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The renaissance of desorption chemical ionization mass spectrometry: characterization of large involatile molecules and nonpolar polymers

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Abstract

The present overview (1) presents a short historical perspective of desorption chemical ionization (DCI), (2) discusses the effect of the changes of some important experimental parameters, revealing which conditions minimize the occurrence of pyrolytic processes, (3) identifies the range of analytical problems where, in our own experience, DCI is more likely to provide unique performance, (4) outlines a possible mechanism for the overall DCI mass spectrometry (DCI-MS) analysis of large nonpolar molecules, and (5) presents several successful applications of DCI-MS, taken from our previous and recent research. (Int J Mass Spectrom 212 (2001) 505–518) © 2001 Elsevier Science B.V.

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1. Introduction

The title is provocative. Actually, no renaissance of desorption chemical ionization mass spectrometry (DCI-MS) is under way. Instead, this interesting technique was abandoned and forgotten even before it was fully developed and understood. The lacking comprehension of the processes involved in DCI is testified by both early and recent literature which called the technique with a variety of different names to stress specific devices used or supposedly predominant mechanisms for ion formation, including "direct CI," "direct exposure CI," "in-beam CI," and "surface ionization."

The consecutive introduction and success of fast atom bombardment (FAB), matrix-assisted laser desorption (MALDI), atmospheric-pressure chemical ionization (APCI), and electrospray ionization (ESI), which progressively drew the attention of mass spectroscopists, explains only in part the early oblivion of DCI. In my opinion, a more subtle reason for this lack of interest is that the DCI technique appears much simpler than it actually is. The consequence of this apparent simplicity is that most mass spectroscopists utilized DCI seldom and without optimizing the experimental conditions, which in turn produced poor results and a generalized mistrust. On the other hand, the frequent occurrence of plain chemical ionization processes and the uncomplicated apparatus required

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Dedicated to R. Graham Cooks on the occasion of his sixtieth birthday.

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induces the false impression that DCI does not differ substantially from CI, discouraging deep investigation of the peculiar features of this technique. Quite frequently, the DCI probe was just considered a fast way to introduce a solid sample into the ion source, as an alternative to the direct introduction probe. This gave rise to an extensive literature, where inadequate DCI data were obtained by using wrong operating conditions, such as, for example hot ion-source, excessive sample loading, and slow heating rate.

The present report intends to revalorize the DCI-MS technique by presenting several applications in which DCI-MS proved to provide excellent performance and unique information. To explain these results, the most appropriate experimental condition will be identified and explained. This comprehension leads us to suggest which are the analytical problems most likely to be solved by DCI-MS.

2. Historical background (desorption chemical ionization mass spectrometry in the ’70s and ’80s)

The first ancestor of DCI was introduced in 1973 by Baldwin and McLafferty [1], who used an extended tip on a conventional solid-sample insertion probe to “expose” a thin film of a peptide sample to the CI plasma, resulting in the production of a considerable abundance of the protonated molecular ion, which was impossible to obtain by conventional CI. The experiments were conducted without heating the probe, but rather by heating the ionization chamber.

Almost in the same time, Beuhler and coworkers emphasized the effectiveness of “rapid heating” and “fast vaporization” of a peptide sample from a conventional copper probe to prevent both pyrolysis and extensive fragmentation of the molecular species [2–4].

Modern DCI evolved by combining these two basic principles: direct exposure of a thin sample film to the CI plasma and fast heating of the probe carrying this sample film [5–13]. Important concepts were gradually introduced, such as the “flash” or “ballistic” heating of the probe [6,10], the maintenance of the ion-source walls at the lowest possible temperature [12], and the dependence of the CI plasma composition on the temperature of the DCI emitter [14,15].

Few papers undertook the task of discussing the possible mechanisms of sample vaporization/desorption and ionization in the light of the various experimental conditions adopted by different research groups [15–18]. One paper in particular provides an extensive overview of the early DCI results [17].

3. The desorption chemical ionization experiment

Shortly after the introduction of the first prototypes, DCI probes became commercially available from most mass spectrometer manufacturers. Their construction schemes shared most technical features whereas retaining minor differences from one another. However, the DCI experiment can be carried out under substantially identical conditions in any instrument. A brief description of the general operating procedure is provided in the next paragraphs. Based on our experience, these conditions are optimized for the “difficult” samples, where either the high molecular weight or the presence of labile chemical structures may maximize the risk of inducing pyrolytic processes.

The DCI experiments require the ionization chamber for CI and the presence of a reagent (or moderating) gas at a pressure analogous to that used for regular CI. An important condition is that the ion source should be kept at ambient temperature or, at least, as low as possible. To achieve this, the electron-emitting filament should be switched on only for the time strictly necessary.

A specific probe is requested, which ends with an elongated tip constituted by a rhenium wire (the DCI emitter) forming either a single eye or a coil. When inserted, the coil is positioned in the center of the ion-chamber, along the line linking the electron-emitting filament and the anode. The DCI emitter is part of an electric circuit, where the current can be raised rapidly to relatively high values. Initially, the

DCI emitter is loaded with 1–2 μL of a very diluted (i.e. 10^{-5} M) solution of the sample. Then, the solvent is evaporated, leaving an extremely thin film of the sample at the surface of the emitter wire. If the solvent has a relatively high boiling point, its evaporation can be accelerated using the fore-vacuum facility of the mass spectrometer.

Upon insertion of the probe tip into the ionization chamber, the analysis is started and the mass analyzer should execute fast scans along the mass range of interest. Cycle scan times below 0.8 s are preferable. Subsequently, the current passing through the DCI emitter is rapidly increased from zero to the upper limit (generally above 1 A), determining a sudden heating of the wire by Joule effect, from ambient to above 1000 °C. This heating may be carried out at 40–80 °C s^{-1}, so that the analysis is completed in less than 30 s.

By looking at the total ion current, an intense signal should be recorded for no more than three scans. The observation of a smooth signal increment and decline, lasting for several seconds, is generally associated with an extensive pyrolysis of the sample. This pyrolysis is frequently a consequence of excessive sample loading. For the final emitter cleaning, it is generally sufficient to maintain the wire above 1000 °C for about 30 s. Then, the current can be switched off and the probe retreated.

4. Critical experimental parameters and mechanism inferred

As mentioned in the introduction, the existence of critical parameters in DCI, as in any experimental technique, has been frequently unrecognized. In order to obtain the best performance from DCI-MS, it is essential to understand and to control a number of experimental parameters, which are briefly discussed below.

No matter what the purpose of the investigation is, it is extremely important to keep the sample loading on the DCI-emitter at a low level. Excessive sample loadings transform the DCI probe into a normal heated probe. In such a case, fast heating of the DCI-emitter invariably produces the thermal decomposition of the sample. Thus, the mass spectra of pyrolytic products superimpose the regular spectrum of the analyte. Correct sample loadings are in the low- to hundreds of nanograms range, whereas loadings in microgram range are excessive.

Once the sample loading is minimal, then setting a high DCI-emitter current gradient is crucial to vaporize intact molecules from the probe. The reasons for the beneficial effect of fast heating on the thermal stability of vaporized species has been extensively discussed elsewhere [3]. Gradients in the order of 50–100 mA s^{-1} are correct and correspond to DCI-emitter heating from ambient to 1000 °C in 10–20 s. Maintaining the emitter at the highest temperature for few second after the slope cleans the wire, but a too long cleaning time warms up the ion source, an effect that should be avoided. In fact, the third important parameter is the ion-source temperature, that should be kept close to ambient, in order to achieve effective cooling of the vaporized species, preventing their fragmentation and thermal degradation. To maintain the walls of the ion source as cold as possible, it is essential to switch off both the electron emitting filament and the DCI-emitter when they are not needed, and any other unnecessary heating device. The maintenance of the ion plasma at ambient temperature does not affect the long-term performance of the ion source, unless an involatile reagent gas is utilized.

The last critical parameter is the speed of the mass analyzer scanning. Fast heating of the wire produces almost instantaneous vaporization of the thin film of analyte deposited on it, at least when the sample is constituted by a single substance. The scan speed should be fast enough to capture the rapidly surging signal arising from the ionization of these vapors, before they are pumped away or condense. In this case, the signal lasts for no more than 1–1.5 s. When the sample contains a mixture of components, these are vaporized subsequently as a function of their relative volatility. For example, in polymer analysis, the oligomers with increasing molecular weight are vaporized in sequence, yet in a short time. In such a case, the scanning of the mass analyzer should be

made synchronous with the period of vaporization of the entire oligomer series. Otherwise, the scan speed must be much faster than the vaporization period, so that several mass spectra are collected, each representing a portion of the oligomer distribution, and then added together. Both approaches yield accurate molecular weight distributions, provided that long interscan periods are unnecessary for resetting the mass analyzer. This point opens the question of which is the most appropriate mass analyzer to be used in DCI experiments. Linear quadrupoles allow very fast scanning but have a relatively low upper mass limit and modest sensitivity at the higher mass values. Magnets are adequate in terms of mass range and sensitivity but the scan speed is somewhat limited by hysteresis. Time-of-flight analyzers and quadrupole ion traps with extended mass range are likely to have excellent potentiality, but their hyphenation with DCI has never been commercially implemented.

All the observations made for different classes of substances analyzed by DCI-MS point to a mechanism in which the fast vaporization of the analytes and their rapid and efficient thermal deexcitation play the key roles. The latter process is particularly important. Maintaining the ion-source walls cold assures that the internal energy of the CI moderating gas remains low. In turn, the occurrence of multiple collisions of this cold moderating gas with the analyte molecules (or ions) immediately after they are vaporized, removes the excess of internal energy from them, leaving these molecules in a thermally stable configuration. This explains why, for certain analytes, DCI may appear as the least energetic among the "soft" ionization techniques. However, the first step is the sublimation of the sample; if this process cannot take place, as for the polar substances, because pyrolytic transformation channels require less energy than sublimation, DCI fails completely. On the other hand, when the efficiency of molecular "cooling" is reduced either because the moderating gas temperature is high or because an excessive sample loading prevents the gas to come in contact with the inner layers of the sample, again fragmentation and thermal decomposition processes of the analyte molecules become active.

5. Target analytes for desorption chemical ionization mass spectrometry

The early analytical applications of DCI-MS almost exclusively dealt with the characterization of polar biological molecules [1–18], such as peptides and polysaccharides. This trend was justified by the importance of biochemical research, as well as the lack of adequate desorption and ionization methods for these substances at the time when DCI-MS was initially developed. Newer techniques such as FAB, MALDI, and ESI proved to provide much better results than DCI on biopolymers, determining the decline of the latter method. The only biological molecules for which DCI favorably competes with the other techniques in terms of analytical performance, are those carrying a relatively short polar moiety (a peptide, a glycoside, etc.) on a nonpolar substrate, as it occurs in many antibiotics [12,13,18–24].

In our own experience, large antibiotic molecules could always be neatly characterized by DCI-MS, both in the positive and the negative ion mode [23,24]. A large abundance of the molecular ion was generally observed and varying the ion-source temperature and other operating parameters modulated the fragmentation. However, when we approached linear polypeptides and polysaccharides, a definite molecular mass limit was observed, beyond which only pyrolytic products were produced [24]. Otherwise, the polar groups had to be derivatized [22,25–27].

For the previous reasons, it can be concluded that the large biopolymers and, in general, the highly polar molecules do not represent the kind of analytes that one may consider to investigate by DCI-MS in these days. For example, the polar groups are likely to achieve much more effective charging by ESI than by DCI, and their thermal degradation is prevented in ESI. However, the large and nonpolar molecules undergo much less efficient ionization than the polar substances in ESI, and are often not compatible with

the range of solvents used by this technique. The same considerations apply to FAB and APCI. In contrast, MALDI finds wide application also in the characterization and molecular weight distribution of nonpolar polymers.

Unlike the highly polar substances, any kind of large and nonpolar compound can be regarded as a potentially ideal analyte for DCI-MS. Typical classes of compounds with these structural features include organized macromolecules (cavitands, carcerands, catenanes, etc.), dendrimers, fullerenes, technological materials, dyes, nonpolar polymers, and even neutral organometallic compounds. For all these substances, DCI is likely to provide optimal structural characterization, yielding extremely clean mass spectra with dominant molecular ion and excellent signal-to-noise ratio.

Each analysis requires very little time, allowing high throughput analysis and rapid optimization of the experimental parameters. Several manufacturers, who produced automated sample introduction devices, attempted further productivity improvement in the past but none of these equipments proved commercially successful. Mixtures of analytes can be efficiently approached and molecular weight distributions can be determined under the appropriate experimental conditions. Sample impurities do not generally constitute serious interference, at least in the positive ion mode. In the electron capture mode, the relative abundance of the sample constituents is biased by the selectivity associated to their relative electron affinity.

In the subsequent sections, several applications of DCI-MS to the structural characterization of large, nonpolar, and involatile molecules are presented, taken from our own research work.

6. Organized macromolecules with technological properties

Several materials synthesized in the recent years for technological applications (optics, electronics, drug targeting) have the chemical structure of a single macromolecule or a sequence of oligomeric species. Generally, the search for the macromolecule to be synthesized is driven by the properties requested, and its optimal structure is identified upon extensive theoretical modeling and computation. Once synthesized, the reaction products and by-products have to be determined. When these products have the structure of a macromolecule, their separation and identification is possibly problematic.

We studied a series of macromolecular liquid crystals carrying a rigid resorcin-arene tetrameric substrate and as many as twelve flexible alkyloxybenzoyl groups [28]. The balance of the rigid and flexible units modulated the degree of order in the liquid phase. The molecular weight of these macrostructures varied in the 3000−4500 Da range, far beyond the limit at which the organic molecules are considered vaporizable. It is generally accepted that the molecules with such high molecular weight tend to pyrolyze when heated before producing appreciable vapor pressure.

In spite of the previous concepts, the DCI mass spectra of these liquid crystals exhibited a dominant molecular ion and little fragmentation in both ion polarities. An example of these spectra is shown in Fig. 1 with the corresponding molecular structure. The molecular ion cluster yields the most intense peak at *m/z* 4068.7 corresponding to the chemical formula containing two ^{13}C. In the same study [28], it was shown that these cluster peaks could be separated at the base line when the magnetic mass analyzer is scanned with sufficient resolution (m/Dm = 4000). A strong ion-source temperature effect was also demonstrated: the complete disappearance of the molecular ion and the onset of an extensive consecutive fragmentation was induced by increasing the ion-source temperature from 90 to 200 °C.

Other organized macroscopic structures of technological interest are the molecular receptors. These include calixarenes, cyclodextrins, cyclophanes, cavitands, hemicarcerands, and carcerands. In a decade, we investigated and confirmed the chemical structure of at least one hundred of such receptors using DCI-MS. Most of them possess a strong structural backbone and molecular weights comprised in the 1000–2000 Da range; therefore, their characterization does not represent a real analytical challenge. How-

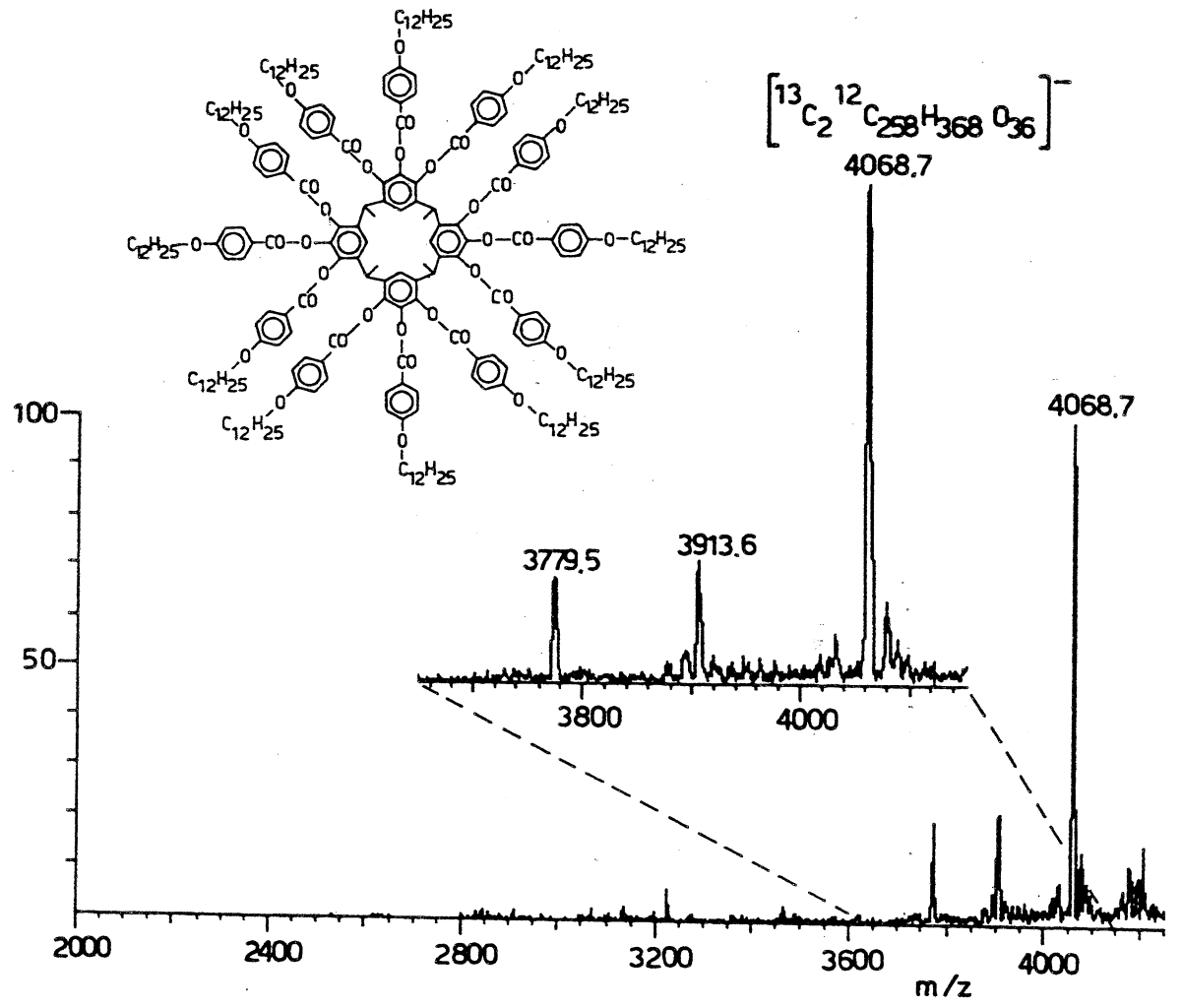

Fig. 1. Electron-capture (negative-ion) DCI mass spectrum of a macrocycle having the chemical formula $C^{260}H^{368}O^{36}$, recorded at 90 °C ion-source temprature. Reprinted with permission of Heyden & Son Limited from Rapid Communications in Mass Spectrometry 3 (1989) 106.

ever, a conventional heated probe cannot vaporize them intact and their FAB spectra are frequently noisy and interfered, leading to possible misinterpretation. Even when the presence of polar groups makes these compounds amenable to ESI, the formation of a variety of adducts and clusters are promoted (with alkali metal ion and ammonium impurities, with buffer and solvent molecules) [29], which complicate the ESI spectrum. By using DCI with methane or isobutane as a moderating gas, none of these inconveniences is observed. Thus, for the analysis of molecular cages and receptors, DCI really represents the method of choice, as it provides in few minutes clean, reproducible, and structurally informative mass spectra [30]. The same advantages apply to the analysis of fullerene derivatives [31,32].

In another kind of application, DCI has been extensively used as an introduction method for molecular receptors, in order to obtain cavitands [30,33–35] and bridged calixarenes [30,36] in the gas-phase, to remove the excess of internal energy and lastly to react them with appropriate molecular guests, yield-

ing stable host/guest complexes. This application has been reviewed elsewhere [37–39] and will not be discussed in detail here. Nonetheless, it is worth noting that the extensive gas-phase formation of host/guest complexes implies that the receptor is sufficiently "cold" to establish attractive supramolecular interactions with the molecular guests, a condition that would not occur if the internal energy of the receptor was the one imparted by the DCI-emitter heating at the temperature of its vaporization (500–600 °C for most cavitands and functionalized calixarenes). Thus, the DCI process must necessarily involve strong cooling of the desorbed receptor before the host/guest interaction can be established. On the other hand, it is still partially unclear at which stage of the overall process the ionization takes place: whether before or during the thermal deexcitation step, or even after the host/guest complex is formed [35].

A different situation is observed for carcerands, whose structure includes one or more molecules of the solvent used in their synthesis. In this case, the guest is encapsulated inside the host cavity and cannot escape nor be exchanged by another solvent molecules, when dissolved in it. The common mass spectrometric problem posed by these organized systems is to characterize in the gas phase the host/guest complex, i.e. the carcerand still retaining its original guest. Quite obviously, in the gas phase the carceplex structure is free from the steric and electronic effects produced by the solvent, its internal energy is intrinsically higher than in solution and the entropic contribution to its dissociation is largely favorable. The consequences are that the constraints for the guest are weaker, the pores of the carcerand are larger, and the stability of the carceplex in the gas phase is much lower than in solution.

A comparison of MALDI [40] and DCI [38,41,42] mass spectra for the same carceplexes indicates that laser photons induce quite extensive release of the guest from the carceplex and even some fragmentation of the carcerand backbone, whereas DCI mass spectra are dominated by the protonated host/guest complexes with the empty carcerands accounting for about 20% relative intensity. An example of a DCI mass spectrum of a carceplex containing one molecule of dimethylformamide is depicted in Fig. 2. It can be deduced that DCI is indeed a very soft ionization technique for nonpolar supramolecular aggregates and that the removal of internal energy from the desorbed species during the process is extremely efficient.

7. Nonpolar polymers

The analytical characterization of polymers by mass spectrometric methods has always found a serious complication in the high molecular weight of the analytes and the limited mass range of the mass spectrometers. The renovated success of time-of-flight mass analyzers interfaced to MALDI sources has recently improved the analytical capabilities of mass spectrometric methods for the study of high mass polymers, but the most important polymer features are still determined on the low oligomers. In fact, for ions above *m/z* 10 000 complicated clusters are always formed and the distinction of mass units becomes difficult. For the mass spectrometric study of these low oligomers, a variety of ionization techniques have been used, including FAB [liquid secondary ionization mass spectrometry (LSIMS)], MALDI, ESI, field desorption, plasma desorption, thermospray, and others. However, to my knowledge, we were the only group using DCI-MS to determine intact oligomeric species [43–46]. Other groups utilized DCI-MS in different experimental conditions to induce the pyrolysis of the polymer and to observe the decomposition products [47,48].

We employed DCI-MS to characterize several classes of synthetic polymers, after extensive testing of the experimental conditions with polymer standards. These included polystyrene and poly(ethylene glycol) with different average molecular weight [43]. The DCI mass spectrum of a polystyrene standard with average molecular weight of 4000 Da is reported in Fig. 3. The peaks correspond to the protonated molecular ions of polystyrene oligomers. No evidence of ion fragmentation is present in the spectrum. From this spectrum, the number-average molecular weight (M_n) and the weight-average molecular weight (M_w) were calculated resulting respectively equal to 3906

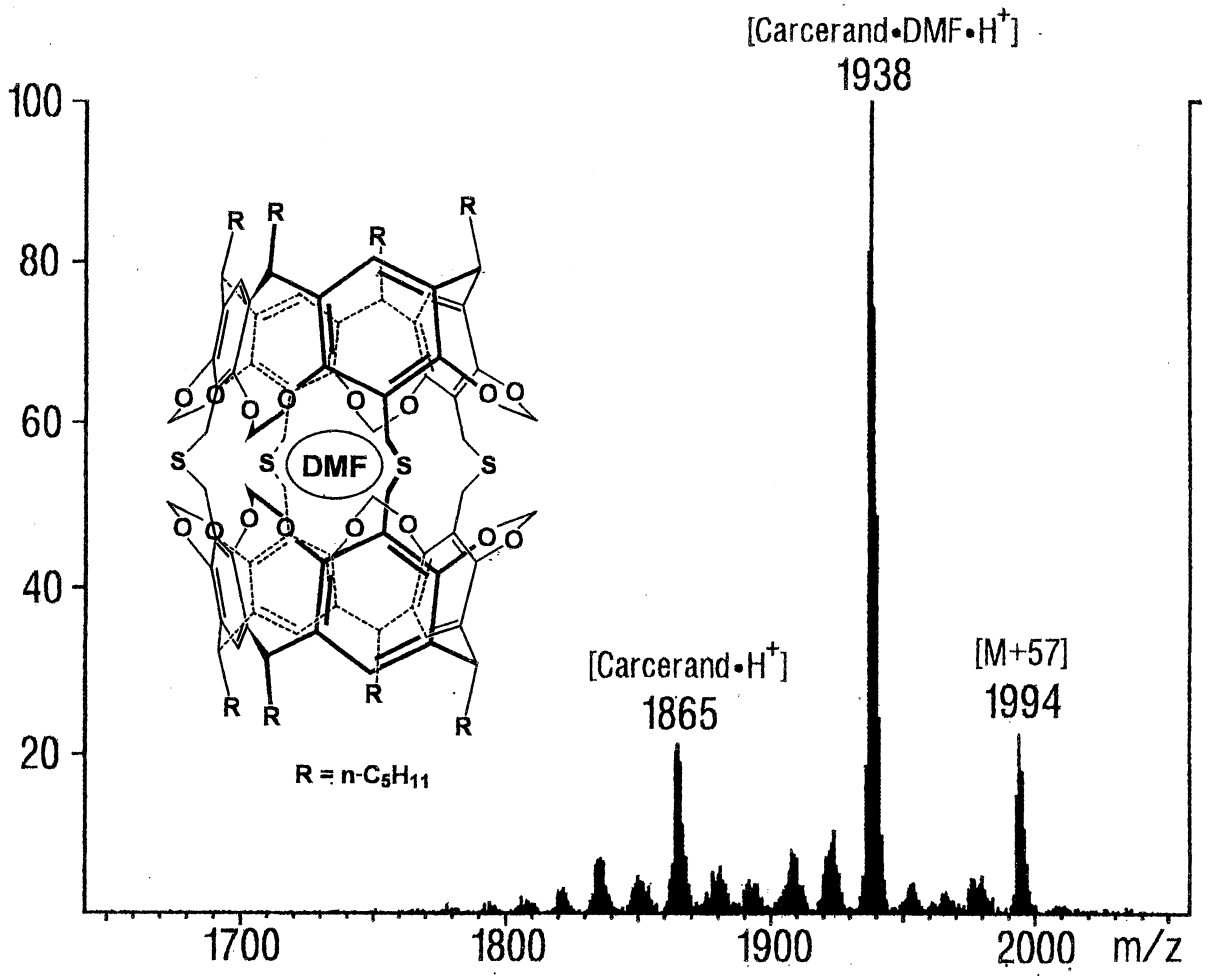

Fig. 2. Positive-ion DCI mass spectrum of the inclusion complex formed by a carcerand and one molecule of dimethylformamide.

and 4090, in excellent agreement with the theoretical value. Similar results were obtained for all the other polystyrene standards in both ion polarities, whereas poly(ethylene glycol) (PEG) provided accurate analytical results only for the standard with the lowest average molecular weight (PEG 2000). DCI mass spectra of poly(ethylene glycol) standards with average molecular weight of 3400 and 5000 Da, respectively, exhibited evidence of fragmentation and partial thermal decomposition, which was attributed to the rather polar character of the polymer [43]. The same occurrence of pyrolytic processes was induced onto the PEG 2000 standard by increasing the temperature of the ion source.

Polymers that we studied in detail, due to their unique properties and specific mass spectroscopic features, were perfluoropolyethers [44]. Unlike the other polymers, the negative ion DCI mass spectra of perfluoropolyethers did not exhibit a distribution of molecular ions, but rather a distribution of fragment ions, with a terminal oxygen atom bearing the negative charge. The odd finding was that the fragmentation was not randomized on the C–O ether bonds, as observed in SIMS [49], but involved exclusively the few oxygen atoms closer to the terminal groups, favoring the formation of high-mass ions. The resulting peak distribution approximated the average molecular weight desumed by nuclear magnetic reso-

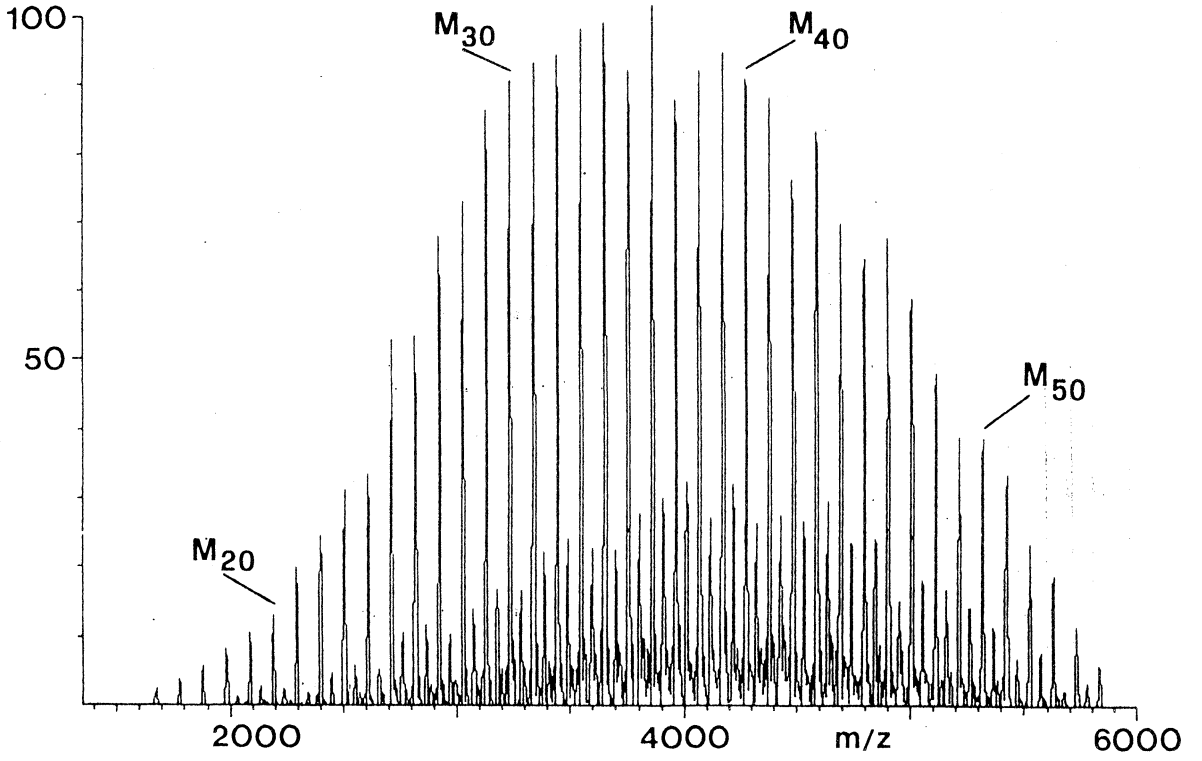

Fig. 3. Positive ion DCI mass spectrum of polystyrene standard, with average molecular weight of 4000 Da. Reprinted with permission of the American Chemical Society from Analytical Chemistry 64 (1992) 1879.

nance with minimal mass shift. This discriminating fragmentation mechanism observed in DCI-MS was again explained by assuming that minimal internal energy deposition occurred upon DCI, favoring the fragmentation channels requiring the least energy, as the ones allowing charge stabilization on a large ion and release of small radicals [44]. In contrast, SIMS deposits a larger amount of energy on the sputtered species, opening several unspecific fragmentation channels at once. The effect is that DCI mass spectra are clean and easy to interpret even for complex copolymers, as they result from simple ion chemistry, leaving only two series of ions, corresponding to each different terminal group. This simplicity combined with appropriate DCI-tandem mass spectrometry (MS-MS) experiments allowed us to determine with ease the relative abundance of different terminal groups and different monomers in co- and ter-polymers, as well as to infer the average molecular weight. We doubt that any other mass spectrometric technique could be as appropriate as DCI for the study of perfluoropolyethers.

Another successful example of identification and quantitation of several terminal groups was provided by a DCI-MS study of synthetic ethylene-propylene-carbon monoxide ter-polymer [45]. Also the relative abundance of monomers and their alternate vs. block sequence was ascertained.

A specific feature of the DCI-MS technique in the study of polymers is its extreme sensitivity. As low as 5 ng of polymer loaded on the DCI-emitter are generally sufficient to observe an acceptable distribution pattern [43]. However, this sensitivity is useless for the characterization of most synthetic polymers, where large amounts of material are available. Applications in which extreme sensitivity is occasionally required for polymer analysis are found in forensic science. We utilized DCI-MS to characterize the

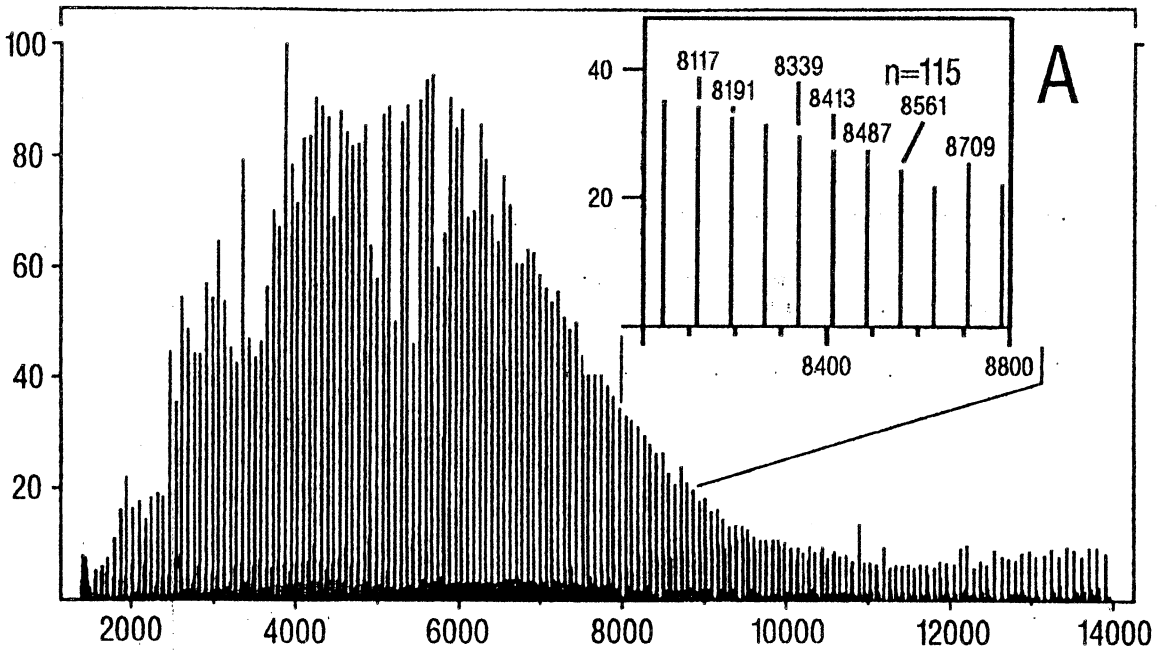

Fig. 4. Positive ion DCI mass spectrum of lubricant sampled from Adonis® condom and dissolved in dichloromethane. Expanded area shows that each peak is a protonated molecular ion, with regular intervals of 74 Da, corresponding to dimethylsiloxane repeat units. Reprinted with permission of the Forensic Science Society, U.K., from the Journal of Forensic Science Society 34 (1994) 245.

lubricants applied to a large series of latex condoms [46]. For most condoms, the lubricant turned out to be polydimethylsiloxane with large oligomer distribution and average molecular weight of about 6000, corresponding to a viscosity of 200 cSt. A typical example of DCI mass spectrum of such a lubricant is shown in Fig. 4. From DCI mass spectra, a few condoms proved to have lubricants containing either polydimethylsiloxanes with different molecular weight distributions or additives with spermicide activity (for example ethoxylated nonylphenols). The latter was vaporized at lower DCI-emitter temperatures than polydimethylsiloxane, so they were clearly distinguished at different analysis times. Again, the spectrum in Fig. 4 exhibits peaks corresponding to protonated molecular ions up to *m/z* 14 000 and no evidence of fragmentation nor thermal decomposition of the polymer. Upon accurate analytical protocol assessment with donors, the DCI-MS analysis was applied to two vaginal cotton swabs extracts obtained from alleged rape victims. The results, depicted in Fig. 5, clearly demonstrated that a lubricated condom was utilized by the first assailant, not in the second case, confirming the sensitivity and the selectivity of the method. The sensitivity of DCI-MS was also exploited in the water determination of other oligomeric mixtures, namely nonionic surfactants such as polyoxyethylene-lauryl ethers and -nonylphenols [50].

8. Organometallic compounds

Organometallic compounds have been traditionally regarded by mass spectroscopists as difficult samples. If they are sufficiently volatile to be vaporized by a heated probe, they tend to contaminate the mass spectrometer, resulting in memory effect and loss of performance. Moreover, the electron ionization and CI spectra are often interfered by impurities and difficult to interpret. FAB (LSIMS) spectra generally exhibit poor signal-to-noise ratio, unless the organometallic analyte is singly charged. Moreover, all tech-

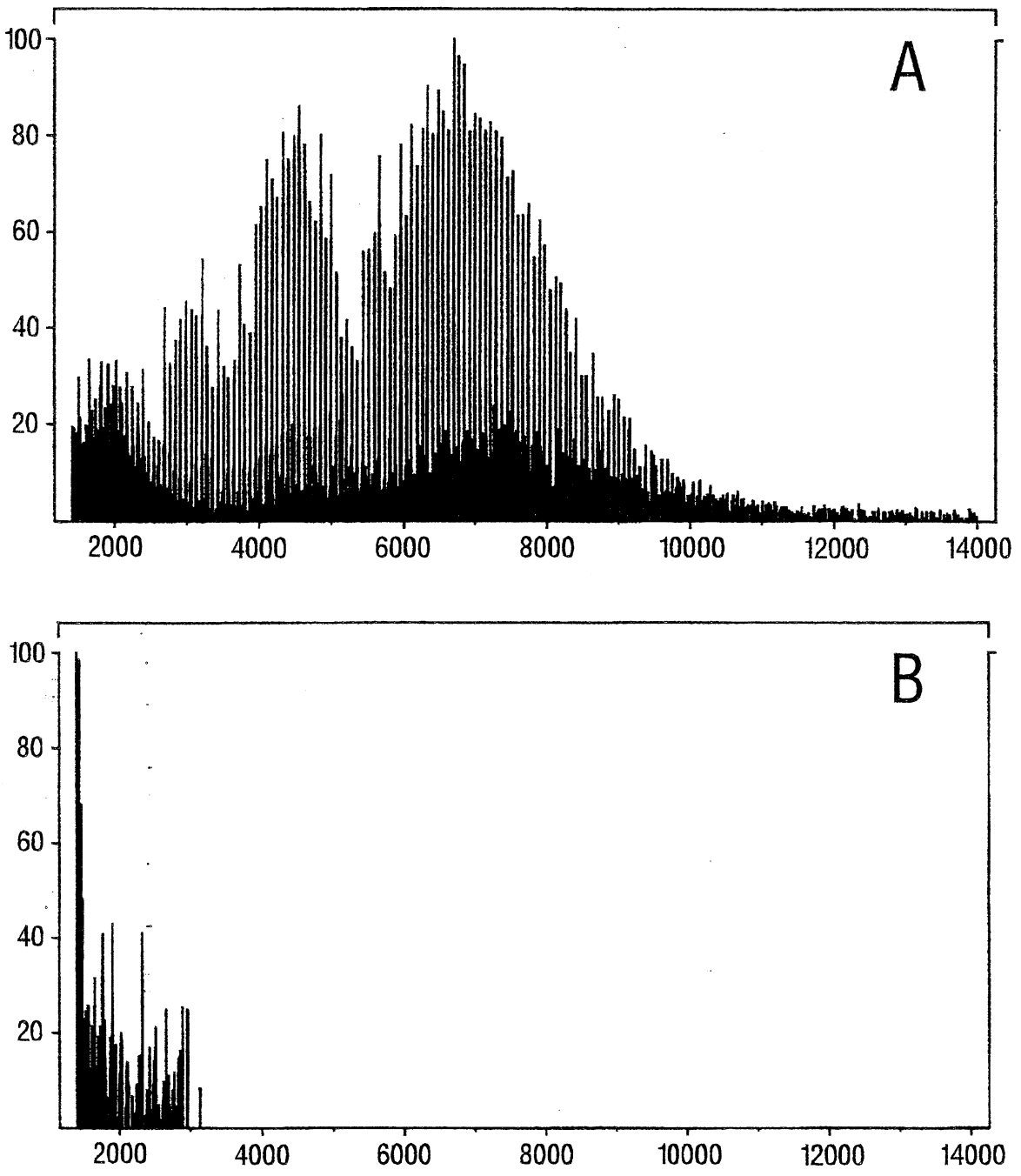

Fig. 5. Positive ion DCI mass spectra of vaginal cotton swab extracts obtained from alleged rape victims. (a) Case 1; (b) Case 2. Reprinted with permission of the Forensic Science Society, U.K., from the Journal of Forensic Science Society 34 (1994) 245.

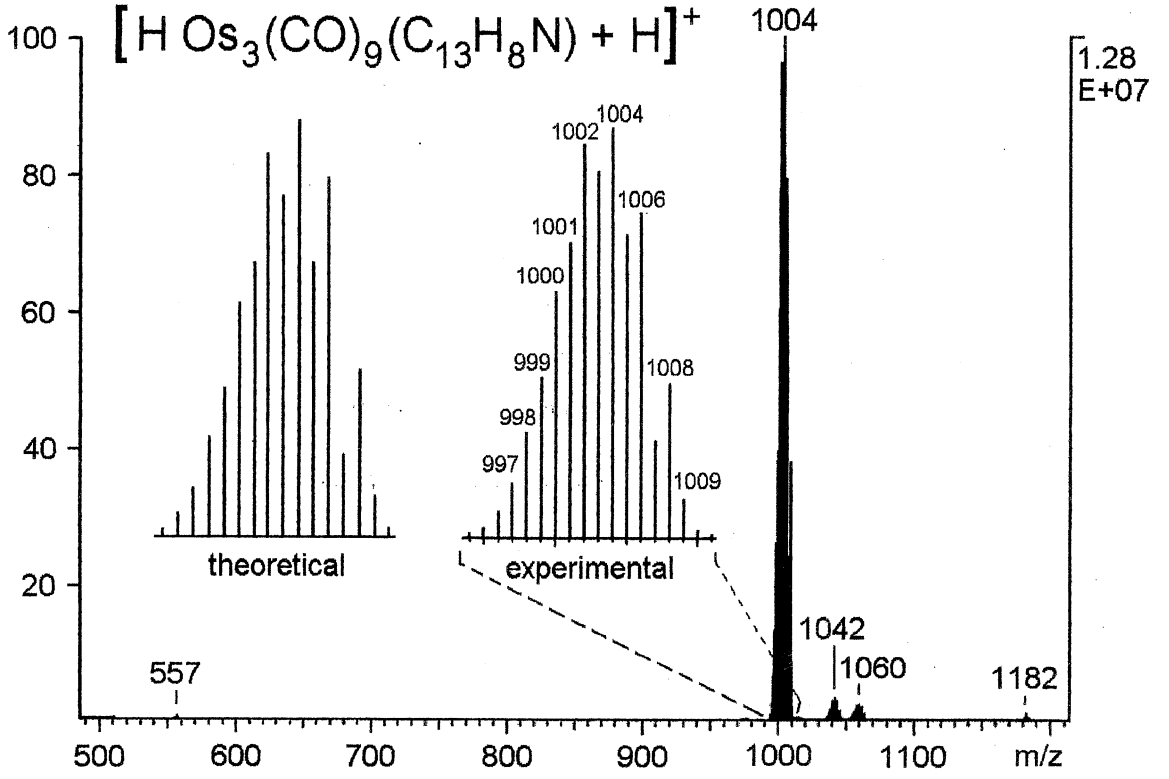

Fig. 6. Positive ion DCI mass spectrum of a triosmium complex. The insets compare the distribution of peak abundances for the experimental molecular ion cluster with the theoretical one desumed from isotope abundances for all the elements present.

niques involving a liquid matrix (FAB, ESI) may produce adducts between the metal moiety and matrix components, which are detected in the mass spectrum.

DCI-MS applies only to the neutral organometallic compounds, but for these analytes it displays unique advantages with respect to the other MS techniques. Little sample loading is required: few ng of product are sufficient to record optimal spectra, virtually eliminating the risks of contamination and memory effect. Secondly, the DCI mass spectra generally show an intense and very clean signal. Since the entire sample loaded is vaporized, little or no interference arises from minor impurities, whose total amount in the ion source is negligible. Lastly, the molecular ion generally represents the base peak, but the fragmentation can be activated by increasing the ion-source temperature or by decreasing the heating rate of the DCI-emitter. These conclusions arise from experience on cobalt, molybdenum, ruthenium, and osmium complexes with organic ligands [51] and estradiol derivatives [52,53], even if this mass spectroscopic experience has not been systematized yet. An example of DCI mass spectrum of an organometallic compound, containing three osmium atoms, is provided in Fig. 6. In the mass range from 500 to 1200 Da only the molecular ion cluster is present in large abundance, together with low intensity adducts with isobutane (the reagent gas) ions. An expanded view of the molecular ion cluster is depicted in the inset together with the theoretical isotope distribution, demonstrating that the correspondence is virtually perfect. Consecutive losses of carbon monoxide units can be activated by collision-induced dissociation and MS-MS or simply by raising the ion-source temperature.

9. Conclusions

Even though many efficient soft ionization techniques have come to the fore in the recent years, it is unfortunate that a powerful ionization system such as DCI has been put aside so early. Several applications exist in chemistry, where DCI-MS still provides unsurpassed performance and should be considered as the ionization method of choice.

Among the positive aspects of the technique, the following should be mentioned. DCI-MS is: (1) fast, as it allows to carry out as much as 20–30 analysis per hour; (2) sensitive, as one nanogram of material is generally sufficient to record a good spectrum; (3) clean, since minimal sample loading prevents the contamination of the mass spectrometer; (4) cheap, since it requires minimal investment and inexpensive consumables; (5) noise-free; (6) easy-to-use, and (7) widely applicable.

As in the Renaissance was common practice to celebrate the beauty of a woman in a sonnet, the wished renaissance of DCI-MS may demand a sonnet to become true:

The DCI sonnet
So easy to use
You will be amused,
So fast and so clean
You know what this means,
Its signal so strong
You'll praise it for long.
So why
Don't you try
The nice DCI?

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