

# Intermolecular Processes in the Ion Trap Mass Spectrometer

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**Abnormal (M + 1)/M ratios in the ion trap mass spectrometer were examined to resolve questions about their source. Compounds showing minimal fragmentation provide normal (M + 1)/M ratios except under conditions of space charging (high ion concentration). Substances providing abundant alkyl ions form (M + H)<sup>+</sup> ions through proton transfer to neutrals. Concentrations causing this effect in the ion trap mass spectrometer and the sources of the proton in the case of methyl decanoate are discussed.**

Formation of (M + 1)<sup>+</sup> ions is commonly observed in electron impact mass spectrometry as sample pressure is raised (1). Onset of the ion-molecule reaction is usually earlier with compounds that can both readily supply and accept a proton. The process is particularly favored with aliphatic molecules containing oxygen or nitrogen (1) since the alkyl fragment ions of such species have relatively high gas-phase acidities (2). Aliphatic alcohols, amines, ketones, and esters are typical examples. In mass spectrometers depending on ion storage, such as ion traps and ion cyclotron resonance spectrometers, the problem is magnified since long residence times result in collisions even at low sample pressure.

In recent publications, mostly in this journal, several authors have addressed this problem and come to somewhat different conclusions. Ghaderi et al. first described (2) the process in a Fourier transform ion cyclotron resonance (FTICR) spectrometer and used the term "self-CI (chemical ionization)" in application to ion storage devices. When methyl stearate was used as an example, (M + H)<sup>+</sup> was the most abundant ion detected at 20-ms residence time with a sample pressure of 10<sup>-7</sup> Torr. When the ions were confined for 200 ms, the (2M + H)<sup>+</sup> ion was the most abundant ion. Olson and Diehl (3) extended the term "self-CI" to explain the enhanced (M + 1)/M ratio in spectra produced on a gas chromatograph/Fourier transform infrared/ion trap detector (GC/FTIR/ITD) combination instrument. Self-CI was seen to be a minor process with naphthalene but significant with dicyclohexylamine and short-chain esters. Somewhat surprisingly, they found the effect not even noticeable with certain compounds of high proton affinity including phenol, aniline, alcohols, and nonanal. Concentration dependence was easily observed as the substances eluted in a gas chromatograph peak. Although no exact sample sizes are mentioned, it is important to note that much of the sample was split off prior to transfer to the ITD. About the same time, Ratnayake et al. (4), examining the use of the ITD for certain lipids including fatty esters, isopropylidene derivatives, and phenolic acetates, remarked on increased (M + 1)/M ratios as well as other differences in the spectra. Since the magnitude of the (M + H)<sup>+</sup> ions was

found to be concentration dependent, these authors also considered them due to self-CI, although they did not use the term.

Eichelberger and Budde (5), surveying the use of the ITD for environmental analysis, noted excessive (M + 1)/M and (M/2) + 1 ratios using >50 ng of polycyclic aromatic hydrocarbons. With pyrene, analysis of the peak profiles revealed saturation of the data system with consequent peak broadening as well as a shift of the peak area toward higher mass. Since the ITD normally measures abundance at 1 mass unit intervals rather than analyzing the shape of each peak, this area would be incorrectly assigned to the next higher mass. The peak shift was attributed to space charging by C. Campbell of the Finnigan Corporation (personal communication in ref 5). Consequent limitation of the dynamic range available to the ITD was regarded by these authors as a limitation of the instrument. They also noted that the manufacturer was about to modify the software to automatically adjust the ionization time appropriate to sample size (automatic gain control (AGC), Finnigan MAT).

Shortly thereafter, noting the paper by Olson and Diehl (3), these authors pursued the matter further (6) using both anthracene-*d*-10 and hexachlorobenzene, i.e., compounds incapable of forming (M + 1)<sup>+</sup> ions. Since peaks continued to be observed at M + 1, they concluded that all of the abundance at this mass was caused by space charging rather than self-CI. Space charging was considered to reduce the effective radio frequency (rf) potential experienced by an ion, shifting it to higher mass. In fact, Armitage et al. (7), in agreement with Fisher (8), have shown that the effect of space charging is the same as adding a direct current (dc) potential to the ring electrodes of the ion trap. The resulting region of ion stability is both theoretically and experimentally skewed to higher masses. A further effect is that ions at lower mass fall outside the stability region and are lost. Though this conclusion was not specifically stated, the communication by Eichelberger et al. (6) could be read to imply that space charging is also the explanation for the abundant M + 1 ions observed by Olson and Diehl (3) using dicyclohexylamine and short-chain esters.

Meanwhile, we had acquired versions of Finnigan ion traps equipped with the AGC software modification. Even with this modification, we found the (M + 1)/M ratios excessive, and we suggested once again that the phenomenon was due to self-CI (ASMS Conference, June 5-10, 1988) (9). As proof, we pointed out that these excessive ratios were obtained only on the molecular ions, even when considerably more abundant fragment ions were present. Further experiments involving peak shape analysis and deuterated samples confirmed this point. These experiments are now discussed in detail below with further information on the sources of the proton.

More recently, a communication by McLuckey et al. (10) outlined thoroughly the conditions necessary for self-CI in the ion trap. Using methane, these authors obtained a rate constant for its self-reaction consistent with that obtained with other mass spectrometers. In the case of ethyl formate, they showed, both by peak profile analysis and MS/MS, that the  $M + 1$  ion was a true  $(M + H)^+$  ion. Furthermore, sources of the proton were found to include the molecular ion ( $m/z$  74) and the fragment ion (31) rather than water or other substances. A high  $(M + 1)/M$  ratio was obtained even under regular electron impact (EI) conditions in the trap, i.e., without using long ion storage times. These authors concluded that a 50-ng sample of any substance capable of reacting with itself (or its fragment ions) with a rate constant of ca.  $3 \times 10^{-9}$   $\text{cm}^3/\text{molecule s}$  is expected to show about 5% excess  $(M + H)^+$  as it elutes from a typical gas chromatograph. These authors made the important point that automatic gain control, while preventing space charging, should cause no change in the  $(M + 1)/M$  ratio because, for a fixed number of ions, the percentage of self-CI depends only on the amount of neutrals present. Experiments presented below suggest that their theoretical estimate of the quantity of sample necessary for self-CI may be low.

### EXPERIMENTAL SECTION

Chemicals used in this work were of the highest quality available from commercial sources and were used without purification. Both the Model 700 ITD and the ITMS were purchased from the Finnigan Corp., Sunnyvale, CA. The latter was used in the supplied configuration with an open split between the Hewlett-Packard Model 5880 gas chromatograph, while the former was adapted with a short, direct inlet from a Hitachi gas chromatograph. Versions 3 and 4 of the software were used in both instruments. Transfer lines were maintained at 250 °C, while the ITD was fixed at 225 °C and the ITMS at 100 °C. Samples were run isothermally on the GC at temperatures such that the sample eluted in 3–4 min. The mass range was scanned at the default setting of 5555  $\text{amu/s}$ .

### RESULTS AND DISCUSSION

A 70-ng sample of naphthalene- $d_8$  was first investigated to replicate closely the experiments of Olson and Diehl (3) with ordinary naphthalene. As Figure 1a shows, without AGC a normal  $(M + 1)/M$  ratio was obtained with an ionization time of 1 ms. At 12 ms (Figure 1b) the  $(M + 1)/M$  ratio is clearly excessive, and by 25 ms (Figure 1c),  $M + 1$ , rather than  $M + 2$ , i.e.,  $(M + D)^+$  expected from self-CI, dominates the spectrum. Examination of the peak profiles (inset, Figure 1c) as the compound elutes from the GC shows, in agreement with a similar study on pyrene by Eichelberger and Budde (5), that the effect is due to peak distortion from space charging. When the sample size is tripled (Figure 1d), still with a 25-ms ionization time, the peak is broadened so that the data system indicates the presence of many ions beyond  $M^{++}$ . Furthermore, peaks at lower mass are diminished in abundance, as predicted by the perturbed stability diagram shown by Armitage et al. (7). Under these conditions the molecular ion appears to shift back to its correct position in spite of the excessive broadening. The reason for this is not entirely clear, but at this point the peak is so distorted that estimation of its centroid is difficult.

Using ordinary naphthalene, Olson and Diehl (3) had found the  $(M + 1)/M$  ratio to be about 17% high. It appears that their results are best explained by the space charging phenomenon. Under normal conditions, there is no evidence for self-CI in naphthalene before space charging occurs.

To determine whether self-CI might occur under more extreme conditions with naphthalene, the sample was studied by using other modes available with the ITMS. Ions other than the candidate ion were first ejected from the trap by using a combination of rf and dc on the ring electrode. The selected

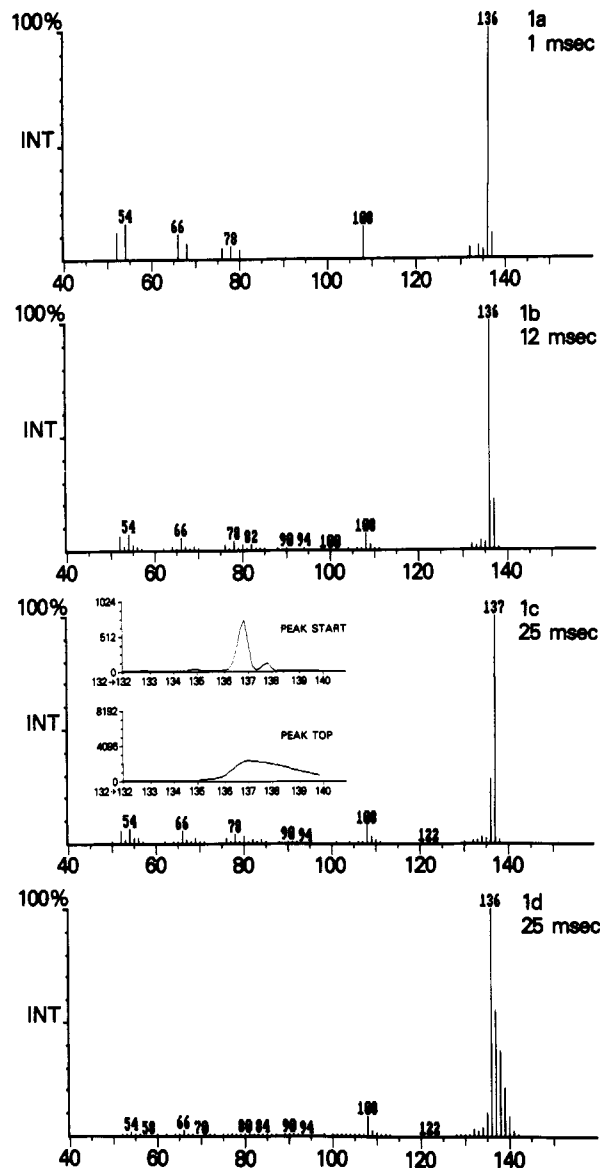


Figure 1. Mass spectra of naphthalene- $d_8$  at varying ionization times with 70 ng (a, b, c) and 210 ng (d) of sample entering the ion trap.

ion was then retained in the trap for varying times to allow accumulation of product ions from reaction with neutral naphthalene- $d_8$ . In this fashion, by isolation of  $m/z$  136 ( $M^{++}$ ) and retention in the trap for up to 50 ms, no increase was seen in  $M + 2$ ; the only effect noted was the appearance of about 0.2% of the dimer ( $2M$ ) $^{++}$  at  $m/z$  272 and 5% of  $(2M - D)^+$  at  $m/z$  270. Similarly, isolation of the odd-electron ion representing loss of acetylene ( $C_2D_2$ ) at  $m/z$  108 resulted only in the production of 52% of the molecular ion by charge exchange, even when it was held for 50 ms. On the other hand, the even-electron ion ( $C_4D_3$ ) $^+$  at  $m/z$  54 whose conjugate base has a low proton affinity was completely lost after 50 ms, as it formed a mixture of ions of  $m/z$  108 (33%), 122 (1%), 136 (54%), and of  $M + D$  (11%) (self-CI) at  $m/z$  138.

Compounds such as aliphatic acid methyl esters show the self-CI effect much more readily (2, 10). For example, Tulloch found it necessary to resort to trimethylsilyl rather than methyl esters in order to analyze the deuterium content of a series of specifically deuterated decanoic acids (11). When the chain length of the acid was increased to C16 (palmitic acid), self-CI of the methyl esters diminished considerably. We have examined both methyl decanoate and methyl palmitate using an ordinary magnetic sector spectrometer (LK-B-9000), and Figure 2A confirms Tulloch's observations re-

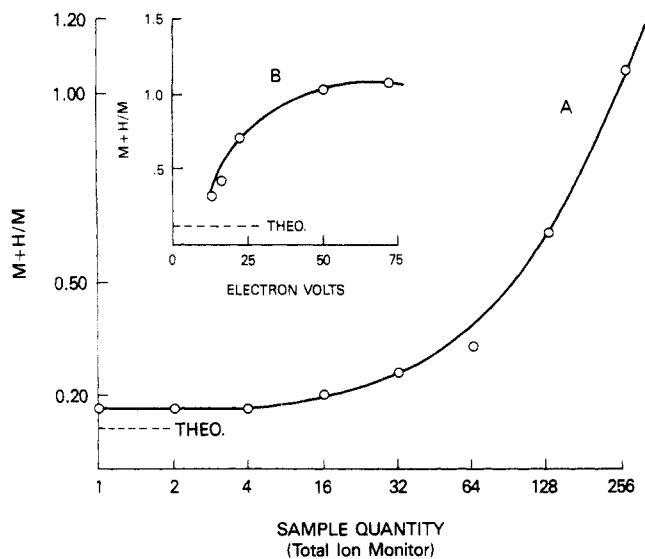
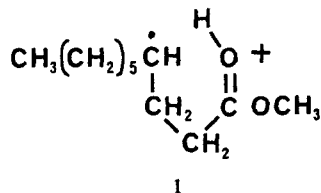


Figure 2. Variation in  $(M + H)/M$  ratios with sample pressure (A) and ionizing voltage (B) obtained with the LKB-9000 spectrometer.

garding the increase in the  $(M + 1)/M$  ratio of methyl decanoate with sample pressure. Interestingly, even at the lowest pressures the  $(M + 1)/M$  ratio was about 0.18 instead of the theoretical value of 0.12, and it appeared to plateau at this value, suggesting the existence of a second, pressure-independent, proton-transfer process.

In a later report (12), Tulloch and Hogge used deuterium labeling to show that the  $(M + H)^+$  protons derived mostly from protons attached to C-4, C-5, and C-6 (37, 15, and 9%, respectively) of the ester. They suggested that the reaction involved combination of rearranged forms of the molecular ion such as 1 with neutral ester. The failure of methyl pal-



mitate to show the same effect was ascribed to protection afforded by its longer alkyl chain as it wrapped around the protonated ester group, shielding it from further reaction. These authors also pointed out that their data did not rule out the possibility that rearrangement ions such as  $m/z$  74 and 87 might be alternative sources of the proton since these species are deuterated in accord with the neutral ester. On the other hand, Ghaderi et al. (2) ascribed the source of the protons to the many fragment ions occurring in these ester spectra whose conjugate bases have low proton affinity. In fact, this is the only conclusion possible from the appearance of their spectrum of methyl stearate confined for 20 ms where  $(M + H)^+$  was by far the most abundant ion.

Before further examination of this process using the ITMS, it was necessary to prove unequivocally that self-CI rather than space charging was responsible for the excess abundance at  $M + 1$ . By use of 6 ng of perdeuterated methyl palmitate, with AGC on, a correct  $(M + 1)/M$  ratio is obtained (Figure 3a), but at 24 ng  $M + 2$ , i.e.,  $(M + D)^+$  at  $m/z$  306, exceeds the molecular ion in intensity (Figure 3b). The peak profiles retain their symmetry (inset, Figure 3b) showing that under these conditions the AGC is correctly performing its function of preventing space charging. We therefore confirm Ghaderi's observation that self-CI does occur with long-chain methyl esters, at least under ITMS conditions. As with naphthalene- $d_8$ , increasing the number of ions in the trap by a factor

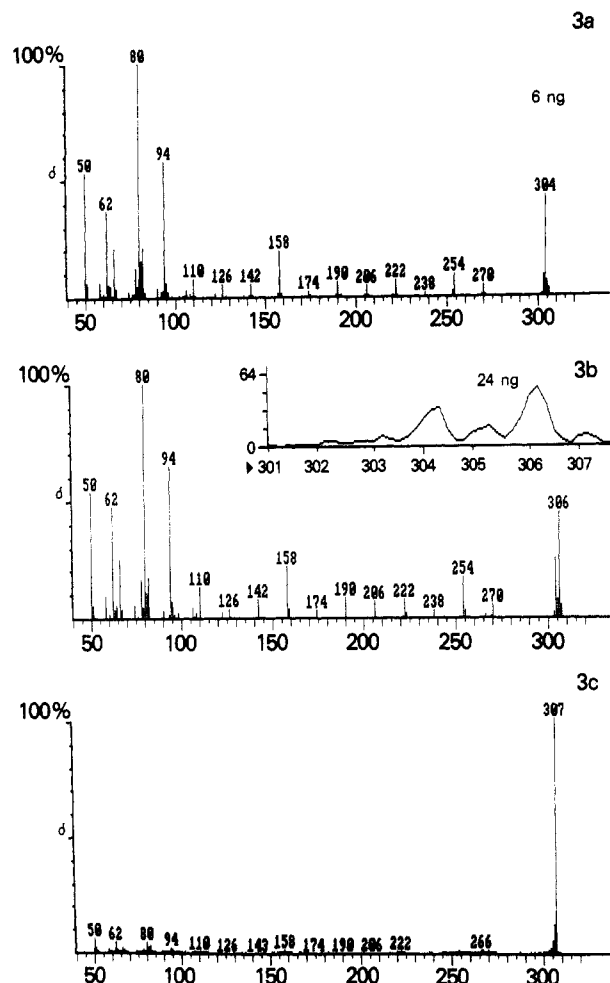
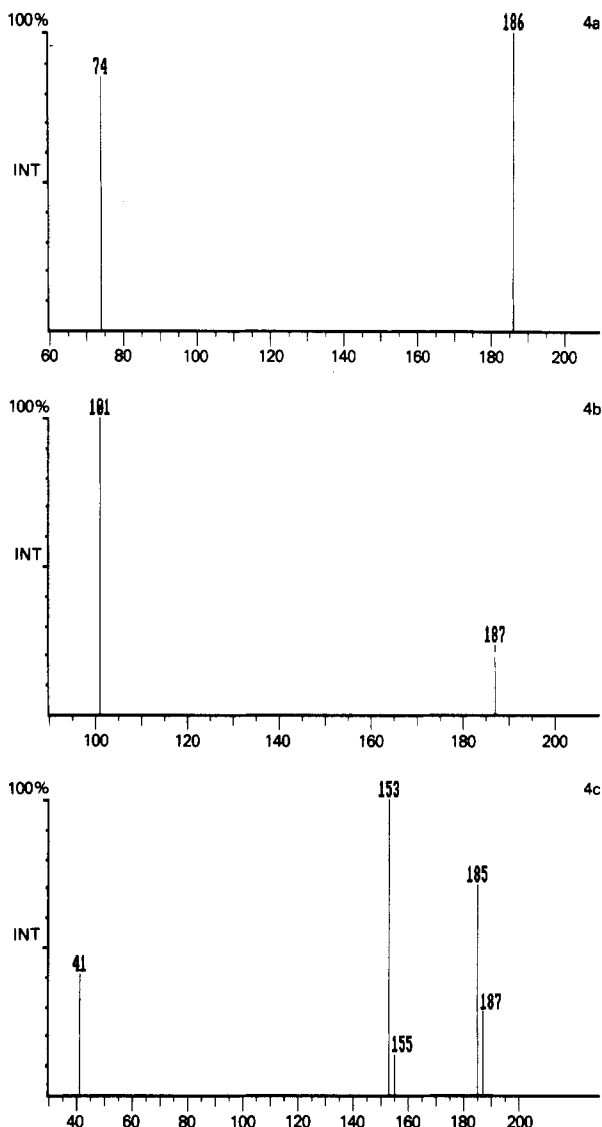


Figure 3. Spectra of methyl palmitate- $d_{34}$  in "AGC on" mode: (a) 6 ng with 1-ms ionization time; (b) 24 ng with 1-ms ionization time; (c) 24 ng with 20-ms ionization time.

of 20 by increasing the ionization time again shifts  $(M + D)^+$  1 mass unit higher (Figure 3c), distorting the appearance of the isotope cluster. Again, intensity at lower masses is lost under these extreme conditions of space charging.

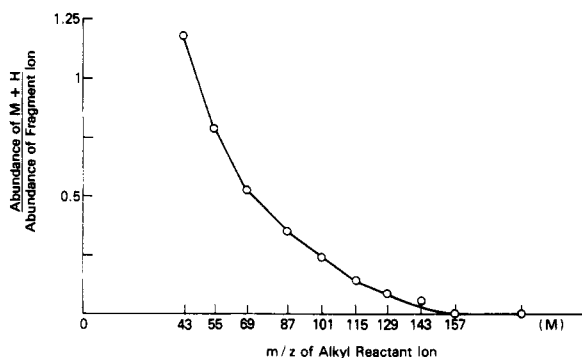
Under operating conditions defined above where self-CI but not space charging occurs, major ions in the spectrum of methyl decanoate were examined to determine the extent to which they participate in the self-CI process. In this experiment, the ionization times were adjusted for each candidate ion in relation to its normal abundance to ensure the same initial number of ions in the trap. Examining first the rearrangement ion at  $m/z$  74 (Figure 4a), one can see that no protons are transferred to neutral ester even after 50 ms. The only process observed is charge exchange to form about an equal number of ester molecular ions at  $m/z$  186. In contrast, even-electron alkyl ions such as  $m/z$  101 do indeed supply protons, forming even-electron  $(M + H)^+$  ions at  $m/z$  187 (Figure 4b). The abundance of these ions diminishes smoothly with mass of the reacting ion as shown in Figure 5, reaching zero at  $M - \text{C}_2\text{H}_5$ . Lower mass ions such as  $m/z$  41, whose conjugate bases have very low proton affinity, cause subsequent fragmentation of the  $(M + H)^+$  ion as shown in Figure 4c. Losses of  $\text{H}_2$ , methanol, or both appear to be major pathways. We have also noted interesting differences in the nature of the fragmentation depending on the structure of these reactant ions. This will be discussed in a forthcoming publication.

These studies fail to provide any evidence for the process involving 1 as suggested by Tulloch and Hogge (12). Even when  $m/z$  186 was confined for 50 ms, far longer than allowed



**Figure 4.** Spectra obtained by reaction of low-mass ions with neutral methyl decanoate: (a)  $m/z$  74 reactant ion; (b)  $m/z$  101 reactant ion; (c)  $m/z$  41 reactant ion.

**Methyl Decanoate 50ng Injected on DB-1**



**Figure 5.** Tendency of fragment ions from methyl decanoate to donate proton to neutral ester. A 50-ng sample of methyl decanoate was injected on DB-1.

under normal EI conditions with magnetic mass spectrometers, the only reaction observed was  $\approx 3\%$  dimerization to form  $2M^{+}$ . Essentially identical results were obtained when all the above experiments were repeated using methyl palmitate.

If the fragment ions are the sources of the proton causing self-CI, the ratio of  $(M + 1)/M$  should decrease as the ionizing

energy is lowered and the fragmentation diminishes. Unfortunately, it is not possible to study this process in the ITMS where all ions are necessarily produced at  $>100$  eV. Using a magnetic spectrometer (LKB-9000) (Figure 2, curve B) shows that this is correct, although again, the theoretical value of  $\approx 0.11$  was not reached at the lowest voltage where ions are detectable.

### CONCLUSIONS

Under suitable conditions virtually all compounds are capable of self-CI. If the process is not one of simple proton transfer, then either dimerization to form  $2M^{+}$  (or  $(2M + H)^{+}$ ) or transfer of some other fragment may be expected. The proton-transfer process is important when alkyl fragments whose conjugate bases have low proton affinity are present in profusion. When the spectrum is dominated by a molecular ion, as in the case of naphthalene, peak distortion due to space charging can be expected with the ITMS and ITD long before self-CI occurs. This is likely the reason that Olson and Diehl (3) failed to observe self-CI with aniline and phenol although their results with alcohols and nonanal are not so easily explained.

In general our results are in accord with the principle that odd-electron ions react with neutral compounds by forming odd-electron ions through charge exchange, while even-electron ions form even-electron products through proton or alkyl group transfer. These are all the products of bimolecular reactions, and it is perhaps not surprising that electron parity is maintained. Although the transferring proton can arise from interaction between molecular ions and neutrals as in, for example, methane and methyl formate, with larger molecules the source of protons is more likely to be the fragment ions whose conjugate bases have low proton affinity.

Finally, the point made by McLuckey et al. (10) is worth reiterating: The automatic gain control feature of the ITMS and ITD will not affect the magnitude of self-CI observed in these spectrometers. Other measures must be taken to ensure that the sample load entering the trap is appropriate for the sample structure since this feature alone determines the magnitude of its tendency to exhibit self-CI. It is obvious that a good ratio can be realized even under these excessive conditions if scans are examined near the base of chromatographic peaks. One can even envision a program that would continuously examine the  $(M + 1)/M$  ratio over a gas chromatographic peak and alert the analyst to the presence of either phenomenon.

**Registry No.**  $d_2$ , 7782-39-0; naphthalene, 91-20-3; methyl palmitate, 112-39-0; methyl decanoate, 110-42-9.

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