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REGULAR PAPER

Peak Confluence Phenomenon in Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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When two ions with very small mass difference are analyzed by Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry, the two peaks in the mass spectrum approach to each other by increasing the number of ions and finally merge into a single peak, even though the width of the peaks is sufficiently small compared to the distance between the peaks. It seems that Coulomb force between the two ion packets modulates their cyclotron motions produced by an rf electric field in the FT-ICR trap. We studied the phenomenon theoretically using a model of two charged particles which are confined in a plane perpendicular to a uniform magnetic field. In the case that the two ions appear as a single peak the two ion packets are coupled and rotate around the center of mass with oscillating radius and the position of the peak in the spectrum is determined by the frequency of rotation of the center of mass which corresponds to the weighted average of the mass of the two ion packets. It is found that there is an oscillating force acting between the two ion packets and when the force is resonant with the oscillating radius, the two ion packets are decoupled and appears as two separate peaks in the spectrum. Various factors which affect the phenomenon are discussed.

1. Introduction

In FT-ICR spectrometers[1)~3)] ions are confined in a trap under the influence of electric and magnetic fields. Motion of an ion projected to a plane perpendicular to the magnetic field is circular motion whose frequency is given by the cyclotron resonance frequency $f_c = 1/2\pi \cdot qB/m$ where B is the magnetic field intensity and m and q are mass and charge of the ion respectively. In FT-ICR the cyclotron motion is accelerated for a short period by an rf electric field containing the cyclotron frequency of ions. With an increase in velocity the motion of ions becomes coherent and the ions form a packet executing a large cyclotron orbit. These ions induce an rf electric signal at detector electrodes of the trap.[4)] The signal is amplified, digitized and Fourier transformed to yield a frequency domain spectrum. The mass-to-charge ratio of ions is determined by the cyclotron resonance condition.

When two kinds of ions with very small mass difference are confined in the trap and their numbers are increased, the two peaks in the spectrum come close to each other and finally merge into a single peak, even though the width of each peak is sufficiently small compared to the distance between them.[5)] Figure 1 presents such an example. The figure shows variation of mass spectrum of CO^+(m/z 27.9949) and $C_2H_4^+$(m/z 28.0313) as

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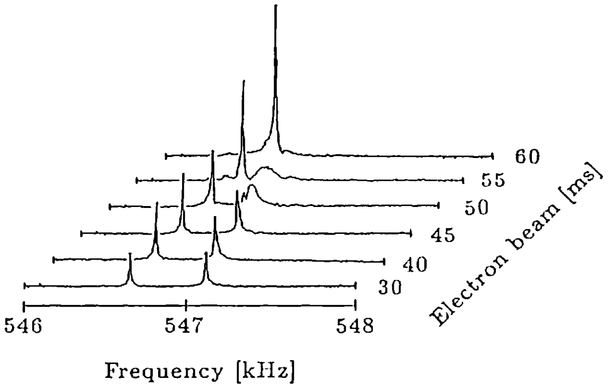

Fig. 1. Experimental results of CO^+ and $C_2H_4^+$ spectra varying the electron beam irradiation time. The FT-ICR spectrometer employed in this experiment is described in detail elsewhere.[6),7)] The magnetic field strength was 0.998 T. The background pressure in the vacuum chamber was below 1×10^{-8} Torr. The same amounts of CO and C_2H_4 samples were introduced through a leak valve and the total pressure was kept at 4.6×10^{-8} Torr. The gas was ionized by a 70 eV pulsed electron beam.[5)]

a function of the number of ions in the trap. The phenomenon has connection neither with peak broadening caused by collisions of ions with neutral molecules[8)] nor with the Coulomb broadening due to the space charge of ions.[9)~14)] It is suggested that with the increase in the number of ions the interaction of two ion packets becomes important and they cannot rotate independently with their own cyclotron resonance frequencies. In this paper we wish to treat theoretically this phenomenon using a simple two-charged-particle model.

2. Theory

2.1 Formulation of the two-charged-particle model

In formulating a model which represents the phenomenon the following points were taken into consideration. i) Due to the inhomogeneity of the electric field in FT-ICR traps there are two modes of ion motion other than the cyclotron motion of ions. One is the trapping oscillation in the direction of the magnetic field within a electrostatic potential well formed by the trap electrodes[15)] and the other is the magnetron motion which is a precession of the center of the cyclotron motion along an equipotential contour in the plane perpendicular to the magnetic field.[16)] The frequencies of these periodic motions are much smaller than the cyclotron frequency and these motions can be treated separately and not included in the present model. ii) The size of the ion packets is small compared to the radius of their cyclotron orbit which is the order of millimeters in the typical experimental conditions,[17)] thus a packet can be treated as a charged particle having mass and charge multiplied by the number of ions in the packet. We therefore treat the phenomenon with two charged particles moving in the plane perpendicular to the magnetic field at the center of the trap.

2.2 Coupled motion of the two charged particles

The Lagrangian function of two-charged-particle system can be written as follows

$$\mathscr{L}=\frac{n_1m_1\dot{r}_1^2}{2}+\frac{n_2m_2\dot{r}_2^2}{2}-\frac{n_1n_2e^2}{4\pi\varepsilon_0|\boldsymbol{r}_1-\boldsymbol{r}_2|}+\frac{n_1eB(x_1\dot{y}_1-\dot{x}_1y_1)}{2}+\frac{n_2eB(x_2\dot{y}_2-\dot{x}_2y_2)}{2} \tag{1}$$

where e is the charge of an electron and ε_0 is the permittivity of free space. The z-axis points to the direction of the magnetic field $\boldsymbol{B}$ whose magnitude is constant. The notations m_1 and m_2, n_1 and n_2, and $\boldsymbol{r}_1=(x_1, y_1)$ and $\boldsymbol{r}_2=(x_2, y_2)$ are masses, numbers and position vectors of the two kinds of ions 1 and 2, respectively.

Using the center-of-mass coordinate system the equation can be rewritten as

$$\mathscr{L}=\frac{M\dot{R}^2}{2}+\frac{m\dot{r}^2}{2}-\frac{n_1n_2e^2}{4\pi\varepsilon_0|\boldsymbol{r}|}+\frac{(n_1+n_2)eB(X\dot{Y}-\dot{X}Y)}{2}+\left(\frac{1}{n_1m_1^2}+\frac{1}{n_2m_2^2}\right)\frac{eBm^2(x\dot{y}-\dot{x}y)}{2}-\frac{(m_1-m_2)n_1n_2eB(X\dot{y}-\dot{X}y+x\dot{Y}-\dot{x}Y)}{2M} \tag{2}$$

where M is the total mass of the system, m is the reduced mass, $\boldsymbol{R}=(X, Y)$ is the position vector of the center of mass and $\boldsymbol{r}=(x, y)$ is the relative position vector of the two charged particles. The last term of Eq. (2) having cross terms of $\boldsymbol{R}$ and $\boldsymbol{r}$ is negligible because the masses of two ions are approximately equal ($m_1\approx m_2$). Hence the Lagrangian function can be separated into the $\boldsymbol{R}$-component and the $\boldsymbol{r}$-component. By using the cylindrical coordinates the former becomes

$$\mathscr{L}_{cm}=\frac{M\dot{R}^2}{2}+\frac{M(R\dot{\Theta})^2}{2}+\frac{(n_1+n_2)eBR^2\dot{\Theta}}{2} \tag{3}$$

where the variables X and Y are changed as $R\cos\Theta$ and $R\sin\Theta$ respectively. Because the motion takes place in the static magnetic field, the present system is time independent and is symmetrical with respect to R and Θ. Therefore the system satisfies the conservation of both P_R, the momentum about R, and M_Z, the angular momentum about Θ. Partial differentiation of Eq. (3) gives P_R and M_Z as

$$P_R=\frac{\partial\mathscr{L}_{cm}}{\partial\dot{R}}=M\dot{R}=\text{const.}, \tag{4}$$

$$M_Z=\frac{\partial\mathscr{L}_{cm}}{\partial\dot{\Theta}}=MR^2\dot{\Theta}+\frac{(n_1+n_2)eBR^2}{2}=\text{const.}. \tag{5}$$

According to Eqs. (3) and (4) the Lagrangian equation of motion with respect to R can be written as follows

$$\frac{d}{dt}\frac{\partial\mathscr{L}_{cm}}{\partial\dot{R}}-\frac{\partial\mathscr{L}_{cm}}{\partial R}=-\frac{\partial\mathscr{L}_{cm}}{\partial R}=-R\dot{\Theta}\{M\dot{\Theta}+(n_1+n_2)eB\}=0. \tag{6}$$

In the case that R and $\dot{\Theta}$ are not equal to zero,

$$-\dot{\Theta}=\overline{\omega_c}=\frac{(n_1+n_2)eB}{M} \tag{7}$$

and R=const. are obtained. As a result the motion of the center of mass is circular motion and its angular frequency $\overline{\omega_c}$ is the weighted average of the angular cyclotron frequencies of the two particles.

From Eq. (2), the Lagrangian function of r-component in the approximate form with $m_1 \approx m_2$ is obtained:

$$\widetilde{\mathscr{L}}_{\rm rel} = \frac{m\dot{r}^2}{2} + \frac{m(r\dot{\theta})^2}{2} - \frac{n_1 n_2 e^2}{4\pi\varepsilon_0 r} + \left(\frac{1}{n_1 m_1^2} + \frac{1}{n_2 m_2^2}\right)\frac{eB(mr)^2\dot{\theta}}{2} \tag{8}$$

where the cylindrical coordinates $(x, y) = (r\cos\theta, r\sin\theta)$ are used. Since the variables θ and t are not appeared in Eq. (8), both the angular momentum about θ: M_z, and the total energy E are conserved,

$$\begin{aligned} M_z &= \frac{\partial \widetilde{\mathscr{L}}_{\rm rel}}{\partial \dot{\theta}} \\ &= mr^2\dot{\theta} + \left(\frac{1}{n_1 m_1^2} + \frac{1}{n_2 m_2^2}\right)\frac{eB(mr)^2}{2} = \text{const.}, \end{aligned} \tag{9}$$

$$\begin{aligned} E &= \dot{r}\frac{\partial \widetilde{\mathscr{L}}_{\rm rel}}{\partial \dot{r}} + \dot{\theta}\frac{\partial \widetilde{\mathscr{L}}_{\rm rel}}{\partial \dot{\theta}} - \widetilde{\mathscr{L}}_{\rm rel} \\ &= \frac{m\dot{r}^2}{2} + \frac{mr^2}{2}\left\{\frac{M_z}{mr^2} - \left(\frac{1}{n_1 m_1^2} + \frac{1}{n_2 m_2^2}\right)\frac{eBm}{2}\right\}^2 \\ &\quad + \frac{n_1 n_2 e^2}{4\pi\varepsilon_0 r} = \text{const.}. \end{aligned} \tag{10}$$

We then have

$$\dot{\theta} = \frac{M_z}{mr^2} - \left(\frac{1}{n_1 m_1^2} + \frac{1}{n_2 m_2^2}\right)\frac{eBm}{2} \tag{11}$$

and

$$\dot{r} = \sqrt{\frac{2[E_{\rm eff} - U(r)]}{m}} \tag{12}$$

where

$$E_{\rm eff} = E + \left(\frac{1}{n_1 m_1^2} + \frac{1}{n_2 m_2^2}\right)\frac{eBmM_z}{2} = \text{const.} \tag{13}$$

is the effective total energy of the relative motion and

$$U(r) = \frac{M_z^2}{2mr^2} + \left(\frac{1}{n_1 m_1^2} + \frac{1}{n_2 m_2^2}\right)^2\frac{m^3(eBr)^2}{8} + \frac{n_1 n_2 e^2}{4\pi\varepsilon_0 r} \tag{14}$$

is the potential energy. The region of the relative motion is restricted within the range in which the relation $E_{\rm eff} - U(r) \geq 0$ and $r > 0$ are satisfied. Because $U(r)$ is asymptotic to r^{-2} at $r \to 0$ and to r^2 at $r \to \infty$, it forms a potential well. Therefore the relative distance r oscillates between the minimum r_1 and the maximum r_2 which are the crossing points of $E_{\rm eff}$ and $U(r)$. From Eq.(12),

$$dt = \sqrt{\frac{m}{2[E_{\rm eff} - U(r)]}}\,dr. \tag{15}$$

Integration of this equation yields the period of oscillation of r as

$$T = \sqrt{2m}\int_{r_1}^{r_2}\frac{dr}{\sqrt{E_{\rm eff} - U(r)}}. \tag{16}$$

The relative motion can be expressed as rotational motion whose angular frequency is given by Eq. (11) and its radius oscillates with a period given by Eq. (16). The motion is restricted in the neighborhood of the center of mass of the system. In this case the signal induced at the detector electrodes of the trap is mainly caused by the cyclotron motion of the center of mass and results in a confluent peak in the mass spectrum.

2.3 Decoupled motion of the two charged particles

In order to derive the condition for letting the charged particles escape from the confinement the complete form of the Lagrangian function of the relative motion must be treated. Taking into account of the orbit of the center of mass the complete Lagrangian function of the relative motion is obtained from Eq. (2) as

$$\mathscr{L}_{\rm rel}=\frac{m\dot{r}^2}{2}+\frac{m(r\dot{\theta})^2}{2}-\frac{n_1n_2\mathrm{e}^2}{4\pi\varepsilon_0 r}+\left(\frac{1}{n_1m_1^2}+\frac{1}{n_2m_2^2}\right)\frac{\mathrm{e}B(mr)^2\dot{\theta}}{2}$$
$$-\frac{(m_1-m_2)n_1n_2\mathrm{e}BR}{2M}$$
$$\times\{(\overline{\omega_c}+\dot{\theta})r\cos(\overline{\omega_c}t-\theta+\Theta_0)-\dot{r}\sin(\overline{\omega_c}t-\theta+\Theta_0)\} \qquad (17)$$

where Θ_0 is the initial phase of the motion of the center of mass. The last term of Eq. (17) represents a driving force which induces oscillation of the relative distance between the two particles. The frequency of the force is given by

$$f=\left|\frac{\overline{\omega_c}-\dot{\theta}}{2\pi}\right|. \qquad (18)$$

The force is resonant with r-oscillation at a frequency $f=1/T$. The resonance makes the amplitude of r-oscillation larger and finally the two particles are released from the restraint and begin to rotate independently at their own cyclotron frequencies. The variation of f is monotonous with respect to r and becomes minimum at $r=r_1$, the minimum distance between the two particles. Assuming that as initial conditions $r=r_0$, $\dot{r}=0$ and $\dot{\theta}=0$ at $t=0$ Eqs. (9) and (11) become

$$M_z=\left(\frac{1}{n_1m_1^2}+\frac{1}{n_2m_2^2}\right)\frac{\mathrm{e}B(mr_0)^2}{2} \qquad (19)$$

and

$$\dot{\theta}=\frac{M_z}{mr^2}-\frac{M_z}{mr_0^2}, \qquad (20)$$

then Eq. (14) is reduced to

$$U(r)=\frac{M_z^2}{2mr^2}+\frac{(M_zr)^2}{2mr_0^4}+\frac{n_1n_2\mathrm{e}^2}{4\pi\varepsilon_0 r}. \qquad (21)$$

From Eqs.(10), (13) and (19) it follows

$$E_{\rm eff}=\frac{n_1n_2\mathrm{e}^2}{4\pi\varepsilon_0 r_0}+\frac{M_z^2}{mr_0^2}. \qquad (22)$$

We find immediately that one of the solutions of $E_{\rm eff}-U(r)=0$ is $r=r_0$. It is confirmed that r_0 is equal to r_1 by analyzing the derivative of $U(r)$. From Eqs. (18) and (20) the minimum driving frequency f_0 is given by

$$f_0=\frac{\overline{\omega_c}}{2\pi}. \qquad (23)$$

The resonance condition is that the frequency of r-oscillation is higher than the minimum frequency:

$$\frac{\overline{\omega_c}}{2\pi}\leq\frac{1}{T}. \qquad (24)$$

When many ions are in the packets a strong Coulomb force makes the amplitude of

r-oscillation larger and the period of r-oscillation T becomes large. As a result the resonance condition is not satisfied. The two ion packets remain coupled and continue to be attracted to the center of mass. These remarks agree with our experimental observations.[5] The number of ions not satisfying the resonance condition can be estimated from the experimental condition which does not induce peak confluence. In the case of the pulsed electron beam of 60 ms the corresponding numbers of CO^+ and $C_2H_4^+$ ions were found to be $n_1 \approx 3.8\times10^5$ and $n_2 \approx 6.2\times10^5$ respectively. In this estimation the theoretical values of total ionization cross section for CO and C_2H_4 given by Otvos and Stevenson[18] were employed. From the above results, if the numbers of CO^+ and $C_2H_4^+$ ions are expressed as $n_1=3.8\times n_0$ and $n_2=6.2\times n_0$ respectively, the value of n_0 which satisfies the resonance condition is $n_0 \lesssim 10^5$. Because we kept the ratio of the partial pressure of CO and C_2H_4 constant throughout the experiment, the ranges for n_1 and n_2 which satisfy the resonance condition were not determined separately. This numerical results will be compared with our theory in the next subsection.

2.4 Derivation of the resonance condition by the perturbation method

The analysis of the relative motion can be made by the perturbation method. Let the last term of Eq. (21) be a perturbation term $\delta U(r)$ and the rest terms be denoted as $U_0(r)$. From the potential without perturbation, Eq. (15) becomes

$$\begin{aligned} \mathrm{d}t &= \sqrt{\frac{m}{2[E_{\mathrm{eff}}-U_0(r)]}}\,\mathrm{d}r = \sqrt{m\Big/\left(2E_{\mathrm{eff}}-\frac{(M_z r)^2}{m r_0^4}-\frac{M_z^2}{m r^2}\right)}\,\mathrm{d}r \\ &= \frac{m r_0^2}{M_z}\frac{r\mathrm{d}r}{\sqrt{a^2s^2-(r^2-a)^2}} \qquad ;\ a=\frac{m r_0^4 E_{\mathrm{eff}}}{M_z^2},\ s=\sqrt{1-\frac{M_z^4}{m^2 r_0^4 E_{\mathrm{eff}}^2}}, \\ &= -\frac{m r_0^2}{2M_z}\frac{\mathrm{d}\eta}{\sqrt{a^2s^2-\eta^2}} \qquad ;\ \eta=a-r^2, \\ &= \frac{m r_0^2}{2M_z}\mathrm{d}\phi \qquad ;\ \eta=as\cos\phi\,. \end{aligned} \tag{25}$$

The period without perturbation T_0 can be obtained by integrating Eq. (25) from 0 to 2π:

$$T_0=\frac{\pi m r_0^2}{M_z}\,. \tag{26}$$

The perturbation term yields the shift of the period δT. The shift of the infinitesimal period $\delta \mathrm{d}t$ is derived from Eq. (15):

$$\begin{aligned} \delta\mathrm{d}t &= -\frac{\partial}{\partial E_{\mathrm{eff}}}\sqrt{\frac{m}{2(E_{\mathrm{eff}}-U_0-\delta U)}}\,\delta U\mathrm{d}r = -\frac{\partial}{\partial E_{\mathrm{eff}}}\delta U\mathrm{d}t \\ &= -\frac{n_1 n_2 e^2}{4\pi\varepsilon_0}\frac{\partial}{\partial E_{\mathrm{eff}}}\frac{\mathrm{d}t}{r}\,. \end{aligned} \tag{27}$$

Integrating,

$$\begin{aligned} \delta T &= -\frac{n_1 n_2 e^2 m r_0^2}{4\pi\varepsilon_0 M_z}\frac{\partial}{\partial E_{\mathrm{eff}}}\int_0^{\pi}\frac{1}{\sqrt{a(1-s\cos\phi)}}\mathrm{d}\phi \\ &= -\frac{n_1 n_2 e^2 m r_0^2}{2\pi\varepsilon_0 M_z}\frac{\partial}{\partial E_{\mathrm{eff}}}\frac{K\left(\sqrt{\frac{2s}{1+s}}\right)}{\sqrt{a(1+s)}} \end{aligned} \tag{28}$$

where $K(x)$ is the first elliptic integral and can be approximated by taking the first few terms of the expansion in the case that $\delta U(r) \ll U_0(r)$:

$$K(x)=\frac{\pi}{2}\sum_{n=0}^{\infty}\left[\frac{(2n-1)!!}{2^n n!}\right]^2 x^{2n}$$
$$\approx\frac{\pi}{2}\left(1+\frac{x^2}{4}\right). \tag{29}$$

Thus δT is given as

$$\delta T\approx-\frac{n_1n_2e^2mr_0^2}{8\varepsilon_0M_z}\frac{\partial}{\partial E_{eff}}\frac{2+3s}{\sqrt{a(1+s)^3}}=\frac{5n_1n_2e^2mr_0^2}{16\varepsilon_0M_zE_{eff}\sqrt{a(1+s)^3}}$$
$$\approx\frac{5n_1n_2e^2}{16\varepsilon_0}\sqrt{\frac{m}{E_{eff}^3}}. \tag{30}$$

The result shows that δT is positive and the period is made larger by the perturbation term.

Using Eqs. (7), (19), (24), (26) and (30) the resonance condition can be rewritten as

$$\frac{5n_1n_2e^2}{32\pi\varepsilon_0}\sqrt{\frac{m}{E_{eff}^3}}\leq\frac{M|m_1-m_2|\ |n_1m_1-n_2m_2|}{eB(n_1+n_2)(n_1m_1^2+n_2m_2^2)}. \tag{31}$$

The effective kinetic energy of the relative motion E_{eff} is defined as the difference in the kinetic energies of the two charged particles. The radius of the rotation of the center of mass R is substituted for the cyclotron radii of particles,

$$E_{eff}\approx\frac{(eBR)^2}{2}\left|\frac{n_1}{m_1}-\frac{n_2}{m_2}\right|. \tag{32}$$

Hence Eq. (31) becomes

$$\left(\frac{n_1n_2}{M|n_1m_2-n_2m_1|}\right)^{3/2}\frac{(m_1m_2)^2(n_1+n_2)(n_1m_1^2+n_2m_2^2)}{R^3B^2|m_1-m_2|\ |n_1m_1-n_2m_2|}\leq\frac{16\pi\varepsilon_0}{5\sqrt{2}}. \tag{33}$$

In the case the two numbers n_1 and n_2 are equal ($n_1=n_2=n$) Eq. (33) becomes

$$\frac{n(m_1m_2)^2(m_1^2+m_2^2)}{R^3B^2(|m_1-m_2|)^{7/2}(m_1+m_2)^{3/2}}\leq\frac{8\pi\varepsilon_0}{5\sqrt{2}}. \tag{34}$$

The Eq. (33) represents the resonance condition which determines whether the motion of the two ion packets is coupled or decoupled. A number of factors which affect the condition can be drawn from the examination of the left-hand side of the equation. The behavior of the two spectral peaks observed by experiment should conform to these factors. If the left term is large with respect to the right term which is constant, the resonance does not take place and the two peaks are merged into a single peak in the spectrum and if the left term is made smaller than the right term, the resonance takes place and the peaks are observed as separate peaks. When the mass difference of the two ions $|m_1-m_2|$ is decreased, the left term increases rapidly. The term also increases with the numbers of the two ions n_1 and n_2. These effects are experimentally observed as illustrated in Fig. 1. In order to examine the validity of Eq. (33) comparison was made with experiment. The following experimental values were substituted in the equation: $B=0.998$ T, $m_1=27.9949$ amu, $m_2=28.0313$ amu, $n_1=3.8\times n_0$, $n_2=6.2\times n_0$ and $R=1.0$ cm, and the equation was solved to obtain n_0 which satisfies the resonance condition. The value of n_0 was found as $n_0\lesssim1.5\times10^5$ which is favorably compared with the experimental result.

In addition the equation predicts that low magnetic field B and small radius of the rotation of the center of mass R make the resonance difficult. The radius R is proportional to both the amplitude and the length of the rf pulse which accelerates the cyclotron motion of ions.[4] This suggests that by raising the kinetic energy of ions a confluent peak may be separated. Lastly the equation indicates that the decoupling motion of the two ion packets becomes difficult at high mass ions. These predictions are to be confirmed by future experiments.

3. Conclusion

The phenomenon of confluent two ion peaks with small mass difference is well understood theoretically by analyzing the motion of two charged particles confined in a plane perpendicular to a uniform magnetic field. Analysis of motion in the center-of-mass coordinates shows that the center of mass of the two particles rotates at a frequency which corresponds to the weighted average of the cyclotron frequencies of the two particles. The relative motion of the two particles is described as coupled rotation around the center of mass and oscillation of the distance between the two particles. A more exact treatment of the Lagrangian function yields a force which drives the oscillation. A condition which causes resonance between the force and the oscillating radius is derived. When the condition is satisfied, the two particles are released from the coupling and begin to rotate independently at their own cyclotron frequencies. This situation results in the separation of two peaks in the spectrum. At high concentration of ions the ion packets which have been released from the coupling fall again in the confinement after some delay at least in a Poincare period and the two states take place alternatively. It seems that the two mass spectral peaks come close to each other as the period of the coupling increases compared to the period of the decoupling.

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