Study of the Quasi-peaks in the Ion Cyclotron Double Resonance

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Quasi-peaks which do not correspond to any reactant ion in the ion-molecule reaction were observed in the ion cyclotron double-resonance spectrum. The field-sweep quasi-ICDR spectrum was also observed. Expressions giving the frequencies of the quasi-peaks observed in the ion cyclotron double-resonance spectrum were obtained; the results agreed with those obtained previously. Both the ion mass and ion drift-voltage dependences of the quasi-peaks were shown. A close agreement between the calculated and measured values was obtained. A method to repress the quasi-peaks is discussed.

It has been demonstrated that ion cyclotron double-resonance (ICDR) spectroscopy is useful in elucidating the mechanism of ion-molecule reactions.[2)] In an ion-molecule reaction, $R^+ + M \longrightarrow P^+ + N$, R^+ is the reactant ion, P^+, the product ion, and M and N, the reactant molecule and the neutral product. The signal from the product ion can be continuously monitored while an irradiating rf field is swept through the range of cyclotron frequencies. When the irradiating frequency matches the cyclotron frequency of the reactant ion, the energy from the irradiating rf field is absorbed by the reactant ion and the translational energy of reactant ion is increased. Since most reaction-rate constants are dependent on the ion velocity, the concentration of the product ion will change, and this change is presented as a peak in the ICDR spectrum. If the product ion is observed at its cyclotron frequency of f_1 while the irradiating frequency, f_2, is swept, the signals will be observed for values of f_2 corresponding to the cyclotron-resonance frequencies of the reactant ions which yield the product ion. At a low irradiating-field strength, a change in the monitored ion intensity reflects a change in the reaction rate constant as the kinetic energy of reactant ion is increased.[3)] At a high irradiating-field strength, however, intense peaks which do not correspond to any reactant ion are observed in the ICDR spectrum. These quasi-peaks accompanying a negative response are recorded symmetrically about the irradiating frequency of $f_2=f_1$. These peaks have been recognized as spurious peaks by Freiser, McMahon, and Beauchamp.[4)] However, it is important to recognize the detailed nature of these quasi-peaks in order to avoid an erroneous interpretation of the ICDR spectrum.

The motion of an ion which moves under the simultaneous application of the magnetic and electric fields appropriate for an ICR cell has been described in detail.[5)] The electrostatic trapping field of the same polarity as the ions under investigation is used to prevent ion loss in the direction parallel to the magnetic field. The ions execute an oscillatory motion in the trapping field. The frequency, f_t, of this oscillatory motion is given by[6,7)]

$$f_t = \frac{1}{2\pi}\left[\frac{8e}{m(d_x^2+d_z^2)}\left(V_t - \frac{V_{ud}+V_{ld}}{2}\right)\right]^{1/2}, \qquad (1)$$

where e/m is the charge-to-mass ratio of an ion, d_x, the spacing between the drift plates, d_z, the spacing between the trapping plates, V_t, the trapping voltage, and V_{ud} and V_{ld}, the drift voltages applied to the upper- and lower-drift plate respectively. The quasi-peaks discussed herein were observed using a square-type cell ($d_x=d_z$); the cell has been described in detail previously.[2d)]

In the present paper, we wish to report the features of the quasi-peaks, especially the drift-voltage dependence of their resonant frequencies for the quasi-peaks, and present a method to suppress them.

Experimental

The quasi-ICDR spectra recorded with a JEOL JIC-3B spectrometer have been described in detail.[7)] The ICR cell was of a three-section square type (2.5 × 2.5 × 14 cm) similar to the conventional one.[2a)] Single-resonance spectra of krypton and *t*-butyl alcohol were obtained by fixing the marginal oscillator frequency of 100.00 kHz, while that of 2-methylpropene was obtained by means of a Twin-T bridge detector with the oscillator frequency fixed of 99.986 kHz and sweeping the magnetic field using a field-modulation phase-sensitive detection scheme. The double-resonance experiments were carried out in the pulsed-modulation mode while sweeping the frequency of the irradiating oscillator. The field-sweep quasi-ICDR spectra of 2-methylpropene were obtained by fixing the observing and irradiating frequencies at 99.986 and 118.00 kHz respectively, using a pulsed-modulation mode of the irradiating field. The other experimental conditions were as follows: energy of ionizing electron, 70 eV; modulation frequency, 80 Hz; trapping voltage, +0.25 V; upper analyzer-drift voltage, 0 V, and lower analyzer-drift voltages in the −1.2—0 V range.

Results and Discussion

a) Frequency-sweep Quasi-ICDR Spectra. The quasi-ICDR spectrum of the *m/e* 84 ion of krypton at 2×10^{-5} Torr is shown in Fig. 1. Irradiation at $f_2=120.9$ and 79.6 kHz resulted in a decrease in the intensity of the peak due to the ion with *m/e* 84. The peaks observed with the frequencies of 120.9 and 79.6 kHz correspond to the *m/e* 69.5 and 105.5 ions which were not present in the single-resonance spectrum of krypton. Therefore, these peaks are not the actual double-resonance peaks. The spectrum exhibits the quasi-peaks symmetric about the frequency of the irradiating rf field of $f_2=f_1$.

Figure 2 shows the quasi-icdr spectrum of $(CH_3)_2$-COH^+ (*m/e* 59) of *t*-butyl alcohol obtained at 2.2×10^{-5} Torr. Irradiation at $f_2=124.6$ and 76.0 kHz caused a decrease in the intensity of the peak due to the ion with *m/e* 59. The spectrum indicates the quasi-peaks at the distances of f_1+2f_t and f_1-2f_t respectively from

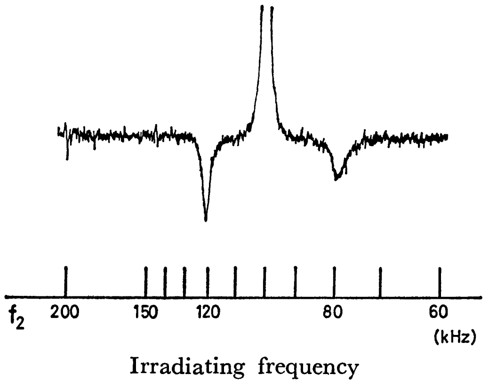

Fig. 1. Frequency-sweep quasi-ICDR spectrum of the *m/e* 84 ion of krypton with the pressure of 2×10^{-5} Torr, the observing rf field of 0.04 V/cm, the irradiating rf field of 0.32 V/cm, the trapping voltage of +0.25 V, and the upper and lower analyzer-drift voltages of 0 and −0.55 V. The large spike appearing at the 100 kHz frequency results from the interaction of the irradiating and observing oscillators, while the small spike at the 200 kHz frequency is due to the irradiating oscillator exciting the first sub-harmonic of the observing frequency.

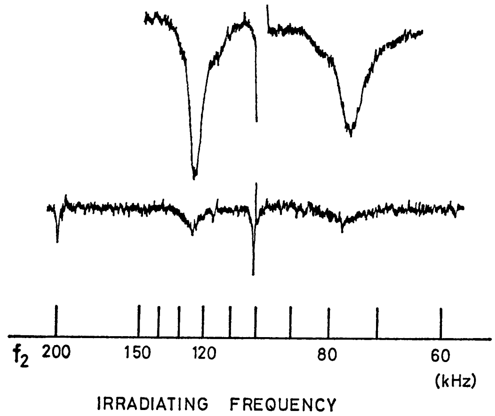

Fig. 2. Frequency-sweep quasi-ICDR spectrum of the $(CH_3)_2COH^+$ (*m/e* 59) of *t*-butyl alcohol with the pressure of 2.2×10^{-5} Torr; the other conditions are identical with those under which Fig. 1 was recorded. The sharp spike appearing at the 100 kHz frequency results from the interaction of the irradiating and observing oscillators, while the small feature at the 200 kHz frequency is due to the irradiating oscillator exciting the first overtone of the marginal oscillator.

the frequency of $f_2 = f_1$. The peak observed with the frequency of 124.6 kHz corresponds to the *m/e* 47.3 ion, which was not present in the single-resonance spectrum of *t*-butyl alcohol. The *m/e* 59 ion derived from electron-impact ionization of *t*-butyl alcohol is an α-cleavage product that is, a primary ion.[8] Therefore, these peaks observed with the frequencies of 76.0 and 124.6 kHz corresponding to the *m/e* 47.3 and 77.6 ions are not the actual double-resonance peaks.

When ICDR studies were made of 2-methylpropene, the following results were obtained. In the case of $C_3H_5^+$ (*m/e* 41), irradiation at $f_2 = 123.7$ and 75.4 kHz resulted in a decrease in the intensity of the peak due to the $C_3H_5^+$, as is shown in Fig. 3a. Irradiation at $f_2 = 121.3$ and 79.6 kHz give rise to a decrease in the intensity of the peak due to the $C_4H_7^+$ (*m/e* 55), as is shown in Fig. 3c. In another case, that of $C_4H_8^+$ (*m/e* 56), the intensity of the peak due to the $C_4H_8^+$ is decreased by the irradiation at $f_2 = 121.1$ and 79.2 kHz, as is shown in Fig. 3d. The peaks observed with the frequencies of 123.7 and 75.4 kHz; 121.3, and 121.1 kHz correspond to the *m/e* 33.1 and 54.4; *m/e* 45.3, and 46.2 ions respectively, but these ions were absent from the single-resonance spectra. The quasi-peaks appearing at the frequencies of 79.6 and 79.2 kHz corresponding to the *m/e* 69.1 and 70.7 ions are not associated with any resonable ion-molecule reaction. Therefore, these peaks observed in the double-resonance spectra are also false peaks.

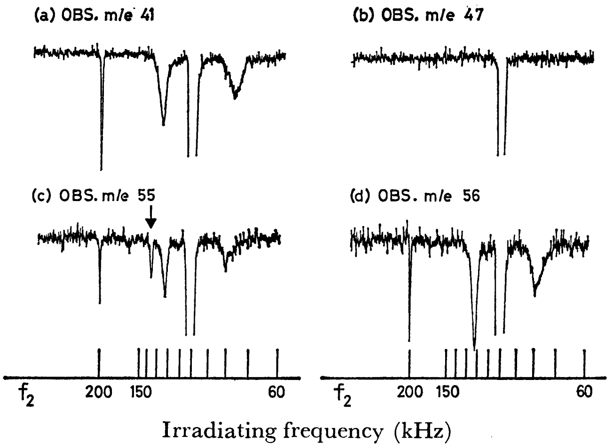

Fig. 3. (a) Frequency-sweep quasi-ICDR spectrum of the $C_3H_5^+$ (*m/e* 41) of 2-methylpropene with the pressure of 3×10^{-5} Torr, the observing rf field of 0.02 V/cm, the irradiating rf field of 0.24 V/cm, the trapping voltage of +0.25 V, and the upper and lower analyzer-drift voltages of 0 and −0.3 V. (b) Frequency-sweep quasi-ICDR spectrum of the *m/e* 47 ion of 2-methylpropene with the conditions are identical with those under which (a) was recorded. The ion corresponding to *m/e* 47 is absent from the single-resonance spectrum of 2-methylpropene; therefore, the quasi-peaks are not observed either. (c) Frequency-sweep quasi-ICDR spectrum of the $C_4H_7^+$ (*m/e* 55) of 2-methylpropene with the conditions are identical with those under which (a) was recorded. The peak at 134.6 kHz (indicated by an arrow) is the actual double-resonance peak corresponding to the reaction producing *m/e* 55. (d) Frequency-sweep quasi-ICDR spectrum of the $C_4H_8^+$ (*m/e* 56) of 2-methylpropene with the conditions are identical with those under which (a) was recorded. In this figure, the large spikes appearing at the 100 kHz frequency result from the interaction of the irradiating and observing oscillators, while the sharp spikes appearing at the 200 kHz frequency are due to the irradiating oscillator exciting the first sub-harmonics of the observing frequency.

b) Frequencies of Occurrence of the Quasi-peaks.

From the experimental results described above, it follows that the quasi-peaks occur when the difference between the observing and irradiating frequencies is equal to $2f_t$, *i.e.*; $|f_1 - f_2| = 2f_t$, where f_t is given by

Eq. 1. This result agrees with that of Freiser *et al.*4)

In the ICR spectrometers,2a–d) naked electric wires are usually employed as the rf feeders in the vacuum chamber of the icr detector, because the coaxial cable used in a ultra high-vacuum is absent. Similarly, a naked wire is also employed to feed the electrostatic trapping voltage to the icr cell. As a result of the use of the naked wires, the observing and irradiating rf voltages are picked up by the wire for trapping voltage. In the ICR cell, thus, leakage of the rf field results from the rf voltages superimposed on the trapping voltage. Therefore, the generation of quasi-peaks is considered to be caused by the ejection of the ion from the trapping field by the leakage of the rf field. That is, when the observing frequency is fixed and the irradiating frequency is swept, the oscillatory motion of an ion increases in its amplitude in the trapping field at $|f_1-f_2|=2f_t$. Then, the ion is neutralized when it strikes the trapping plate, and the ion is ejected from the trapping field. Therefore, the quasi-peaks are observed with the frequencies of the irradiating rf field which are given by

$$f_2 \doteq f_1 \pm 2f_t, \tag{2}$$

and the frequency-sweep quasi-ICDR spectrum is recorded as the quasi-peaks accompanying the negative response. Equation 2 has been reported in a slightly different form.4) Using as practical units V_t, V_{ud}, and V_{1d} in volts, M in atomic mass unit, and f_1, f_2, and f_t in Hz, the frequencies, f_{2q}, of the occurrence of the quasi-peaks observed are given by

$$f_{2q} = f_1 \pm 246\left[\frac{V_t-(V_{ud}+V_{1d})/2}{M}\right]^{1/2} \text{ kHz.} \tag{3}$$

The frequencies of the occurrence of all the quasi-peaks described in the preceding item are calculated from Eq. 3; they are listed in Table 1. The calculated results agree well with the experimental values.

As predicted by Eq. 3, the frequencies of the occurrence of the quasi-peaks vary with the square root of the ion mass or the difference between the trapping voltage and half of the drift voltage. On the other hand, the frequency of the irradiating rf field of the actual double-resonance peak is independent of the trapping and drift voltage. The variation in the frequency of occurrence of the quasi-peak observed in 2-methylpropene with the square root of the ion mass is shown in Fig. 4. Under these conditions the trapping and drift voltages remain constant; the observation of several ionic species confirms the inverse linear variation in the frequency of the occurrence of the quasi-peaks with the square root of the ion mass, as predicted by Eq. 3. Moreover, the variation in the frequency of the occurrence of the quasi-peak of $C_4H_7^+$ (*m*/*e* 55) in 2-methylpropene with

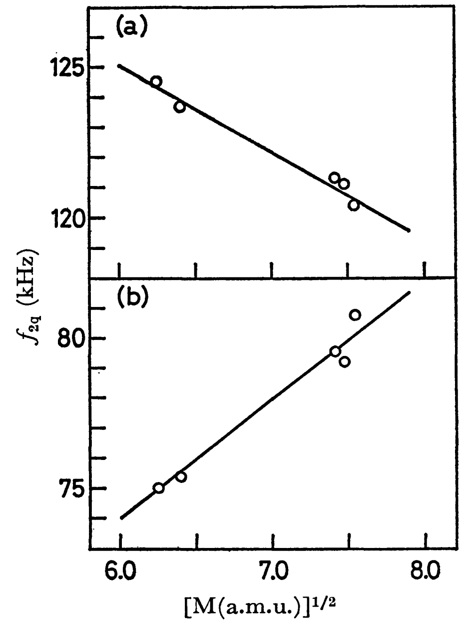

Fig. 4. Linear variation in the frequency of occurrence with the square root of the ion mass for 2-methylpropene. (a) $f_{2q}>f_1$, (b) $f_{2q}<f_1$.

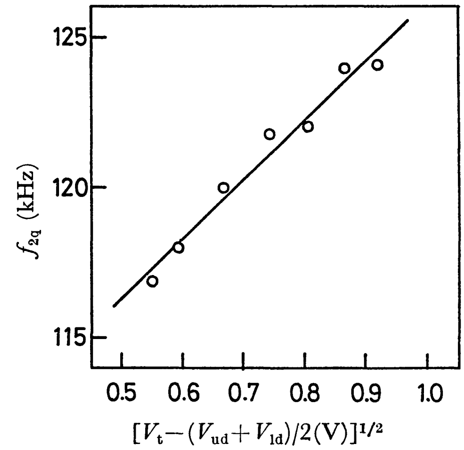

Fig. 5. Linear shift in the frequency of occurrence with the square root of the difference between the trapping voltage and half of the analyzer-drift voltage for $C_4H_7^+$. The trapping voltage is fixed at +0.25 V.

TABLE 1. OBSERVED AND CALCULATED FREQUENCIES FOR SOME IONIC SPECIES

Compound	Observed ion *m*/*e*	Observed ion Species	Frequencies of occurrence (kHz) Obsd		Calcd	
Krypton	84		120.9	79.6	119.45	80.55
t-Butyl alcohol	59	$(CH_3)_2COH^+$	124.6	76.0	123.21	76.80
2-Methylpropene	39	$C_3H_3^+$	124.5	≈75	124.89	75.07
	41	$C_3H_5^+$	123.7	75.4	124.28	75.69
	55	$C_4H_7^+$	121.3	79.6	120.96	79.01
	56	$C_4H_8^+$	121.1	79.2	120.78	79.20
	57	$C_4H_9^+$	120.4	80.8	120.59	79.38

the square root of the difference between the trapping voltage and half of the drift voltage is illustrated in Fig. 5. When the trapping voltage is fixed, the observation of the quasi-peaks at several drift voltages confirms the linear variation in the frequency of the occurrence of the quasi-peak with the square root of the difference between the trapping voltage and half of the drift voltage.

Compared with the quasi-peaks, the most remarkable feature of the actual double-resonance peak is the constancy of the frequency of the irradiating rf field. The frequencies of the irradiating rf field at which the actual double-resonance peak corresponding to the ion-molecule reaction,

$$C_3H_5^+ + C_4H_8 \longrightarrow C_4H_7^+ + C_3H_6,$$

is observed at several drift voltages, are independent of the drift voltage, as Table 2 shows.

Table 2. Observed and calculated frequencies as functions of the analyzer-drift voltage for the $C_4H_7^+$ of 2-methylpropene

Analyzer-drift voltages (V)		Frequencies of occurrence (kHz)		Irradiating frequencies(kHz) Obsd in $C_4H_7^+$—$[C_3H_5^+]$[a)]
Upper	Lower	Obsd	Calcd	
0	−1.2	≈124	124.59	b)
0	−1.0	124.0	123.44	134.30
0	−0.8	122.0	122.24	134.87
0	−0.6	121.85	120.96	134.60
0	−0.4	120.10	119.61	134.60
0	−0.2	118.0	118.15	135.0
0	−0.1	116.9	117.38	134.4
0	−0.0	b)	116.57	b)

a) $C_4H_7^+$—$[C_3H_5^+]$ indicated that $C_4H_7^+$ is observed when $C_3H_5^+$ is irradiated.

b) Too weak for the frequency to be determined.

c) Field-sweep Quasi-ICDR Spectrum. If the magnetic field, H, is swept, while the observing and irradiating frequencies described in Eq. 3 are fixed and the trapping and drift voltages are held constant, an oscillatory ion in the trapping field is translationally excited at the field of $H=aM$ (a is the costant); then, the field-sweep quasi-ICDR spectrum is obtained. Figure 6 shows the field-sweep quasi-ICDR spectra of 2-methylpropene obtained by sweeping the magnetic field with $f_2/f_1=118.00/99.986$. The spectrum exhibits the quasi-peaks of each ion which is observed in the single-resonance spectrum, but the relative intensity ratio of the quasi-peaks is not proportional to the ionic concentrations of each ion, because the exact f_2/f_1 ratios are not satisfied for any of them except for the m/e 55 ion. The quasi-peaks intensities decrease with a decrease in the strength of the irradiating rf field. This behavior of the quasi-peak intensity indicates that the generation of quasi-peaks can be minimized by the reduction of the leakage of the rf field. By using the shielded feeders, the quasi-peak intensity decreased by approximately 80 db compared with the previous result. This experimental result reveals that the generation of quasi-peaks is due to the ejection of the ion from the trapping field by the leakage of the rf field.

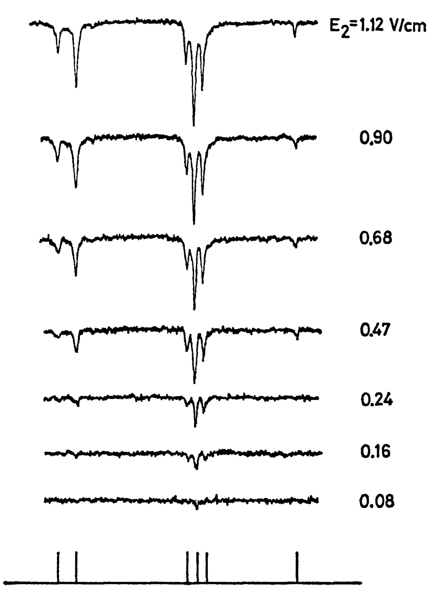

Fig. 6. Field-sweep quasi-ICDR spectra of 2-methylpropene at various irradiating field strengths. f_2/f_1 is fixed in the ratio of 118.00/99.986. The pressure is 3×10^{-5} Torr; trapping voltage, +0.25 V; upper and lower analyzer-drift voltages, 0 and −0.2 V.

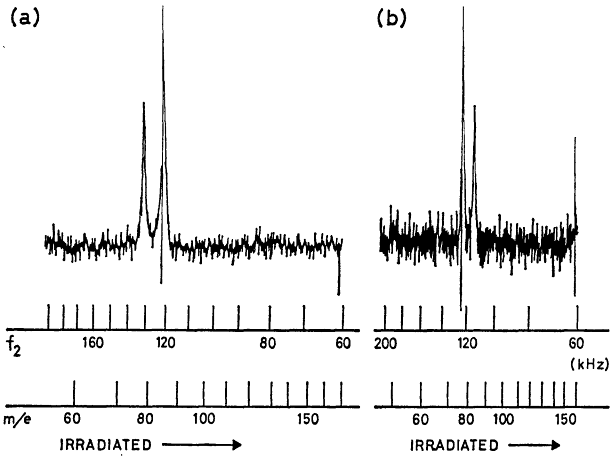

Fig. 7. (a) Double-resonance spectrum of $C_6D_6^+$ in a 1: 1 mixture of benzene and benzene-d_6 with the pressure of 2×10^{-5} Torr, the observing rf field of 0.05 V/cm, the irradiating rf field of 0.24 V/cm, the trapping voltage of +0.25 V, and the upper and lower analyzer-drift voltages of 0 and −0.4 V. (b) Double-resonance spectrum of $C_6H_6^+$ in a 1: 1 mixture of benzene and benzene-d_6 with the conditions are identical with those under which (a) was recorded. In this figure, the large spikes appearing at the 122.8 kHz frequency result from the interaction of the irradiating and observing oscillators, while the sharp spikes at the 61.4 kHz frequency are due to the irradiating oscillator exciting the first sub-harmonics of the observing frequency.

The double-resonance spectra of the $C_6D_6^+$ and $C_6H_6^+$ molecular ions in a mixture of benzene-d_6 and benzene (1: 1 ratio) are shown in Figs. 7a and 7b respectively.

The irradiation of $C_6H_6^+$ caused an increase in the intensity of $C_6D_6^+$, and the intensity of $C_6H_6^+$ was increased when $C_6D_6^+$ was irradiated. These double-resonance responses indicate that the charge-transfer reaction occurs between $C_6D_6^+$ and $C_6H_6^+$ as follows:

$$C_6H_6^+ + C_6D_6 \rightleftarrows [C_6H_6 \cdot C_6D_6]^+ \rightleftarrows C_6D_6^+ + C_6H_6.$$

This charge-transfer reaction corresponds to the equilibrium reaction reported by Field, Hamlet, and Libby.[9] The double-resonance spectra were obtained using a strong irradiating rf field (the strength of the irradiating field is 4.8 times as strong as that of the observing field), but the quasi-peaks are not observed in the spectra.

We may conclude from the experimental results described above that the quasi-peaks are caused by the leakage of the rf field, especially by the leakage of the strong irradiating rf field. The suppression of the leakage of the rf fields is important for eliminating the quasi-peaks and thus for the proper interpretation of the double-resonance spectra.

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