Analysis of Base Oil Fractions by ClMn(H$_2$O)$^+$ Chemical Ionization Combined with Laser-Induced Acoustic Desorption/Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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Laser-induced acoustic desorption (LIAD), combined with chemical ionization with the ClMn(H$_2$O)$^+$ ion, is demonstrated to facilitate the analysis of base oils by Fourier transform ion cyclotron resonance mass spectrometry. The LIAD/ClMn(H$_2$O)$^+$ method produces only one product ion, [ClMn + M]$^+$, for each component (M) in base oils, thus providing molecular weight (MW) information for the analytes. With the exception of one sample, no fragmentation was observed. The mass spectra indicate the presence of homologous series of ions differing in mass by multiples of 14 Da (i.e., CH$_2$). All peaks in the spectra correspond to ions with even *m/z* values and hence are formed from hydrocarbons with no nitrogen atoms, in agreement with the compositional nature of base oils. The MW distributions measured for two groups of base oil samples cover the range 350−600 Da, which is in excellent agreement with the values determined by gas chromatography. Moreover, the hydrocarbon types (i.e., paraffin and cycloparaffins with different numbers of rings) present in each base oil sample can be determined based on the *m/z* values of the product ions. Finally, the results obtained by using LIAD/ClMn(H$_2$O)$^+$ indicate that the efficiency of the technique (combined desorption and ionization efficiency) is similar for different hydrocarbon types and fairly uniform over a wide molecular weight range, thus allowing quantitative analysis of the base oils. Hence, the product ions' relative abundances were used to determine the percentage of each type of hydrocarbon in the base oil. In summary, three important parameters (MW distributions, hydrocarbon types, and their relative concentrations) can be obtained in a single experiment. This mass spectrometric technique therefore provides detailed molecular-level information for base oils, which cannot be obtained by other analytical methods.

Lubricants play an important role in almost every aspect of the civilized world, most notably in transportation vehicles and industiral machinery. Lubricants are typically composed of base oil (80−90%) and various additives (10−20%). Traditional base oils contain saturated hydrocarbons derived from petroleum vacuum gas oils via one or a combination of several refining processes, such as solvent extraction, hydrotreating, and hydroisomerization. The saturated hydrocarbons include normal paraffins, isoparaffins, and one- to six-ring cycloparaffins (or naphthenes). Isoparaffins and the alkyl chains in cycloparaffins can have different degrees of branching. The base oil components of a lubricant and their detailed structures and relative concentrations play key roles in determining the performance of a lubricant, such as cold flow property, viscosity, volatility, and thermal stability.

The ability to carry out a detailed and accurate determination of the molecular weight (MW) distribution and the types of saturated hydrocarbons (i.e., normal paraffin, isoparaffin, or cycloparaffin) in base oils would be highly desirable for the development of high-performing lubricants but has proven challenging. Conventional analytical methods, such as nuclear magnetic resonance (NMR) spectrometry,[1−3] supercritical fluid chromatography[4,5] (SFC), and gas chromatography[6,7] (GC), have been widely used to characterize petroleum products. However, without isolation of the individual petroleum components, these techniques can only provide general information on the average carbon number, types of chemical classes or the presence of certain functional groups in the bulk sample.

In contrast, mass spectrometry (MS) can provide detailed molecular-level information for hydrocarbons and their mixtures. High-energy (70 eV) electron ionization (EI) causes significant fragmentation of the ionized hydrocarbon molecules. Based on the fragmentation patterns, a method called "group type analysis" is often used to sort the contributions from different molecules to certain peaks and to reconstruct the molecular distribution from

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the peak areas.[8,9] However, this method cannot be used to determine the carbon number distribution for each type of hydrocarbon, and it is not accurate[10] if the samples contain olefins or heteroatom-containing compounds. Soft ionization methods, such as low-energy EI, electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), atmospheric pressure photoionization (APPI), and matrix-assisted laser desorption/ionization (MALDI), also have limitations in saturated hydrocarbon analysis. Low-energy EI is a low-efficiency process and selective for aromatic hydrocarbons.[11,12] Although ESI has recently been demonstrated to successfully evaporate and ionize polar hydrocarbons without fragmentation, nonpolar hydrocarbons cannot be detected.[13−16] APCI and APPI can yield $[M − H]^-$, $[M + H]^+$, or $[M]^{+\bullet}$ ions for nonpolar and polar hydrocarbons, including those containing heteroatoms, but not for saturated hydrocarbons.[17,18] Up to date, the most successful ionization techniques for saturated hydrocarbon analysis have been field ionization (FI) and field desorption (FD) wherein hydrocarbons are ionized by electron tunneling at a very high electric field strength (10^8 V/cm).[19−22] However, these techniques suffer from low ionization efficiency and significantly varied response factors for hydrocarbons with different MW or different types. The latter makes mass spectrometric quantitation of hydrocarbons in mixtures especially problematic. Further, for highly branched isoparaffins, FI and FD sometimes cause a significant amount of fragmentation, resulting in an underestimate of the total paraffin (i.e., normal paraffins and isoparaffins) concentration. FI and FD (more significantly FD) can also generate $[M − 2H]^+$ ions,[23] which can complicate the determination of low concentrations of naphthenic hydrocarbons.

During the past few decades, chemical ionization (CI) of hydrocarbons by using atomic ions or organometallic ions (e.g., Fe^+, Ni^+, Ag^+, $FeCH_3^+$, and $CpCo^+$; $Cp = \eta^5$-cyclopentadienyl) has attracted an increasing interest.[24−31] Some of these ions have proven to be useful for MW determination of many hydrocarbons, as well as some synthetic hydrocarbon polymers and petroleum

Table 1. Bulk Characteristics of the Base Oil Fractions Based on NMR, GC, and SFC Analysis (Data Provided by ExxonMobil)

samples		techniques		
group no.	fraction no.	NMR methyl protons (%)	GC avg carbon no.	SFC total paraffins (%)
1	1	19.64	26.6	94.3
	2	28.27	30.4	69.7
2	1	21.29	27.0	76.0
	2	25.16	27.9	60.9
	3	36.51	27.9	0.8

samples.[26c,28−31] However, fragmentation of branched saturated hydrocarbons makes it difficult to obtain MW information for mixtures containing these compounds.

In a previous study, the reactivity of a ligated water cluster of Mn^+, $ClMn(H_2O)^+$, toward a variety of hydrocarbons was studied in a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer.[32] This ion was found to ionize all types of hydrocarbons to exclusively form product ions $[ClMn + M]^+$ via water loss without further fragmentation. This was found to be true even for highly branched saturated hydrocarbons. The purpose of this study is to test the utility of $ClMn(H_2O)^+$ CI in the molecular-level characterization of base oils. Laser-induced acoustic desorption[33a−d] (LIAD) has been demonstrated[29−31,33e,f] earlier to bring even large branched hydrocarbons into the gas phase as intact neutral molecules. Hence, this method was chosen for the evaporation of the neutral base oil samples into the mass spectrometer.

EXPERIMENTAL SECTION

Chemicals. Two groups of base oil samples were provided by ExxonMobil Research and Engineering Co. (EMRE, Annandale, NJ). The samples represent fractions separated from two commercial lube base oils. These fractions contain different types of molecules typically present in hydroprocessed base oils, and they have different chemical compositions. NMR, GC, and SFC analysis were carried out at EMRE. The results of these bulk characterization are given in Table 1. Samples are identified here

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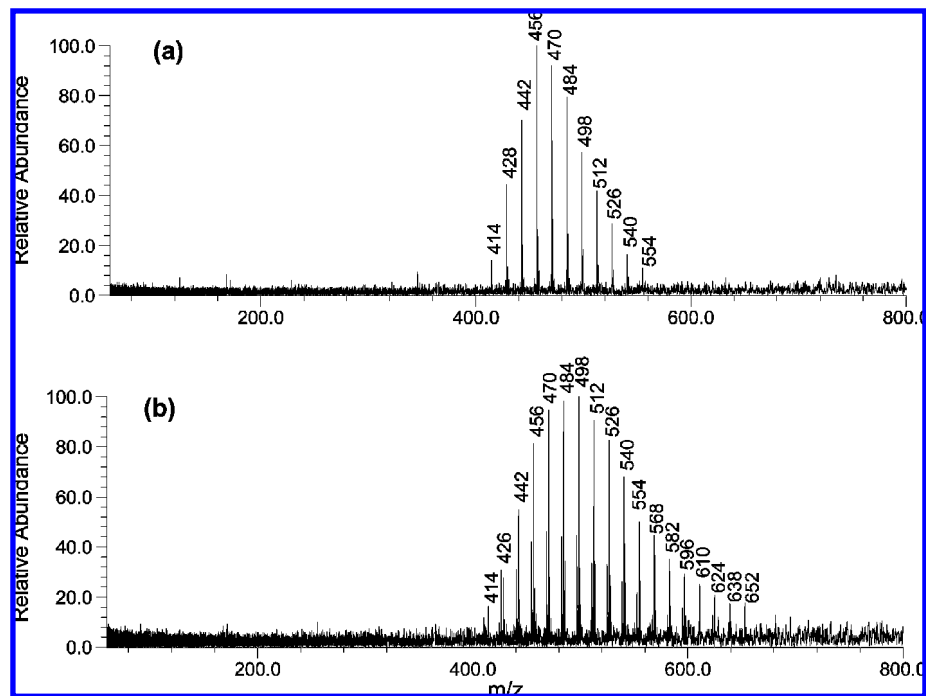
Figure 1. LIAD/ClMn(H₂O)⁺/FT-ICR mass spectra of two base oil samples: (a) G1F1 (single scan); (b) G1F2 (single scan).

with a group (G) and a fraction (F) number (i.e., G1F1, G1F2, etc.). G1F1 and G1F2 are derived from the same parent base oil. G1F1 contains much higher levels of total paraffins than does G1F2. The alkyl chains of the paraffins in G1F1 are less branched, as indicated by the lower percentage of methyl protons. It also has a lower average molecular weight. G2F1, G2F2, and G2F3 were derived from another parent base oil. Sample G2F3 contains mostly naphthenes and has the highest levels of branched paraffins.

The $ClMn(CO)_5$ precursor was synthesized from $Mn_2(CO)_{10}$ by a reaction with Cl_2 in CCl_4.[34] Ti foils (12.7 μm) used in LIAD were purchased from Alfa-Aesar (Ward Hill, MA).

Sample Preparation. Base oil solutions were prepared by dissolving ~1 mg of each base oil sample in ~ 4 mL of hot CS_2 (46 °C). This 4-mL solution was deposited on a 12.7-μm-thick, 2-cm-diameter round Ti foil situated on a hot plate heated to ~50 °C. The solvent was allowed to evaporate, leaving a thin film of the base oil on the surface of the foil. This sample preparation method is fast and simple and requires no matrix or sample pretreatment. The Ti foil with the sample was mounted onto a LIAD probe and inserted into the FT-ICR mass spectrometer.

Instrumentation. FT-ICR Mass Spectrometry. All experiments were conducted in a dual-cell Nicolet model FTMS-2000 FT-ICR mass spectrometer described previously.[29−31] $ClMn(CO)_5$ was introduced into one side of the dual cell via a manual solids probe. The $ClMn(H_2O)^+$ reagent ion (m/z 108) was generated by electron ionization (30-eV electron energy, 7-μA emission current, 80-ms ionization time) of $ClMn(CO)_5$ in the presence of H_2O vapor. The nominal pressure in this cell was between 5.0×10^{-8} and 1.1×10^{-7} Torr. $ClMn(H_2O)^+$ ions were trapped by using a 2-V trapping potential and transferred into the other cell through a 2-mm hole in the conductance limit plate by grounding this plate for 100 μs.

Prior to transfer, a negative potential of −3.5 V was applied for 12 ms to the remote trapping plate of the receiving cell to purge this cell of unwanted ions. At all other times, the three trapping plates were kept at 2 V. The transferred ions were cooled for 1 s by allowing them to undergo IR emission and collisions with argon gas pulsed into the cell (peak nominal pressure ~1×10^{-5} Torr). Subsequent ejection of unwanted ions was performed using stored-waveform inverse Fourier transform (SWIFT) excitation pulses.[35] The isolated $ClMn(H_2O)^+$ ions were then allowed to react with base oil molecules evaporated by multiple laser pulses. Excitation of the ions for detection was achieved by a fast broadband rf sweep (from ~2 kHz to 3 MHz, 121 V_{p-p}, 3200 Hz/μs). The transients (0.065 536 s), recorded as 64K data points, were subjected to Hanning apodization, followed by augmentation of the data by one zero fill prior to Fourier transformation. All the spectra were background corrected by subtracting the background spectra from the reaction spectra. Background spectra were recorded by removing $ClMn(H_2O)^+$ by SWIFT ejection prior to reaction. The experiments were performed and data acquisition was carried out by using a Sun workstation running the Odyssey software version 4.0.

Laser-Induced Acoustic Desorption. The LIAD technique employs laser-generated acoustic waves to evaporate thermally labile or nonvolatile samples as neutral molecules into a mass spectrometer from one side of a 12.7-μm-thick Ti foil when the backside of the foil is irradiated by pulses of laser light. A high-power LIAD probe ("fiberless" probe) was used in this work.[36] A manual solids probe inlet was used for the LIAD probe. The LIAD probe was positioned 5 mm from the FT-ICR cell's trapping plate. Each LIAD experiment involved desorption of base oil molecules by using 30−100 laser shots (Continuum Minilite Nd:YAG laser,

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Scheme 1

$$ClMn(H_2O)^+ \quad + \quad M \quad \xrightarrow{-H_2O} \quad [ClMn + M]^+$$

M = Hydrocarbons
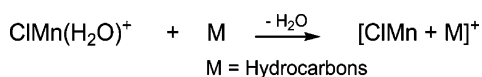
light of 532-nm wavelength, 3-ns pulse width, 10-Hz repetition rate) applied in a circular pattern on the backside of a Ti foil (the side opposite to where the sample was deposited). Each laser shot desorbs molecules from an area of 10^{-3} cm^2 on the Ti foil (laser power density at the metal surface was $\sim 3 \times 10^9$ W/cm^2). Approximately 5% of the foil's total surface area was irradiated when the foil was rotated 360°.

Weight-Average Molecular Weight (M_w). The M_w was calculated as the sum of the product of the square of the mass (M_i) and the signal magnitude (I_i) of each component ($\sum M_i^2 I_i$) divided by the sum of the product of the mass and the signal magnitude of each component ($\sum M_i I_i$).

$$M_w = \frac{\sum M_i^2 I_i}{\sum M_i I_i}$$

RESULTS AND DISCUSSION

In our previous model compound study of $ClMn(H_2O)^+$ chemical ionization, we demonstrated that hydrocarbons (M) form exclusively $[ClMn + M]^+$ product ions (Scheme 1).[32] It is expected that the base oil fractions will behave similarly. Figures 1 and 2 show the FT-ICR mass spectra of two groups of base oil fractions (Table 1) subjected to the $LIAD/ClMn(H_2O)^+$ analysis. In all cases, the center of the mass distribution is ~ 90 Da greater than the average MW of the base oil sample (estimated by GC), confirming that the $ClMn^+$ ion (m/z 90) was incorporated into the hydrocarbon molecules present in the base oils. Further, the mass spectra indicate no fragmentation for the components of the base oils (all ions have even m/z values and hence correspond to pseudomolecular ions; no signals were observed at low m/z) with one exception (sample G2F3 shows a minor amount of fragmentation (Figure 2c), which may be due to the very highly branched hydrocarbons in this sample). The fact that all ions have even m/z values demonstrates that they are formed from hydrocarbon molecules with no nitrogen atoms, which is consistent with the compositional nature of base oils. All the mass spectra indicate the presence of homologous series of ions differing in mass by multiples of 14 Da (i.e., CH$_2$), confirming the presence of homologous series of hydrocarbons. Detailed examination of the mass spectra yielded various types of useful information for the base oil samples studied, as detailed below.

MW Distribution Determination. MW distribution of each base oil sample was obtained from the analysis of the product
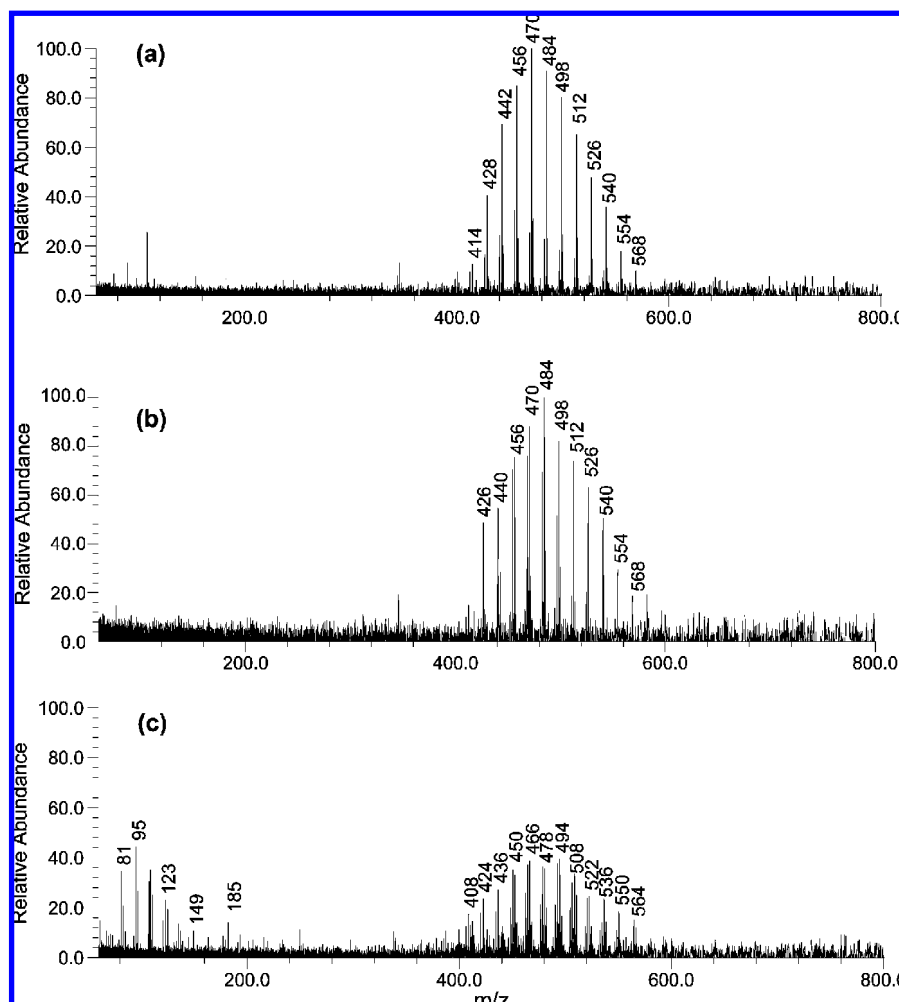
Figure 2. LIAD/ClMn(H$_2$O)$^+$/FT-ICR mass spectra of three base oil samples: (a) G2F1 (average of 7 scans); (b) G2F2 (single scan); (c) G2F3 (average of 8 scans). The origin of the low-mass ions in the last spectrum is currently under investigation.

Table 2. Average Carbon Number and Percentage of Total Paraffins Determined by GC, SFC and the LIAD/ClMn(H₂O)⁺/FT-ICR Method

sample		average carbon no.		total paraffins (%)	
group no.	fraction no.	GC	LIAD/ClMn(H₂O)⁺ ᵃ	SFC	LIAD/ClMn(H₂O)⁺
1	1	26.6	27	94.3	100.0
	2	30.4	30	69.7	76.2
2	1	27.0	27	76.0	79.1
	2	27.9	30	60.9	60.9
	3	27.9	29	0.8	0

ᵃ For simplification purposes, the numbers were calculated according to the formula $(M_w - 2)/14$.

ions' m/z distribution in the measured mass spectra. For example, LIAD/ClMn(H₂O)⁺ of the sample G1F1 produced a mass spectrum centered at m/z 470 (Figure 1a). The average carbon number calculated from the weight-average molecular weight (381, M_w after correcting for ClMn mass of 90) of this sample is C_{27}, which is in good agreement with the result obtained by GC ($C_{26.6}$, Table 1). For sample G1F2, the average carbon number estimated by GC is $C_{30.4}$. Indeed, the peaks in its LIAD/ClMn(H₂O)⁺ mass spectrum are centered at a higher m/z value (m/z 512) than for sample G1F1, and this value corresponds to a carbon number of C_{30} (Figure 1b). A similar situation applies to the three samples in the second group (Table 2). The average carbon numbers (calculated from measured M_w) based on the LIAD/ClMn(H₂O)⁺ method and estimated by GC are 27 versus 27.0, 30 versus 27.9,

and 29 versus 27.9 (Figure 2; Table 2). It is worth noting that these determinations are based on the assumption of uniform ionization/desorption efficiency for a wide carbon number range. The reasonable agreement between GC and FT-ICR results suggests that the assumption is reasonable.

Distribution of Different Types of Hydrocarbons. Information on the different types of hydrocarbons present in the base oil samples can be obtained from a further analysis of the product ions' m/z values. It is worth pointing out here that only hydrocarbons that differ in their extent of unsaturation can be differentiated from each other. Isomeric hydrocarbons, such as normal paraffins and isoparaffins, cannot be differentiated. A narrow mass range (from m/z 460 to 490) of the mass spectra measured for the base oil samples in the first group are shown in Figure 3. The mass spectrum of sample G1F1 (Figure 3a) indicates that almost all the components are paraffins since for both carbon numbers shown (C_{27} and C_{28}), only a single product ion (and its ¹³C-isotope) is observed, and this ion corresponds to the fully saturated hydrocarbon ion ($C_{27}H_{56}$ (m/z 470) and $C_{28}H_{58}$ (m/z 484), respectively). In sharp contrast, a mass spectrum of sample G1F2 (Figure 3b) also shows the presence of a C_{27} cycloparaffin ($C_{27}H_{54}$, containing one degree of unsaturation; m/z 468) and a C_{28} cycloparaffin ($C_{28}H_{56}$; m/z 482). For the base oils in the second group (Figure 4), the presence of a C_{27} paraffin (m/z 470) and a C_{27} cycloparaffin (m/z 468) was observed for samples G2F1 and G2F2 (albeit with different relative abundances than for the samples in the first group). The mass spectrum measured for sample G2F3 is much more complex, containing eight peaks with m/z values ranging from 460 to 490 (Figure 4c). Since the m/z
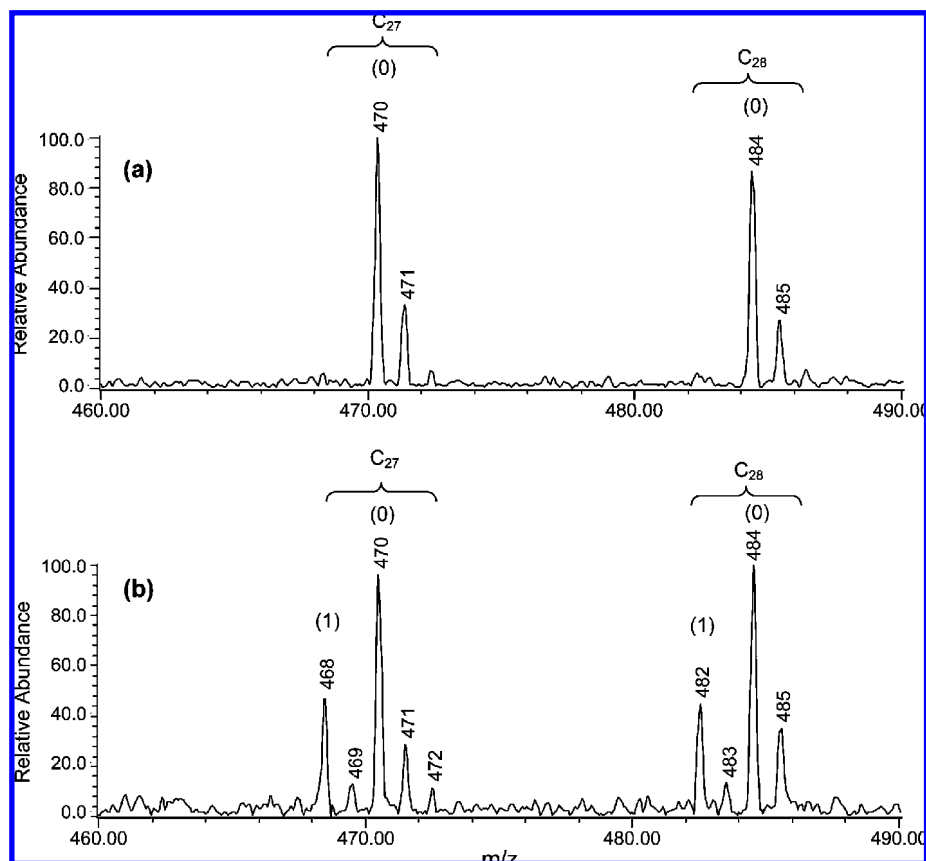
Figure 3. Expanded (m/z 460−490) LIAD/ClMn(H₂O)⁺/FT-ICR mass spectra of two base oil samples: (a) G1F1 (single scan); (b) G1F2 (single scan). The numbers in parentheses represent the number of rings in the cycloparaffins.
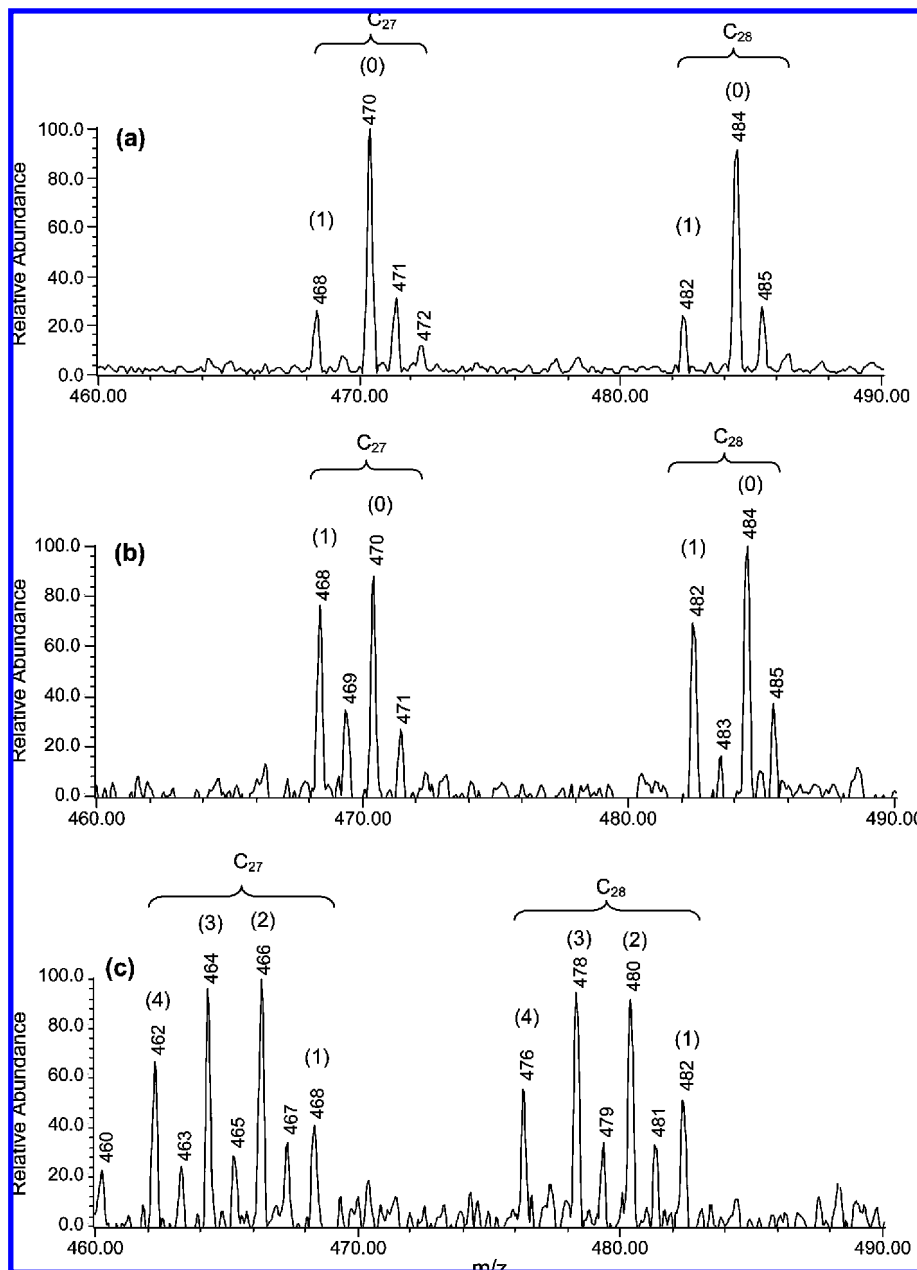
Figure 4. Expanded (m/z 460−490) LIAD/ClMn(H_2O)$^+$/FT-ICR mass spectra of three base oil samples: (a) G2F1 (average of 7 scans); (b) G2F2 (single scan); (c) G2F3 (average of 8 scans). The numbers in parentheses represent the number of rings in the cycloparaffins.

values of product ions decrease by 2 Da for each additional ring (or degree of unsaturation), it is concluded that the product ions of m/z 468, 466, 464, and 462 come from four different C_{27} cycloparaffins: $C_{27}H_{54}$ (1-ring), $C_{27}H_{52}$ (2-ring), $C_{27}H_{50}$ (3-ring), and $C_{27}H_{48}$ (4-ring), respectively. A similar situation applies to the C_{28} alkanes (m/z 482, 480, 478, and 476). No product ions (m/z 470 and 484) from paraffins were observed. This result indicates that sample G2F3 mainly contains one- to four-ring cycloparaffins.

Quantitation. The percentage of different types of hydrocarbons (i.e., paraffin versus cycloparaffin) in the base oil samples can be obtained by considering the relative abundances of the product ions. For instance, further analysis of the relative abundances of the product ions representing different types of hydrocarbons in the two samples in the first group (G1F1 and G1F2) reveals that these samples contain 100 and 76.2% paraffin, respectively (Figure 5). These results are in a good agreement

with the percentages of paraffin (94.3 and 69.7%, respectively) measured by SFC for these two samples (Table 2). An overall comparison of the data obtained by the LIAD/ClMn(H_2O)$^+$ mass spectrometry method and other techniques is shown in Table 2. In every case, the average carbon number and percentage of total paraffins measured by the LIAD/ClMn(H_2O)$^+$ method are in excellent agreement with the results obtained by GC and SFC, indicating quite uniform ionization/desorption efficiency for hydrocarbons of different types and with different molecular weights.

For the second group of samples, the mass spectrometric analysis yields information on the percentage of cycloparaffins containing one, two, three, or four rings, which is not attainable by GC or SFC. For example, for sample G2F1, SFC can only provide the percentage of total paraffins (76.0%) versus all types of cycloparaffins (24.0%), not the percentage of each different type
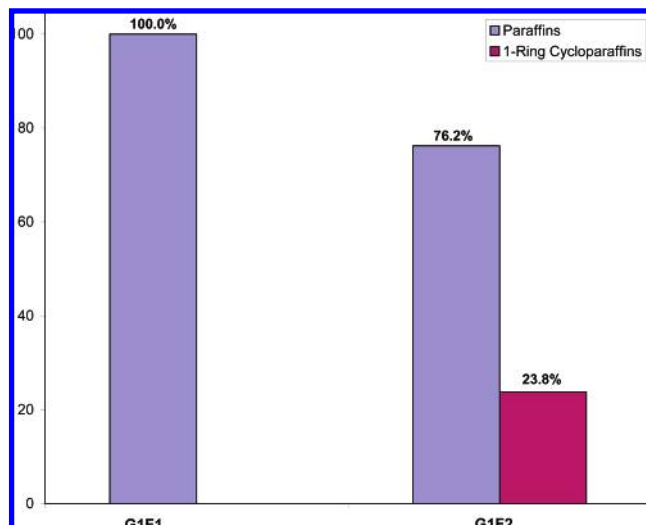
Figure 5. Bar chart of the percentage of total paraffins and 1-ring cycloparaffins in base oils G1F1 and G1F2.
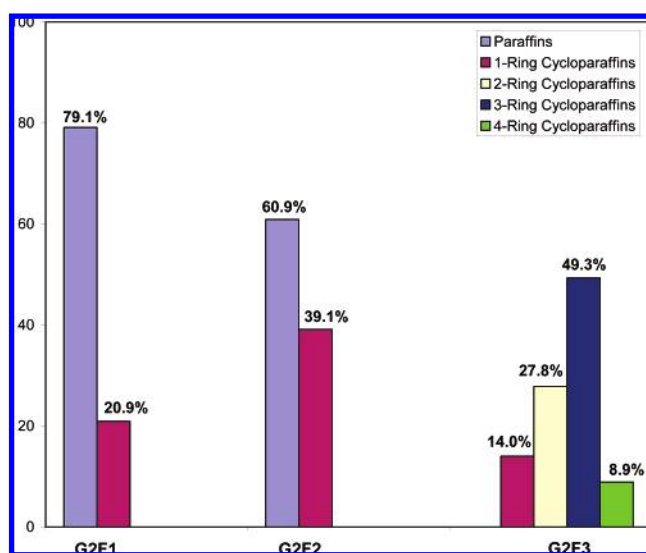
Figure 6. Bar chart of the percentage of total paraffins and 1- to 4-ring cycloparaffins of base oils G2F1, G2F2 and G2F3.

of cycloparaffin. However, this information is readily obtained from the mass spectra. For example, the samples G2F1 and G2F2 were found to contain 20.9 and 39.1% cycloparaffins, respectively (Figure 6), all of which contain only one ring (Figures 4a and b). However, the sample G2F3 contains 100% cycloparaffins, of which 14.0% are one-ring cycloparaffins, 27.8% are two-ring cycloparaffins, 49.3% are three-ring cycloparaffins, and 8.9% are four-ring cycloparaffins (Figures 4c and 6).

CONCLUSIONS

This study demonstrates that the combination of LIAD/ClMn-$(H_2O)^+$ CI with FT-ICR mass spectrometry offers a promising new method for the molecular-level characterization of base oils. Based on an earlier study on many model compounds,[32] chemical ionization with $ClMn(H_2O)^+$ is expected to yield a sole product ion, $[ClMn + M]^+$, for each compound (M) in the base oil samples. This was found to be true, with one exception (sample G2F3). The mass spectra indicate the presence of homologous series of ions differing in mass by multiples of 14 Da (i.e., CH_2). MW distribution of each base oil sample was obtained from the analysis of the product ions' m/z distribution in the measured mass spectra. The average carbon number calculated from the average molecular weight (M_w, after correcting for ClMn mass of 90) for each sample is in good agreement with the result obtained by GC. Information on the different types of hydrocarbons present in the base oil samples can be obtained from a further analysis of the product ions' m/z values. The percentage of the different types of hydrocarbons (i.e., paraffin vs cycloparaffins with one or several rings) in the base oil samples can be obtained by considering the relative abundances of their product ions. The percentages of total paraffins measured here are in a good agreement with the values measured by SFC for these samples. The general agreement of LIAD/ClMn$(H_2O)^+$ results with those obtained in the bulk analyses suggests that this method has a uniform ionization/desorption efficiency for hydrocarbons with varying compositions and molecular weights. This feature presents a key advantage of the technique in hydrocarbon quantification applications. Further, the mass spectrometric analysis also yields information on the percentage of different cycloparaffins (here containing 1, 2, 3, or 4 rings), which is not attainable by GC or SFC. Hence, three important parameters (MW distributions, hydrocarbon types, as well as their percentages) can be obtained in a single experiment. This mass spectrometric technique therefore provides detailed molecular-level information for base oils, which cannot be obtained by other analytical methods.