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Dynamics of ion coupling in an FTMS ion trap and resulting effects on mass spectra, including isotope ratios

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Abstract

We have studied the coupled cyclotron motions of ions at moderate to high density in the ion trap of a Fourier transform mass spectrometer. For the case of two ionic species of similar mass in the ion trap (CO^+ and N_2^+) we present image current detection results over a range of ion densities. At low ion densities the ion motions are independent, resulting in two distinct image current frequencies. At higher ion densities the ion motions are strongly coupled. In the high density limit only one of the coupled motions has the symmetry required to generate an image current. Thus, the FT mass spectrum of the CO/N_2 mixture at high density consists of only a single peak at the frequency of the image current active, coupled cyclotron motion. By analyzing the image current transients in detail we can follow the development of the collective normal modes of the ions in the trap. FTMS spectra of naphthalene ($C_{10}H_8$) as a function of ion density demonstrate that the coupled ion motions can have a substantial effect on the measurement of $^{12}C/^{13}C$ isotope ratios.

Key words: Fourier transform mass spectrometry; Ion coupling; Isotope ratios

1. Introduction

In Fourier transform mass spectrometry (FTMS), static electric and magnetic fields are used to store gaseous ions in an analyzer cell or ICR cell (Fig. 1). The ions are constrained by the magnetic field to move in circular orbits having a frequency

$$\omega = qB/m \tag{1}$$

where q is the charge of an ion, m is its mass, and B is the magnetic field strength. The circular motion of the ion is in the plane perpendicular to the magnetic field. The motion parallel to the magnetic field is constrained by a static electric field applied to the trapping plates. When the frequency of an applied (to the transmitter plates) oscillating electric field is equal to the cyclotron frequency ω, a resonance condition is established and the ions are accelerated to larger cyclotron orbits. An image current is induced in the receiver plates of the cell by the coherent cyclotron motions of the ions and is detected by a sentive preamplifier [1–3].

In FTMS the mass-to-charge ratio of an ion is calculated from its measured cyclotron frequency.

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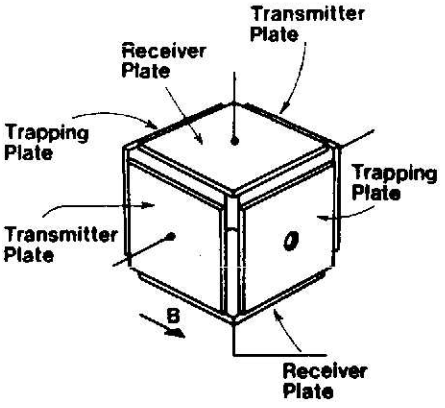

Fig. 1. Schematic of the FTMS analyzer cell.

In principle this can be done very accurately. Previously, ion space charge effects have been identified as one of the factors which needed to be considered in the mass calibration when high density ion clouds are generated in the analyzer cell. Detailed models of the dependence of the ion cyclotron frequency on ion cloud density have been described theoretically [4–8] and studied experimentally [5,6]. In those studies a single charge to mass ratio is considered. In a cubic cell the effective frequency is

$$\omega_{\text{eff}} = \omega/2[1 + (1 - 4K'/\omega^2)^{1/2}] \quad (2)$$

where $K' = 2q\alpha V/ma^2 + q^2\rho G_i/\epsilon_0 m$, a is the separation between the plates of the cell, ρ is the ion density, α is a geometric factor depending on the shape of the trap, G_i is a unitless geometric factor describing the shape of the ion cloud, and ϵ_0 is the permittivity constant and ω is given by Eq. (1) [6,9,10]. When the ion space charge and frequency shift is small compared with the cyclotron frequency, Eq. (2) can be simplified to give the following

$$\omega_{\text{eff}} = \frac{\omega - 2\alpha V/a^2 B - q\rho G_i}{\epsilon_0 B} \quad (3)$$

In Eq. (3) only the first term (ω) depends on the charge-to-mass ratio (q/m). At constant magnetic field, static electric fields, caused by the ion space charge and trapping voltages, shift all of the cyclotron frequencies slightly lower by an approximately constant amount.

In this paper we present results on the effects of high ion densities for the important case where ions

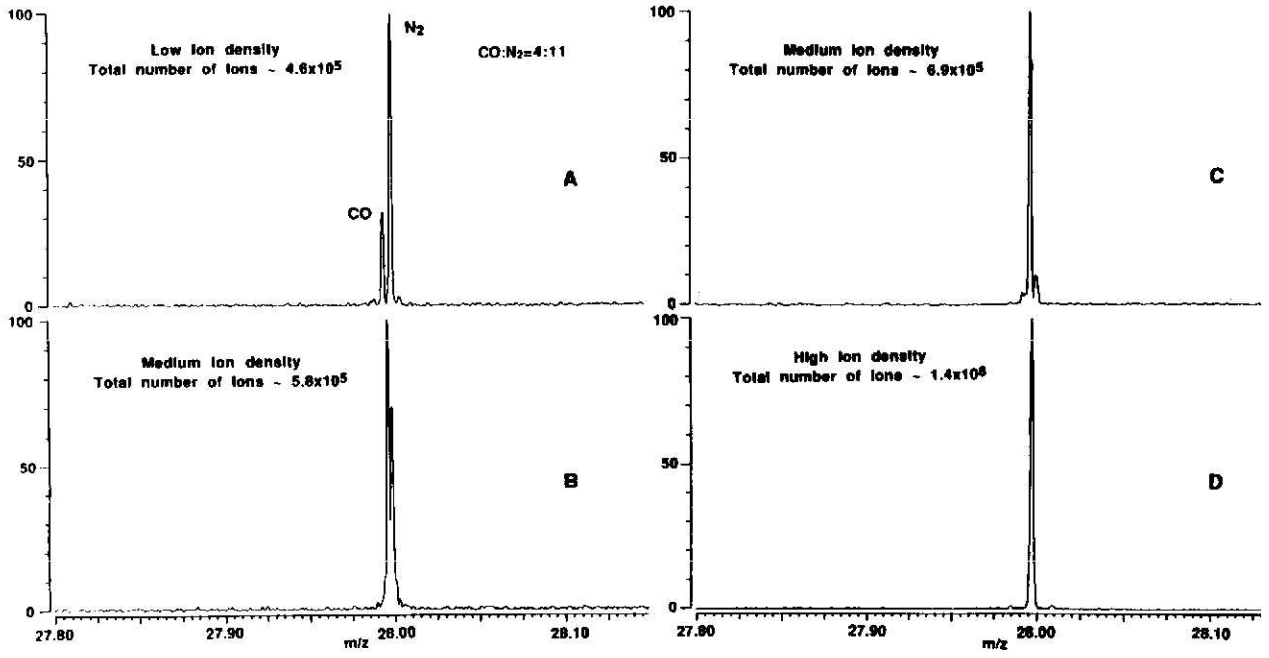

Fig. 2. Mass spectra of CO and N_2 mixture at (A) low, (B), (C) medium, and (D) high ion densities. CO : N_2 = 4 : 11 and total pressure = 1.5×10^{-8} Torr.

of different charge-to-mass ratio exist in the ion trap simultaneously. Figure 2 shows the mass spectra of a CO and N_2 mixture at constant ratio $CO : N_2 = 4 : 11$ as a function of ion density. At very low ion density the CO and N_2 peaks are well resolved and the two peak heights are consistent with the ratio of ions densities. As the ion density is increased, the intensity of the lower frequency peak decreases. At high ion density only one peak, corresponding to a coupled motion of the two ions, can be detected. The ion density dependence of the mass spectra indicates that the two motions of the ions are dramatically coupled as the ion densities increase in the analyzer cell. In a simple model, the coupling of two cyclotron motions is analogous to two coupled harmonic oscillators, such that two new combined motions are generated. In one combination motion, an image current is generated (symmetric mode) and this mode can be detected. In the other combination motion, no net image current is generated (asymmetric mode) and this mode can not be detected. As a result of the coupling, the ratio of the two mass peaks does not simply represent the ratio of the two ion densities. An understanding of these ion coupling effects is important for the quantitative use of FTMS spectra. Ignoring these effects can, for example, lead to substantial errors in isotope ratios.

Similar behavior of trapped ions in a quadrupole trap has been reported previously by Jungman et al. [11], where collective motion rather than independent motion is observed. As a result of the coupling, only one mode can be detected. The two-particle and the high-temperature ion cloud models have been used to give a reasonable explanation of collective oscillations of the stored ions for that case.

2. Experiment

The details of the analyzer cell and FTMS instrumentation have been described in many previous articles [12]. In our experiments, the FTMS analyzer cell is a 5 cm × 5 cm × 5 cm cubic cell which consists of a pair of transmitter plates and two trapping plates and two detector plates. One of the trapping plates supports an electron beam filament to generate ions by electron bombardment. The magnetic field applied was 0.7 T generated by a Varian 12 in electromagnet. The typical trapping voltage is about 1 V. Trapped ions are accelerated by r.f. chirp excitation which was delayed 220 ms for the CO/N_2 experiment and 100 ms for naphthalene experiments with respect to the electron beam pulse. Narrow band and broad band detection were used in the CO and N_2 experiment and naphthalene experiment respectively. In the case of the CO and N_2 experiment the chirp step size is 180 Hz and chirp pulse width is 0.13 ms. In the case of the naphthalene experiment the chirp step size is 200 Hz and chirp pulse width is 0.08 ms. The chirp pulse amplitudes remain unchanged for experiments with different ion densities.

The cell is located in an UHV chamber of base pressure 2×10^{-10} Torr as measured by the ion gauge. Pure N_2 (99.999% Liquid Carbonic) and CO (99.9% Matheson) gas are leaked into the chamber to a typical total pressure of 5×10^{-9} Torr. The molecules are ionized by a pulsed electron beam of energy 70 V and 1 μA current. Different ion densities have been obtained by varying the electron beam pulse width from 5 to 50 ms. An IonSpec FTMS 2000 system is used for pulse generation and data acquisition. Data is transferred to an Ion Spec OMEGA data system for analysis. The split program from IonSpec has been used to split the whole transient spectrum into

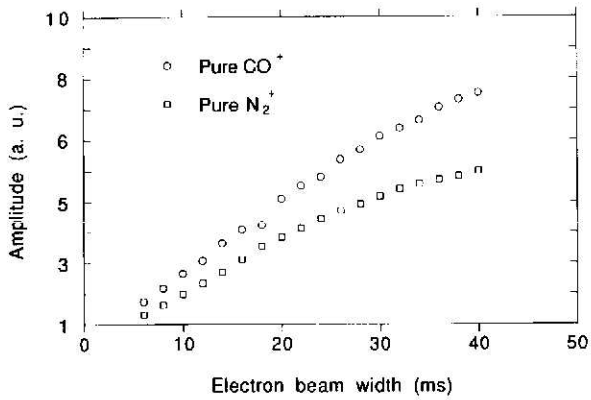

Fig. 3. Pure CO (○) and pure N_2 (□) ion densities (mass peak amplitude) as a function of electron beam pulse width. $P_{CO} = 5 \times 10^{-9}$ Torr, $P_{N_2} = 5 \times 10^{-9}$ Torr, electron beam energy = 70 eV and filament current = 1 mA.

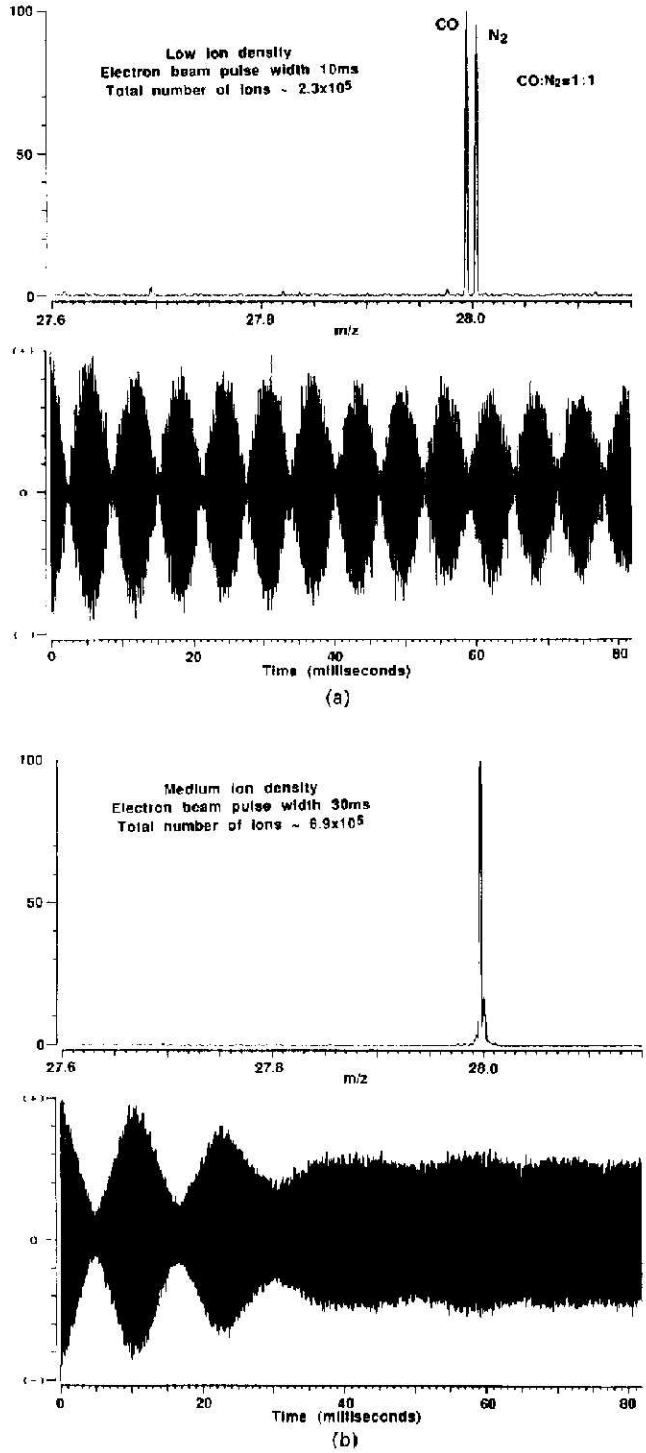

Fig. 4 (opposite and above). Mass and transient spectra of CO and N_2 mixture (CO : N_2 = 1 : 1) at (a) low, (b) medium, and (c) high ion densities. $P_{CO} - P_{N_2} - 3 \times 10^{-9}$ Torr, electron beam energy − 70 eV and filament current = 1 mA.

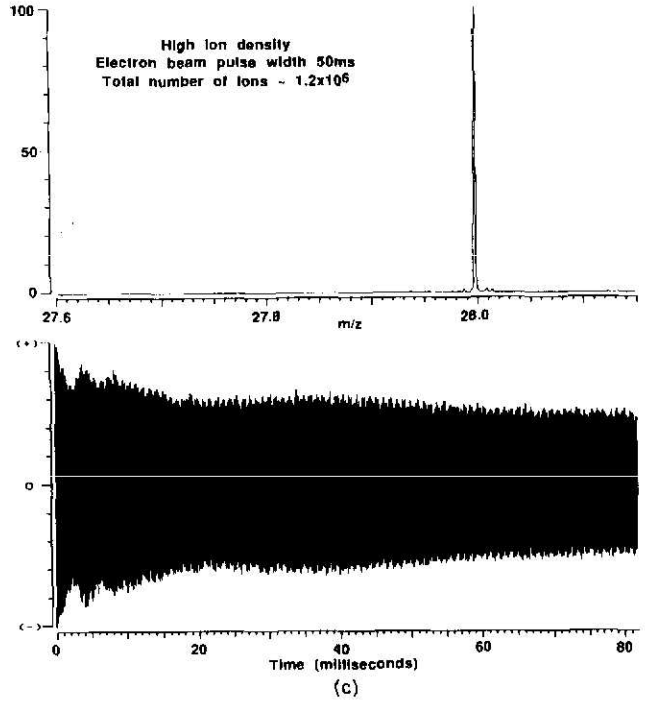

Fig. 4. (continued)

two sections for some of the data analysis as described in the text.

For the naphthalene experiments described here, naphthalene is placed in a sample tube and the vapor is leaked into the chamber at a pressure of 3.7×10^{-8} Torr. The naphthalene is ionized by electron bombardment with a beam energy of 50 V and current of 0.5 μA. The electron beam pulse width was varied, as in the CO/N_2 experiments, to produce different total ion densities.

The electron beam emission current was measured by an electrometer. The total number of ions in each experiment can be calculated by knowing the sample pressures and the ionization cross sections. Details of the experiment and the circuit have been described by Hunter et al. [5].

3. Results and discussion

3.1. Pure CO and pure N_2

In the experiments described here, ion densities are varied by means of changing the electron beam pulse width. Figure 3 shows results of such experiments for pure CO and pure N_2. The FTMS signal is seen to increase linearly over a wide range of electron beam pulse widths. At the highest ion densities (electron beam pulse width > 30 ms) the signal begins to saturate. The frequency of both CO and N_2 shift to lower frequency by similar amounts as the ion densities are increased. These shifts are consistent with previously studied space charge effects [5,6].

3.2. CO/N_2 mixtures

Figure 4 shows the mass spectra of CO and N_2 and the image current transients obtained at $CO : N_2 = 1 : 1$ for low, medium and high ion density. The total numbers of the ions in the cell are 2.3×10^5, 6.9×10^5 and 1.2×10^6 respectively. At very low ion density (Fig. 4(a)) the CO and N_2 mass peaks are consistent with the $CO : N_2$ pressure ratio and the transient is the expected beat pattern indicative of the two ions undergoing

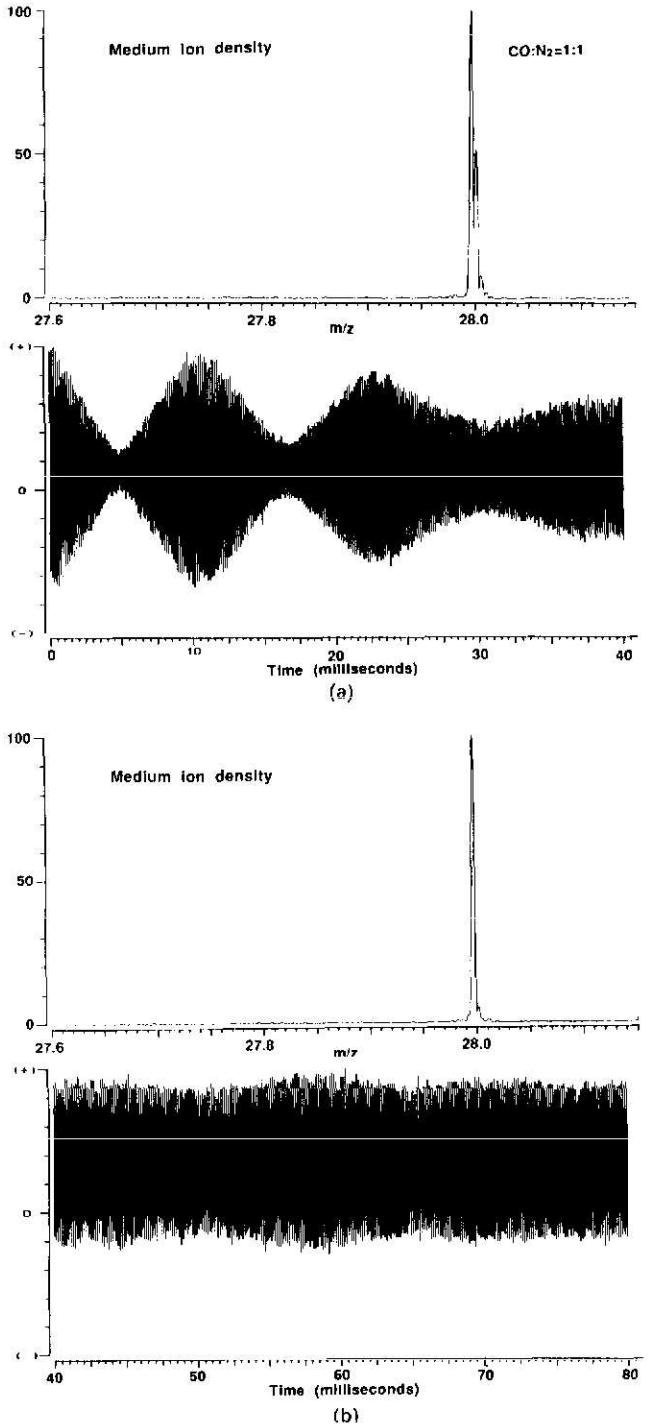

Fig. 5. Mass and transient spectra from split transient of medium ion density CO and N_2 mixture (CO : N_2 = 1 : 1). (a) Mass spectrum from first half of total transient of Fig. 4 medium ion density. (b) Mass spectrum from second half of total transient of Fig. 4 medium ion density.

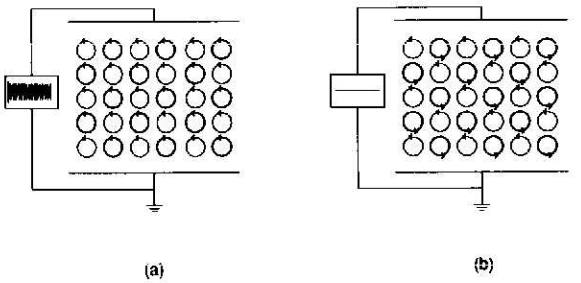

Fig. 6. (a) Image current is generated by the combination mode (ω_+) of two ion cyclotron motion with same phase. (b) No net image current is generated by the combination mode (ω_-) of two ion cyclotron motion with opposite phase.

independent cyclotron motions. At medium ion density (Fig. 4(b)), the higher mass (lower frequency) intensity decreases. Only the early half of the transient exhibits a beat pattern and the later half of the transient does not show a beat pattern. At high ion density (Fig. 4(c)), the spectrum consists of a single peak and the corresponding transient shows very little of the beat pattern. The beat pattern of the transient results from uncoupled CO and N_2 cyclotron motions, while the transient without a beat pattern is indicative of coupled ion motions with only one normal mode of the ion cloud active for generation of an image current. This effect can be further studied by splitting the medium ion density transient into two sections corresponding to the first and second half of the total transient and generating the respective mass spectra (Fig. 5(a) and Fig. 5(b)). After dividing the transient, the mass spectra from the first half has two peaks with a substantial low frequency peak, indicative of less coupling while the mass spectra obtained from the second half of the transient shows a completely coupled single peak. In the transient spectra $t = 0$ is the end of the chirp excitation pulse. Even at high ion densities there is a residual of the beat pattern at the beginning of the transient, which indicates that the two cyclotron motions are uncoupled right after the chirp excitation. Apparently, some time is required for the excited ion cloud to reach equilibrium. At the highest ion densities, the coupled normal modes of the ion cloud are established more rapidly than at medium ion densities. However, even at the highest ion densities, for the simple two species case of CO/N_2, a time of the order of the inverse of the CO/N_2 beat frequency is required to fully establish the coupled modes of the ion cloud. The frequency shift of the two modes can not be explained by the space charge effects only. The shift of the two frequencies depends on the total ion density, and the density ratio of the two species. Experimentally, we see that the two frequencies shift towards each other before one mode decays in intensity. We can rule out the possibility of ion and neutral collision induced decay of the beat pattern because throughout the experiment the total pressure is very low (10^{-9} to 10^{-8} Torr) and kept constant as the ion density is changed. Thus, in all of our experiments the collision time (>1 s) is always much longer than the total time involved in the experiment.

3.3. Discussion of two species case

At low ion densities, the ion motions in an FTMS ion trap are essentially independent, each cyclotron frequency corresponds to the correct charge-to-mass ratio through the simple Eq. (1). However, at high ion densities the ion motions will not be independent and the ion cyclotron frequencies will represent strongly coupled motions. The cyclotron frequencies are not only affected by the space charge effects but also the cross coupling among the cyclotron modes of the ion cloud. A qualitative picture of what controls the phenomena we have observed can be obtained by considering the normal modes of the ion cloud. A quantitative theory of the normal modes of a non-neutral plasma is quite complex since the outcome depends not only on the ion densities and charge to mass ratios but also on the details of the ion cloud shape [13]. Nevertheless, we can obtain some insight into the problem of the two ion species case ($CO^+ : N_2^+$) by making analogy with the coupled motion of two simple harmonic oscillators [14]. In such a case two combination modes ω_+ and ω_- are obtained. ω_+ (the symmetric combination) corresponds to the cyclotron normal mode in which the ions have the same phase and one observes a net image current, such as can be seen in Fig. 6(a). In contrast, ω_- (the antisymmetric combination) corresponds to a motion in which the

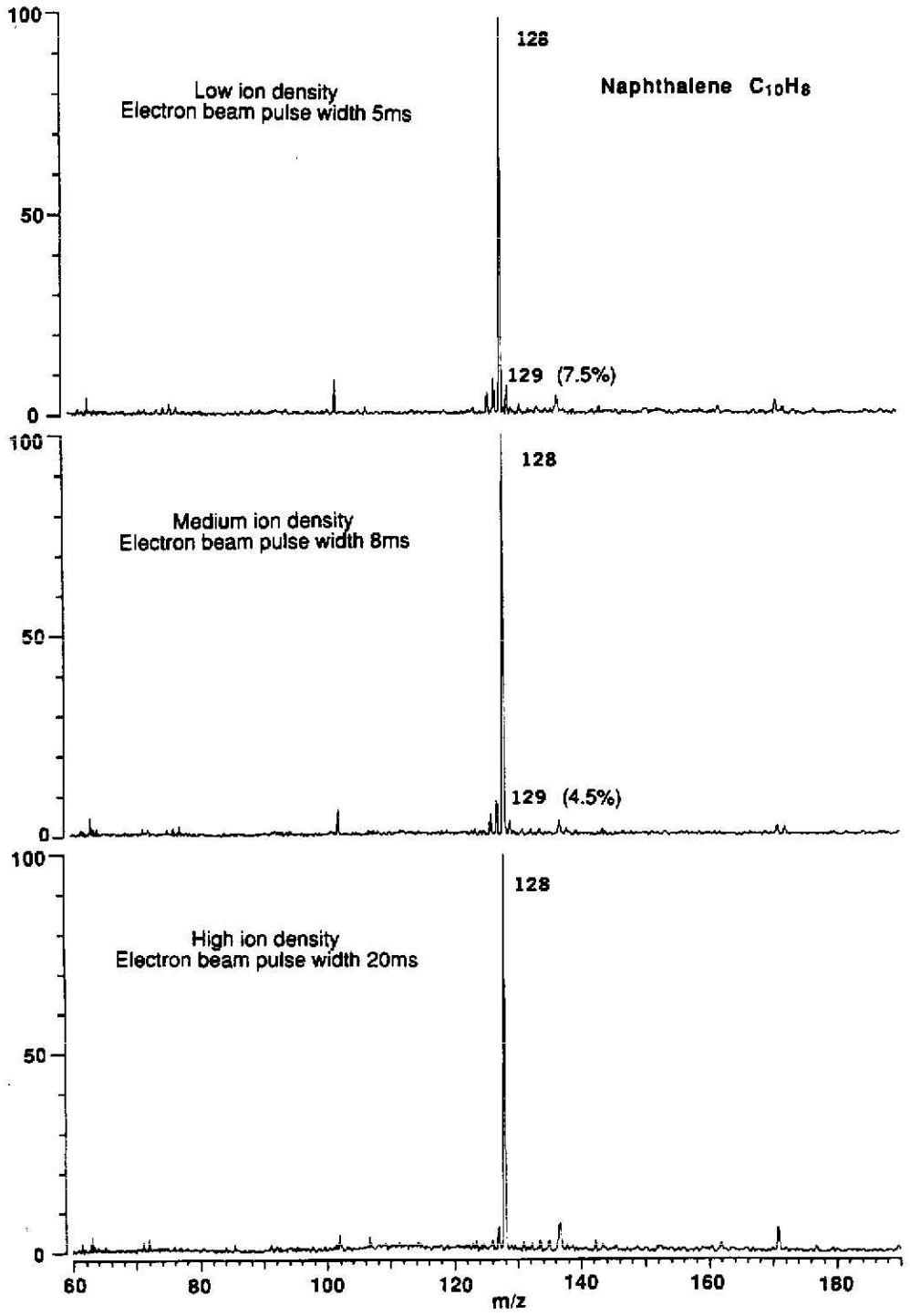

Fig. 7. Naphthalene mass spectra at low, medium and high ion densities from total transient of 16 ms. Electron beam energy = 50 eV, filament current 1.37 μA.

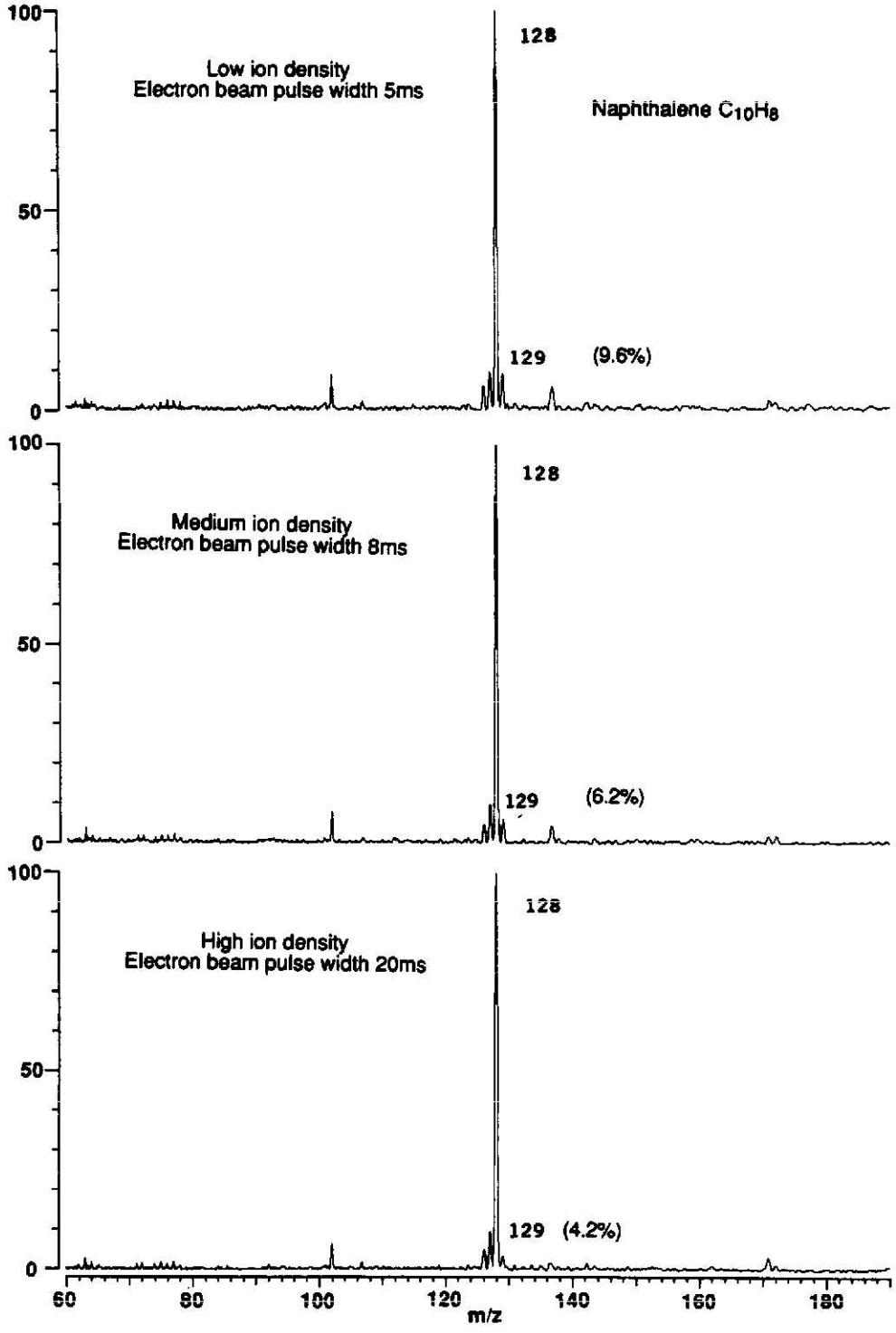

Fig. 8. Naphthalene mass spectra from first half of the split total transient of Fig. 7.

ions are moving in orbits which are 180° out of phase and the net image current is zero such as in Fig. 6(b).

Within this simple picture one expects that as the ion density increases (increased coupling of the two oscillators) the observed frequencies will correspond to coupled motions and that as a function of ion density (coupling) the modes will go over into completely coupled normal modes: one active in the experimental detection method and one inactive. The details of the frequencies and relative intensities of the two modes are a function of the geometry of the ion cloud. This simple model is consistent with our results for the CO^+/N_2^+ mixture in that only the higher frequency (lower mass) mode is detected at very high ion densities. The case of multiple ion species greater than two in the ion trap is still more complex. However, as discussed below a simple picture can still give us qualitative insight into the problem.

3.4. Naphthalene

Very similarly, Naphthalene $C_{10}H_8$ mass spectra have been taken at low, medium and high ion density with 16ms total transient lengths (Fig. 7). As the ion density increases, the ^{13}C isotope peak ($^{13}C^{12}C_9H_8$ $m = 129$) becomes smaller and at high ion density no ^{13}C mass is detected. We split the total image current transient into two parts, 0–8 ms and 8–16 ms. Figure 8 shows the mass spectra from the 0–8 ms part of the transient. As expected the mass spectra obtained from the early part of the transient are less affected by the coupling and have higher isotope ratios compared to the mass spectra from the total transient. At low ion density the ^{13}C isotope peak at 9.6% is very close to the expected natural abundance of 11%. Next to mass 128 there is also a mass 127 peak which survives in the spectra as the ion density is increased. The fact that the spectrum of naphthalene at high density still has multiple peaks is consistent with our simple model. In this case the ion cloud contains ions with several different charge to mass ratios. If we think of this as a number of coupled oscillators at high density, there will be an equal number of coupled normal modes of the ion cloud. The activity of each normal mode for the image current detection method will depend on the details of the particular system. However, it is to be expected that the lowest frequency mode (highest mass) corresponding to the totally symmetric oscillation will be inactive in each case. This is as we observe for naphthalene where the lowest frequency mode is that due to $^{13}C^{12}C_9H_8$ at $m = 129$.

4. Conclusions

(i) At high ion densities in an FTMS analyzer cell the ion cyclotron motions of two ions with a small mass or frequency difference will be coupled.

(ii) The ratios of the two FTMS peaks does not simply represent the density ratio of the two ion species in the analyzer cell at high ion densities. For the two ion species case only one FTMS peak can be detected as a result of coupling of the ion motions at high ion densities.

(iii) It takes some time for the two ion cyclotron motions to couple. Thus, the early part of the transient shows less effects of ion coupling.

(iv) To avoid ion coupling effects in FTMS, lower ion densities, longer detect delay times, higher chirp levels are suggested.

5. Acknowledgment

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