Theory for Longitudinal Ion Cyclotron Resonance Power Absorption: Application to Line Shape for Nonreactive Ion

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The rf electric field in circular concave electrodes for longitudinal ion cyclotron resonance is investigated. The potential equation of this rf electric field is theoretically derived from Laplace's equation. The equation of the motion of an ion which moves under the simultaneous application of the magnetic field and this rf electric field was solved. The solution of this equation is used to obtain the instantaneous and total power absorptions of the ion from the rf electric field. The power absorption expression is used to derive the line-shape expresssions of the longitudinal ion cyclotron resonance.

Ion cyclotron single- and multiple-resonances have been used extensively in recent years to study a wide field of gas-phase chemistry. The reviews[1] describe the use of ion cyclotron resonance (ICR) in the determination of reaction mechanisms, reaction rates, ion structures, relative acidities and basicities, photodetachment processes, the detection of excited states, thermochemistry, and other properties of ions. Recently, the technique of Fourier transform ion cyclotron resonance (FT-ICR) was developed by Comisarow and Marshall,[2] it improves the ICR spectral resolution by orders of magnitude. By combining the high resolution with the inherent high sensitivity of ICR, FT-ICR makes possible new fields of diamagnetic resonance spectroscopy, such as mass spectrometry with regard to organic chemistry, biology, and medicine.

The principle of ICR is based phenomenologically on the classical motion of charged particles in the magnetic and electric fields. An ion moving in a homogeneous magnetic field describes a helical path which is a combination of a translation along the field line and a circular motion in a plane perpendicular to the direction of the magnetic field. The angular frequency or cyclotron frequency, ω, of the circular motion is given by $\omega = eH/mc$, where e/m is the charge-to-mass ratio; H, the magnetic field strength, and c, the speed of light. If an rf electric field with the frequency of ω_1 is applied perpendicular to the magnetic field, and the magnetic field or the rf frequency is swept, the ion resonates at $\omega = \omega_1$ and absorbs energy from the rf electric field; then the ions of a particular e/m ratio are accelerated and the radius of its orbit increases with the time.

ICR is of two types, longitudinal ICR and transverse ICR. In the case of transverse ICR,[1] the guiding center of the circular motion of the ion is migrated at right angles to both the magnetic and electric fields with a uniform drift velocity of v_d. In the other case of longitudinal ICR,[3] the guiding center of the circular motion of the ion is migrated along the magnetic line of force with a uniform traveling velocity of v_z.

In an application of FT-ICR to a wide mass range, a more intence magnetic field than that of the electromagnet used widely is required. Super conducting magnet (SCM)[4] satisfies the requirement mentioned above, and longitudinal ICR is suitable for FT-ICR using SCM.

In this paper, we will propose a potential equation for the longitudinal ICR cell and an exact solution of the equation of the motion of the ion used for driving the power absorption of an ion.

Result and Discussion

RF Electric Field in the ICR Cell. In order to treat the problem, we consider the rf electric field in a vacuum produced by circular concave electrodes arranged cylindrically as is shown in Fig. 1. Let us assume that the frequency of the rf electric field is sufficiently low enough for the displacement current to be neglected, and let us also ignor the axial component of the electric field in the ICR cell. The problem can be reduced to that of solving Laplace's equation:

$$\Delta V = 0, \tag{1}$$

under given conditions, where V is a scalar electric potential. Electric field, $\mathbf{E}$, can be obtained from the potential, V, by using this relation:

$$\mathbf{E} = -grad\ V. \tag{2}$$

Equation (1) is expressed in cylindrical coordinates (r, θ) as:

$$\frac{1}{r}\cdot\frac{\partial}{\partial r}\left(r\frac{\partial V}{\partial r}\right) + \frac{1\partial^2 V}{r^2\partial\theta^2} = 0. \tag{3}$$

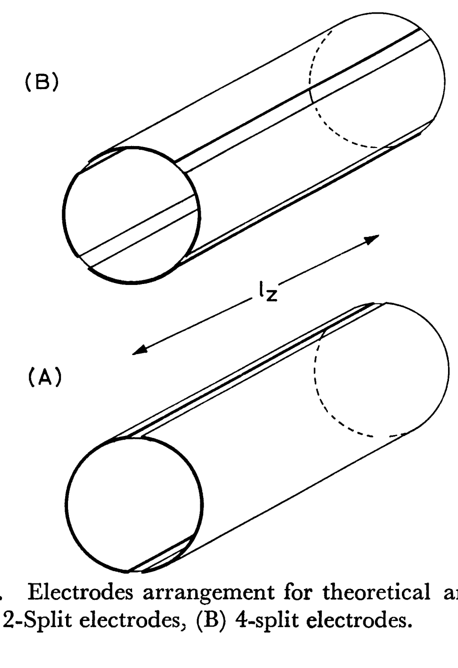

Fig. 1. Electrodes arrangement for theoretical analysis. (A) 2-Split electrodes, (B) 4-split electrodes.

After some analytical treatment, we solve Eq. (3), the result is given by Eq. (A4) (see Appendix). By substituting Eq. (A4) into Eq. (2), we then obtain the expressions of the rf electric field in the case of 2-split electrodes as follows:

$$\mathbf{E}(r)_2 = \left\{-\frac{2(V_1-V_2)}{\pi}\sum_{k=1}^{k=\infty}\frac{(-1)^{k-1}}{r}\left(\frac{r}{R}\right)^{2k-1} \times \cos(2k-1)\theta\right\}\sin(\omega_1 t+\phi_1) \tag{4a}$$

$$\mathbf{E}(\theta)_2 = \left\{\frac{2(V_1-V_2)}{\pi}\sum_{k=1}^{k=\infty}\frac{(-1)^{k-1}}{r}\left(\frac{r}{R}\right)^{2k-1} \times \sin(2k-1)\theta\right\}\sin(\omega_1 t+\phi_1), \tag{4b}$$

where V_1 and V_2 are the electric potentials applied to electrodes, and R, the radius of the cylinder indicated in Fig. 1.

Solution of the Equation of Motion. In absence of reactive collisions, the motion of an ion in the ICR cell can be described as follows:

$$\frac{d\mathbf{v}}{dt} = \frac{e}{m}\mathbf{E}(t) + \frac{e}{mc}\mathbf{v}\times\mathbf{H} - \xi\mathbf{v}, \tag{5}$$

where ξ is the reduced collision frequency that specifies the rate of the momentum relaxation of the ion.[5a)]

The Cartesian coordinates system is chosen so that the static magnetic field, H, is parallel to the z axis and the rf electric field is perpendicular to the z axis. Therefore, the expressions of the rf electric field in the cylindrical coordinates are transformed to those of the Cartesian coordinates.[6)] Equation (4) is transformed as follows:

$$\mathbf{E}(\mathrm{x})_2 = \left\{-\frac{2(V_1-V_2)}{\pi R}\left[1-\frac{x^2-y^2}{R^2} + \frac{x^4-6x^2y^2+y^4}{R^4} - \cdots\right]\right\}\sin(\omega_1 t+\phi_1), \tag{6a}$$

$$\mathbf{E}(\mathrm{y})_2 = \left\{-\frac{2(V_1-V_2)}{\pi R}\left[\frac{2xy}{R^2} - \frac{4x^3y-4xy^3}{R^4} + \frac{6x^5y-20x^3y^3+6xy^5}{R^6} - \cdots\right]\right\}\sin(\omega_1 t+\phi_1). \tag{6b}$$

Equation (5) is now separated into an equation of $\mathbf{v}_z$ only and two coupled equations of $\mathbf{v}_x$ and $\mathbf{v}_y$. The relevant equations of motion are, then:

$$\frac{d\mathbf{v}_x}{dt} = \frac{e}{m}\mathbf{E}_x\sin(\omega_1 t+\phi_1) + \omega\mathbf{v}_y - \xi\mathbf{v}_x, \tag{7a}$$

$$\frac{d\mathbf{v}_y}{dt} = \frac{e}{m}\mathbf{E}_y\sin(\omega_1 t+\phi_1) - \omega\mathbf{v}_x - \xi\mathbf{v}_y, \tag{7b}$$

where $\mathbf{E}_x$ or $\mathbf{E}_y$ only denotes the expression in the brace of Eq. (6).

An ion whose initial velocity, $\mathbf{v}_0$, is due to the thermal velocity leads to a circular motion with the phase angle of ϕ_0; then, $\mathbf{v}_x(0) = -\mathbf{v}_0\sin\phi_0$ and $\mathbf{v}_y(0) = \mathbf{v}_0\cos\phi_0$ at $t=0$. The exact solution of Eq. (7) is given by:

$$\mathbf{v}_x = \mathbf{v}_0\sin(\omega t-\phi_0)\exp(-\xi t) + \frac{e}{m}(\alpha\mathbf{E}_x - \beta\mathbf{E}_y), \tag{8a}$$

$$\mathbf{v}_y = \mathbf{v}_0\cos(\omega t-\phi_0)\exp(-\xi t) + \frac{e}{m}(\beta\mathbf{E}_x + \alpha\mathbf{E}_y), \tag{8b}$$

where;

$$\begin{aligned}\alpha = {} & A\sin(\omega_1 t+\phi_1) - B\cos(\omega_1 t+\phi_1) \\ & - [(A\cos\omega t + D\sin\omega t)\sin\phi_1 \\ & - (B\cos\omega t - C\sin\omega t)\cos\phi_1]\exp(-\xi t), \\ \beta = {} & D\sin(\omega_1 t+\phi_1) + C\cos(\omega_1 t+\phi_1) \\ & + [(A\sin\omega t - D\cos\omega t)\sin\phi_1 \\ & - (B\sin\omega t + C\cos\omega t)\cos\phi_1]\exp(-\xi t),\end{aligned}$$

A, B, C, and D are given in the Appendix.

Line-shape Expression for Nonreactive Ion. *a) Power Absorption of an Average Nonreactive Ion*: The power absorption, A, of an ion from the rf electric field is given by:

$$A = \langle e\mathbf{E}(t)\cdot(\mathbf{v}_x+\mathbf{v}_y)\rangle. \tag{9}$$

The initial velocity of an ion with the phase angle of ϕ_0 will not contribute to the actual power absorption. Substituting Eq. (8) into Eq. (9), the power absorption can be obtained by averaging over the ϕ_1 phase angle, since all the values of ϕ_1 are equally probable. With the approximation that:

$$\omega_1 + \omega \approx 2\omega, \qquad \xi \ll \omega_1, \tag{10}$$

the instantaneous power absorption of an average ion is found to be:

$$A(\omega_1 \neq \omega) = \frac{e^2(\mathbf{E}_x{}^2+\mathbf{E}_y{}^2)}{4m[(\omega_1-\omega)^2+\xi^2]}\{\xi + [(\omega_1-\omega)\sin(\omega_1-\omega)t - \xi\cos(\omega_1-\omega)t]\exp(-\xi t)\}. \tag{11}$$

b) Total Power Absorption for Nonreactive Ion: Ions are produced in a source region with electron impact at a rate of n_0 ions per second; then they move towards the ion collector through an analyzer region at a constant traveling velocity. It has been assumed that the length of the analyzer region is considerably longer than the diameter of the ICR cell and that the distribution of ions is uniform inside the ICR cell. There are a constant number, $n_0\tau$, of ions in the time τ for an ion move through the analyzer, each absorbing energy at the rate given in Eq. (11). Thus, the total power absorption $A(T)$, is obtained by averaging the integration from 0 to τ, the time required for the ions to absorb energy from the applied rf electric field. The averaged total power absorption is given by:

$$\begin{aligned}A(T, \omega_1 \neq \omega) &= \frac{1}{\tau}\int_0^\tau n_0\tau A(\omega_1 \neq \omega)d\tau \\ &= \frac{n_0 e^2(\mathbf{E}_x{}^2+\mathbf{E}_y{}^2)}{4m[(\omega_1-\omega)^2+\xi^2]}\Big\langle \xi\tau + \frac{(\omega_1-\omega)^2-\xi^2}{(\omega_1+\omega)^2+\xi^2} \\ &\quad - \left\{\frac{[(\omega_1-\omega)^2-\xi^2]\cos(\omega_1-\omega)\tau + 2\xi(\omega_1-\omega)\sin(\omega_1-\omega)\tau}{(\omega_1-\omega)^2+\xi^2}\right\} \\ &\quad \times\exp(-\xi\tau)\Big\rangle,\end{aligned} \tag{12a}$$

and:

$$A(T, \omega_1 = \omega) = \frac{n_0 e^2(\mathbf{E}_x{}^2+\mathbf{E}_y{}^2)}{4m\xi^2}\left\{1 - \frac{1}{\xi\tau}[1-\exp(-\xi\tau)]\right\}. \tag{12b}$$

If the pressure is sufficiently high for each ion to undergo many nonreactive collisions, Eq. (12a) is reduced to:

$$A(T,\text{ high-pressure}) = \frac{n_0e^2(\mathbf{E}_x^2+\mathbf{E}_y^2)\tau}{4m}\frac{\xi}{(\omega_1-\omega)^2+\xi^2} \quad (13)$$

by the application of the $\xi t \gg 1$ approximation. This high-pressure power absorption represents the Lorentzian line shape. In the collisionless limit, $\xi \to 0$, Eq. (12a) is reduced to:

$$A(T,\text{ low-pressure}) = \frac{n_0e^2(\mathbf{E}_x^2+\mathbf{E}_y^2)}{4m(\omega_1-\omega)^2}[1-\cos(\omega_1-\omega)\tau]. \quad (14)$$

The line shapes of the total power absorption of longitudinal ICR for the ensemble of ions are represented by Eqs. (12)—(14).

Furthermore, the total power absorption and the line-shape expressions for such reactive ions as the primary, secondary, and tertiary ions are formularized theoretically; results similar to those reported previously[5b] have been obtained. A detailed discussion of the longitudinal ICR power absorption for the reactive ions will be published in the near future.

Appendix

a) Solution of Eq. (3).

To solve Eq. (3), we shall assume V in the following form:

$$V(r,\theta) = R(r)G(\theta)\sin(\omega_1 t+\phi_1). \quad (A1)$$

By substituting (A1) into Eq. (3) and by solving the resultant differential equations, we get the general solution of Eq. (3):[7]

$$V(r,\theta) = \sum_{n=0}^{n=\infty}[(r^n(A_n\cos n\theta+B_n\sin n\theta) + r^{-n}(C_n\cos n\theta+D_n\sin n\theta)]\sin(\omega_1 t+\phi_1), \quad (A2)$$

where A_n, B_n, C_n, and D_n are constants which should be determined from the boundary conditions. If we impose these boundary conditions:

$$\mathbf{E} \neq \infty \quad \text{for } r=0$$
$$V(\theta) = V(-\theta) \quad \text{for } -\pi<\theta<\pi$$

on Eq. (A2), V becomes:

$$V(r,\theta) = \left[a_0+\sum_{n=1}^{n=\infty}\left(\frac{r}{R}\right)^n a_n\cos n\theta\right]\sin(\omega_1 t+\phi_1), \quad (A3)$$

where R is the radius of the cylinder. The potential distribution on the circle at $r=R$ can be expressed by periodic even function of θ as is shown in Fig. 2. Therefore, we can express V by means of a Fourier series. After some algebra, we obtain:

$$a_0 = (V_1+V_2)/2,$$

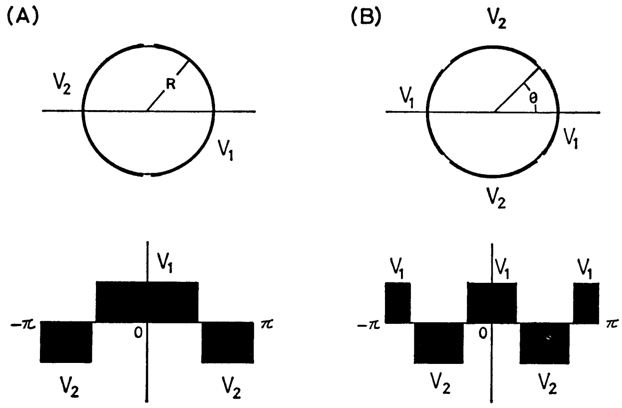

Fig. 2. Potential distribution on circle at $r=R$ of the electrodes (A) and (B), respectively.

$$a_n = [2(V_1-V_2)/n\pi]\sin(n\pi/2)$$

in the case of 2-split electrodes.

When $k=1, 2, 3, \cdots\cdots$, a_n becomes:

$$a_{2k} = 0 \qquad \text{for } n=2k$$
$$a_{2k-1} = 2(V_1-V_2)(-1)^{k-1}/\pi(2k-1) \quad \text{for } n=2k-1.$$

Thus, we finally obtain:

$$V(r,\theta)_2 = \left\{\frac{V_1+V_2}{2}+\frac{2(V_1-V_2)}{\pi}\sum_{k=1}^{k=\infty}\frac{(-1)^{k-1}}{2k-1}\left(\frac{r}{R}\right)^{2k-1}\times\cos(2k-1)\theta\right\}\sin(\omega_1 t+\phi_1) \quad \text{for 2 splits.} \quad (A4)$$

In a similar way, Eq. (A4) can be generalized to the potential equation for $2m$-split electrodes as follows:

$$V(r,\theta)_{2m} = \left\{\frac{V_1+V_2}{2}+\frac{2(V_1-V_2)}{\pi}\sum_{k=1}^{k=\infty}\frac{(-1)^{k-1}}{2k-1}\left(\frac{r}{R}\right)^{m(2k-1)}\times\cos[m(2k-1)\theta]\right\}\sin(\omega_1 t+\phi_1) \quad \text{for } 2m \text{ splits,} \quad (A5)$$

where $m=1, 2, 3, \cdots\cdots$.

By substituting Eq. (A5) into Eq. (2), we obtain this expression of the rf electric field for $2m$-split electrodes:

$$\mathbf{E}(r)_{2m} = \left\{-\frac{2(V_1-V_2)}{\pi}\sum_{k=1}^{k=\infty}\frac{m(-1)^{k-1}}{r}\left(\frac{r}{R}\right)^{m(2k-1)}\times\cos[m(2k-1)\theta]\right\}\sin(\omega_1 t+\phi_1), \quad (A6a)$$

$$\mathbf{E}(\theta)_{2m} = \left\{\frac{2(V_1-V_2)}{\pi}\sum_{k=1}^{k=\infty}\frac{m(-1)^{k-1}}{r}\left(\frac{r}{R}\right)^{m(2k-1)}\times\sin[m(2k-1)\theta]\right\}\sin(\omega_1 t+\phi_1) \quad \text{for } 2m \text{ splits.} \quad (A6b)$$

b) List of Notations Used in the Text.

$$A = [\xi(\xi^2+\omega_1^2-\omega^2)+2\xi\omega^2]/F,$$
$$B = \omega_1(\xi^2+\omega_1^2-\omega^2)/F,$$
$$C = 2\xi\omega\omega_1/F,$$
$$D = [\omega(\xi^2+\omega_1^2-\omega^2)-2\xi^2\omega]/F,$$
$$F = [(\omega_1-\omega)^2+\xi^2][(\omega_1+\omega)^2+\xi^2].$$

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6) The exact solution of Eq. (5), at present, can not be obtained analytically in the cylindrical coordinates.

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