maximum signal strength of mass spectra. Around the maximum value the spectra strength decreases. We should have totally the $\in$ maximum position of signal strength in our observation of mass spectroscopy.

When $\epsilon = 0$, corresponding to that the mass of the sample ion is larger than the mass of the atomic probe ion, the energy difference between the state of the excited sample ion and the state of the excited probe ion is $(1-\sigma)\omega_1$. Therefore, the energy difference increases with decreasing σ. This process results in a small probability of state transformation, and thus weak signal strength of mass spectra. Because the vibration frequency is proportional to the invert of root of ion mass, we can conclude that there will be a weak mass spectra signal for WEIGHT sample ions comparing to mass of atomic probe ion. Combining discussion of the cases $\epsilon \neq 0$ and $\epsilon = 0$ and considering relation between the vibrational frequency and the ion mass, we obtain the spectra strength distribution in whole mass region involving one quantum number excitation, which is shown in Figure 1.

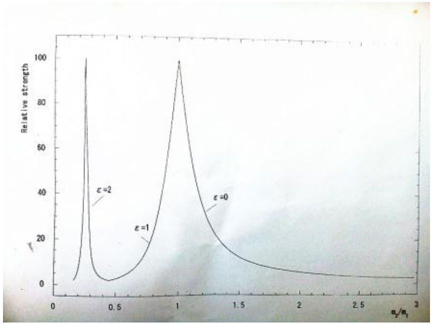

Figure 1. Strength distribution of laser cooling fluorescence mass spectra signal in the case of one quantum number excitation of sample ion. Calculation is carried out on an assumption that the Coulomb interaction term W is 1/20 of fundamental vibration energy of the atomic probe ion, and the maximum value of signal strength is defined as 100.

The signal strength of the sample ion with the mass about 1.5 times of atomic probe ion is 1/8 of the maximum value when the sample ion and the probe ion have the same masses. Therefore, for a measurement that S/N is smaller than 8, it is impossible to observe the mass spectra signal of those ions whose masses are larger than 1.5 times of the mass of the atomic probe ion. If Mg^+ is used as a probe ion, the largest measurable mass number should only be 32 in this case.

3.2. Multi Quantum excitation of Sample ion

In general, a wide measurable region is necessary in the application of mass spectroscopy.For ions with a large mass number, in order to decrease the energy difference of two interacting vibration states, the multi quantum number excitations of sample ions are needed. An effective method is to consider overtone excitation. In the case of $2\omega_2$ excitation, the maximum signal strength point shifts from $m_2 = m_1$ to $m_2 = 4m_1$. If Mg^+ is used as the probe ion, we will get the maximum signal strength at mass number of 96. In the case of $3\omega_2$ excitation, the maximum signal strength point shifts from $m_2 = m_1$ to $m_2 = 9m_1$. Again we use Mg^+ as probe ion, we will have the maximum signal strength at mass number of 216. Figure 2 shows the signal strength distributions at different excitation cases, Mg^+ is used as the probe ion. The probability of the overtone excitation is smaller than that of the single quantum number excitation, thus it is necessary to apply a stronger external electric field in the measurement. Therefore, the external electric field strength can be used as an evidence to distinguish different excitation process that is different measurable region.

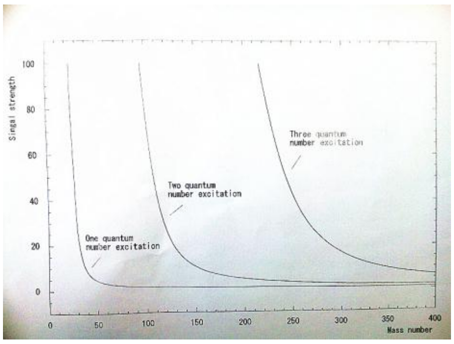

Figure 2. Strength distribution of laser cooling fluorescence mass spectra signal in the case of different quantum number excitation of the sample ion. Calculation is done in the case of Mg^+ is used as a probe ion, on the assumption that Coulomb interaction term W is 1/20 of fundamental vibration energy of the atomic probe ion, and the maximum value of signal strength is defined as 100.

3.3. Coulomb Interaction Term W

We define a quantity $\Delta\delta$ to describe the rate of β^2 that decreases with increasing δ

$$\Delta\delta = \delta(\beta^2 = 1/4) - \delta(\beta^2 = 1/2) = \sqrt{4/3}\,W \tag{3.3}$$

In order to obtain a relatively uniform measurement, a large value of $\Delta\delta$ is needed. Considering relation of $\Delta\delta$ with W, we need a strong Coulomb interaction between ions.

Figure 3 shows the signal strength distribution at different Coulomb interaction strengths W. Because of the repulse force between ions, the distance of two ions at certain average kinetic energy has a minimum value μ , then r can be expressed as

$$r = \mu + D, D \geq 0 \tag{3.4}$$

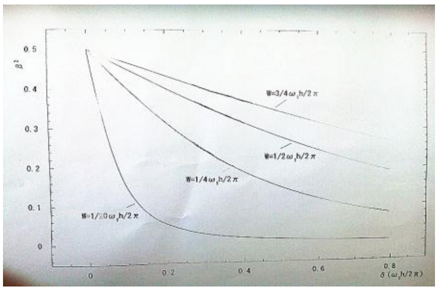

Figure 3. Distribution of probability of state transformation at different values of theCoulomb interaction term W relative to the energy difference of the two perturbed states.

The energy difference is shown by using $\hbar\omega_1$ as an unit.

When parameter D is small enough, $\hat{H}'$ can be expanded as

$$\hat{H}' = \frac{1}{\mu} - (1/\mu)^2 D + (1/\mu)^3 D^2 - (1/\mu)^4 D^3 + \text{cdots.} \tag{3.5}$$

We have

$$W = \frac{1}{\mu}\int \Psi_{mn'} \Psi_{ab} dx - \frac{1}{\mu}\int \Psi_{mn'} \frac{D}{\mu} \Psi_{ab} dx + \frac{1}{\mu}\int \Psi_{mn'} (D/\mu)^2 \Psi_{ab} dx + cdots \tag{3.6}$$

where dx in the integrations represents derivatives of two variables x_1 and x_2 of the two ions and D is a linear function of x_1 and x_2. For harmonic wave functions, the integration is non zero only for the terms in perturbation Hamiltonian that include $X_1^{a-m} X_2^{n'-b}$ term. Considering the expression of perturbation Hamiltonian, as a power expansion of term D/μ which has the relation (D/μ) <1, the high power term is always smaller than low power term. Therefore, it is enough for us to consider lower power term only, which gives a main contribution in the integration. We have the lowest power term which includes term $X_1^{a-m} X_2^{n'-b}$ is $D^{(a-m)+(n'-b)}$. If the terms higher than $(a-m)+(n'-b)$ are neglected, the effective perturbation Hamiltonian for states Ψ_{ab} and $\Psi_{mn'}$ is given by

$$\hat{H}'_{eff} = \frac{1}{\mu}\left(\frac{D}{\mu}\right)^{(a-m)+(n'-b)} \tag{3.7}$$

In the case that mass of the sample ion is larger than that of the probe ion, we can consider only the case of a-m=1 and Δn=n'-b=1, 2, 3 corresponding to the single quantum number excitation and the overtone excitation. Thus we have the effective perturbation Hamiltonian as

$$\hat{H}'_{eff} = \frac{1}{\mu}\left(\frac{D}{\mu}\right)^{1+\Delta n} \tag{3.8}$$

For D/μ is a value smaller than 1, the Coulomb interaction term W of the overtone excitation is always smaller than the value of the single quantum number excitation. The signal strength of mass spectra of the overtone excitation is weaker comparing to that of the single quantum number excitation, at the same energy difference of two interacting states.

To obtain a large Coulomb interaction term W, it is necessary to take parameter μ small. This means that a deep potential well should be used in the experiment. In the case of RF ion trap, the electric voltage applied on electrodes of the ion trap is limited to several thousands because of the problem of discharge. Even though, it is possible to obtain several tens to several hundreds electronic voltage potential depth if we arrange the size of electrodes suitably, which is about one or two order deeper than that in experiment of reference 5. Therefore, we are able to obtain a relatively uniform measurable region until at least several hundreds of mass number.

The stabilization of laser frequency is another important problem in expansion of dynamic region of the measurement. When the atomic ion gas is cooled to its cooling limit, spectra line of the atomic ion fluorescence take a Lorentzian profile with only its natural line width. In the case of Mg^+, its natural line width is about 43MHz. If frequency of cooling laser is adjusted to 10MHz below center frequency of Mg^+ transition, to make noise, coming from laser frequency shift, lower than 1%, we have to stabilize laser to make frequency shift smaller than 280 KHz. On this condition, when the maximum signal strength is half of strength of the atomic ion fluorescence, we can obtain a S/N of our measurement to be about 50 if we neglect other noise resulting factors. If other experimental conditions are the same as the experiment in Ref. 5, the signal of the sample ion with the mass number 100 should be observed by only one quantum number excitation.

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