Compositional elucidation of heavy petroleum base oil by GC×GC-EI/PI/CI/FI-TOFMS

Authors:

Anupam Giri[1], Marion Coutriade[3], Amandine Racaud[3], Pierre-Hugues Stefanuto[2], Koji Okuda[4], John Dane[4], Robert B. Cody[4], Jean-François Focant[2*]

Affiliation:

[1]SABIC, Analytical GTC-EUR, Plasticslaan 1, 4612CX Bergen op Zoom, The Netherlands

[2]University of Liège, Department of Chemistry, Organic & Biological Analytical Chemistry Group, Allée du 6 aout, B6c, B-4000 Liège (Sart Tilman), Belgium

[3]Total Marketing Services, Centre de Recherche de Solaize, Chemin du Canal - BP 22, 69360 Solaize, France

[4]JEOL USA, 11 Dearborn Road, Peabody, MA 01960, USA

To whom correspondence should be addressed:

E-mail: JF.Focant@uliege.be

Phone: +32 4 366 35 31

Fax: +32 4 366 43 87

Abstract

Comprehensive two-dimensional gas chromatography (GC×GC) coupled to time-of-flight mass spectrometry is a powerful separation tool for complex petroleum product analysis. However, the most commonly used electron ionization (EI) technique often makes the identification of the majority of hydrocarbons impossible due to the exhaustive fragmentation and lack of molecular ion preservation, prompting the need of soft-ionization energies. In this study, three different soft-ionization techniques including photo ionization (PI), chemical ionization (CI), and field ionization (FI) were compared against EI to elucidate their relative capabilities to reveal different base oil hydrocarbon classes. Compared to EI (70 eV), PI (10.8 eV) retained significant molecular ion ($M^{+\cdot}$) information for a large number of isomeric species including branched-alkanes and saturated mono-cyclic hydrocarbons along with unique fragmentation patterns. However, for bi-/poly cyclic naphthenic and aromatic compounds, EI played upper hand by retaining molecular as well as fragment ions to identify the species, whereas PI exhibited mainly molecular ion signals. On the other hand, CI revealed selectivity towards different base oil groups, particularly for steranes, sulfur-containing thiophenes, and esters; yielding protonated molecular ions $(M+H)^+$ for unsaturated and hydride abstracted ions ($M-H^+$) for saturated hydrocarbons. FI, as expected, generated intact molecular ions ($M^{+\cdot}$) irrespective to the base oil chemical classes. It allowed elemental composition by TOFMS with a mass resolving power up to 8,000 (FWHM) and a mass accuracy of 1 mDa, leading to the calculation of heteroatomic content, double bond equivalency, and carbon number of the compounds. The qualitative and quantitative results presented herein offer a unique perspective into the detailed comparison of different ionization techniques corresponding to several hydrocarbon classes.

KEYWORDS: Base oil, Hydrocarbons, Ion source, Mass spectrometry, Photo ionization, Field ionization, Chemical ionization

1 | INTRODUCTION

Lubricating oil is widely used in automobile engines and other machines. It plays a critical role to reduce friction, ensuring machines to be energy efficient.[1] The improvement of the quality of lubricating oils is often considered as important as new engine design solutions.[2] Increased government regulations, environment protection requirements, and consumer expectations have resulted in an increasing number of new products on the market. The growing diversity of lubricating oils displays a variety of physiochemical properties and chemical compositions. Thus, the comprehensive fingerprinting of lubricating oil is required for better understanding of physicochemical properties, group type classifications, forensic evidence against adultery, illegal production, identification and tracking source of spillage.[1,2]

Several spectroscopic techniques such as fluorescence, infra-red as well as UV-Vis have been reported for oil analysis.[3-5] Although these techniques can provide rapid screening of oil samples, they are unable to resolve components in samples. The use of chromatographic techniques[6-8] prior to mass spectrometric detection is widely used for characterization of complex petroleum oils. Among different chromatographic techniques, gas chromatography (GC), and in particular two-dimensional GC (GC×GC) is trending since its invention two decades ago.[9,10] It is due to superior compound separation and production of structural elution patterns leading to improved characterization of complex petroleum oils, as reported elsewhere.[11,12] Several detectors, including flame ionization (FID),[13] electron capture (ECD),[14] sulphur chemiluminescence (SCD),[15] nitrogen chemiluminescence (NCD),[6] and most importantly time-of-flight (TOF) mass spectrometric detectors[16] were successfully applied to GC×GC applications. TOFMS, as a fast acquisition mass selective detector, is always the preferred choice for qualitative analysis, allowing to perform acquisition of mass spectra of fast eluting compounds without spectral skewing. The type of source used for ion production prior to mass separation, greatly impacts the formation and the extent of the ionization of molecules.[17] Commonly used electron ionization (EI) has high ion yield and sensitivity, and generates highly reproducible spectra. However, for some group of compounds, particularly for hydrocarbons, EI is too energetic to preserve molecular ions that are crucial for positive identification of the molecule. In contrast, a soft ionization technique like field ionization (FI)[18] produces abundant molecular ion signals. However, FI generates little or no fragmentation at all, providing no structural information (fragments) anymore. Other ion sources include chemical ionization (CI),[19] photo ionization (PI),[11] variable ionization,[12] atmospheric pressure photo ionization (APPI),[20] atmospheric pressure laser ionization (APLI).[21] In general, CI, performed under vacuum or at atmospheric pressure, reveals molecular ions but is highly condition-dependent (reagent gases, flow, humidity, temperature, source geometry etc.).[22] Next to these techniques, PI is (re)emerging as a more universal soft-ionization technique due to its limited dependency only towards the type of lamp used as the photon source. A recent study using PI for the consideration of a wide range of chemical classes revealed that both the retention of molecular ions and the minimal production of structurally significant fragments enables unambiguous identification of a vast majority of analyzed compounds.[11] Despite these significant differences between the soft ionization techniques available for GC-MS, very limited comparative assessments are available, particularly for lubricating oils that exclusively contain hydrocarbons that are highly susceptible to hard ionization.

In this paper, we present a comprehensive comparison of four ionization techniques, EI, PI, CI, and FI for different base oils, which are the major contributors (>80%) of lubricating oils. EI/PI combination ion sources, CI, and FI sources were evaluated under the same GC×GC conditions and same TOFMS detector. Combined ion sources enabling to switch between ionization modes without breaking the vacuum were used as they also allow accurate matching of different ionization data thus providing structural information about different compounds separated by employing same GC×GC chromatographic conditions. The comparison of different ionization data on a wide range of hydrocarbon classes present in base oils were carried out to develop better understanding of ionization mechanisms and extent of fragmentation for a wide range of molecules. Detailed structural elucidation of hydrocarbon classes including, saturated branched alkanes, naphthenic, polycyclic and aromatic compounds were carried out for understanding of the complex molecular composition of base oils.

2 | MATERIALS AND METHODS

2.1 | Samples and chemicals

Several base oil samples belonging to several American Petroleum Institutes (API) groups (I-IV) were analyzed with special emphasis on two samples, base oil 1 (Group I) and base oil 2 (Group II). Base oil 1 was a product of solvent free manufacturing process with less than 90% saturates and more than 0.03% sulfur. Whereas base oil 2 was hydro-processed, containing more than 90% saturates and less than 0.03% sulfur. GC grade solvents, particularly hexane, were used for dilution. Sublimated benzophenone (purity >99%) was obtained from Sigma-Aldrich (St Louis, MO, USA). A gravimetric mixture of paraffins, naphthenes, mono- and poly-aromatics was obtained from AC Analytical Controls, PAC, France.

2.2 | Multidimensional GC (GC×GC) instrumentation

A gas chromatograph (7890B, Agilent Technologies, Wilmington, DE, U.S.A.) equipped with a Zoex ZX2 thermal modulator (Houston, TX, U.S.A.) and an auto-injector (7693A Agilent Technologies) was used for cool-on-column injection. A low-polar (ZB-XLB-HT Inferno, 15.0 m, 0.25 mm ID, 0.1 µm, Phenomenex) and polar (ZB-50HT, 2.0 m, 0.1 mm ID, 0.1 µm, Phenomenex) columns were used for base oil analysis for first and second dimension separation respectively. Deactivated column was used as modulation loop (1.0 m, 0.1 mm ID) and also for TOFMS transfer line (0.5 m, 0.1 mm ID). Helium was used as the carrier gas in constant flow mode.

2.3 | Ion sources and MS configuration

A EI/PI combination ion source, and dedicated CI, and FI sources were used to evaluate and compare different ionization modes for base oil analyses. A unique GC×GC instrument, operating in identical conditions was interfaced with all four ion sources at the exception of an adapted modulation period (P_M) of 6 sec (instead of 5 sec) for the use of the CI source. A detailed description and application of the EI/PI combination ion source (JEOL, Japan) was recently reported.[15] In brief, a minimal modification was made in the EI source block to use it as an EI/PI source. Redesigning of the repeller part allows direct exposure of photon to the ion volume. A deuterium lamp (D_2 lamp, L7293; Hamamatsu, Japan) was used for photon emission. Current PI conditions are strictly single-photon photo-ionization with a maximum energy output of 10.78 eV at 115 nm. The description of CI and FI sources (JEOL, Japan) is available elsewhere. For CI, a reagent gas mixture of methane (95%) and ammonia (5%) was used with a flow rate of 1.0 mL/min. To avoid detector overloading, appropriately diluted base oil samples were introduced to cool on-column (COC) inlet (25-fold dilution for PI, CI, and FI; 200-fold dilution for EI in hexane). Details of ion source parameters used are listed in SI, S1. A time-of-flight mass spectrometer (AccuTOF GCv 4G, JEOL, Japan) was used to acquire data at a mass resolution of >8000 FWHM.

2.4 | Quantitative comparison of ion sources using benzophenone

Mono-dimensional GC (DB-5MS, 29.0 m, 0.25 mm ID, 0.25 μm, Agilent J&W) condition (see SI, S1) was used to assess quantitative aspects of different ion sources using a series of benzophenone solutions ranging from 1 ppb to 1 ppm in triplicate. Critical detection parameters including detector voltages, FI probe conditions, and quality control check for the sensitivity of the instrument were also evaluated under these chromatographic conditions.

2.5 | Data treatment and visualization

GC×GC data were processed and visualized using GC Image v2.5 (Zoex Corporation, Houston, U.S.A.). Global mass spectra were drawn using mMass software (V.3, open source). Signal-to-noise ratios were calculated using MassCenter software (JEOL, Japan). *Ab initio* computations of the vertical ionization potential (IP_V) expressed as a negative of HOMO, appearance potential expressed as HOMO-LUMO gap, were performed for different hydrocarbon classes of base oils using the Spartan'16 program package.[23-25]

3 | RESULTS AND DISCUSSION

3.1 | Chromatographic separation and identification of base oil hydrocarbons

Success of base oil analysis was extremely relied on optimal separation leading to pull base oil components apart to obtain near pure spectra for identification and further characterization. Thanks to comprehensive two-dimensional gas chromatography (GC×GC), by adopting low-polar and polar (ZB-XLB-HT Inferno, ZB-50HT) column set, a best possible separation was achieved for several group of hydrocarbons. GC×GC being widely orthogonal compared to ID separation, compounds were separated in the first dimension based on volatility and polarity in the second. Thus, the molecular mass, one of the most selective information is highly related to the elution order of the corresponding compound. On the other hand, along the second axis relatively apolar saturated alkanes were eluted first followed by saturated and aromatics with increased polarity. Contour plot presented in Figure 1 showed the typical structured pattern of GC×GC separation for several groups of hydrocarbons including, *n*-paraffins, *iso*-paraffins, mono-, di-, polycyclic saturated, and aromatic compounds for different ion sources including EI, PI, CI, and FI. Results revealed that EI, PI and FI profiles were superficially similar to each other, whereas CI was distinctively different. In depth observation of different first dimension retention times (${}^1t_R$) and second dimension retention times (${}^2t_R$) elution zones demonstrated the differences of separations achieved by different ionization techniques and their visualization efficiencies (see SI, S2). As expected, CI exhibited varied sensitivity towards base oil components compared to other ionization techniques. Noteworthy to highlight that infusion of CI reagent gas at 1 mL/min significantly affected ion source vacuum resulting lower carrier gas flow rate leading to slower elution of compounds. Thus, to avoid wraparound of the polar compounds, a 6 sec modulation period (P_M) was used instead of the 5 sec P_M used for EI, PI and FI. The infusion of CI reagent gas further resulted in the distortion of peak shape, as visualized in SI, S2.

n-Alkanes, mono-, di-, tri-methylalkanes and highly branched isoprenoids were the most abundant saturated hydrocarbons detected in base oils. The identification and separation of such acyclic branched hydrocarbons in complex matrix like base oil are extremely difficult by using conventional GC/MS. This is due to two reasons. Firstly, the great number of isomeric possibilities leads to the close retention time. Even the retention times of n-alkanes are distinctively different from each other, their retention times may be close to other structural isomers. Equipped with a 100 m column Krkošova *et al.* reported[26] 196 monomethyl alkanes in diesel fuel using GC/MS in the range of C4-C30. Szabo *et al.*[27] reported 63 isomers for the C19 in exhaled breath. These results are just few examples of huge isomeric probabilities of paraffinic hydrocarbons in complex sample that could pose difficulties in chromatographic separation, justifying the need for GC×GC. Secondly, the use of conventional 70 eV EI ion sources results in extensive fragmentation of molecules with limited or no presence of molecular ions. In this study, the identification of compounds was enabled by comparing the structural elution pattern as well as comparison of mass spectra obtained from standard paraffins, naphthenes, mono- and poly-aromatics, and also by interpretation of mass spectral data obtained by EI, PI, CI, and FI. The interpretation of mass spectral fragmentation pattern was facilitated by *ab initio* calculation of orbital energy. Maclot *et al.*[28] recently demonstrated a strong correlation between the excited states of the ionized molecule with the computed dissociation pathways, as well as with charge localization or delocalization. By combining ion collisions, VUV photo ionization along with *ab initio* calculations, they provided a complete picture of the charge localization and the excitation energy distribution in complex molecular systems after interaction with ionizing radiation.

3.2 | Fragmentation patterns for different ion sources

The evaluation of global mass spectra of a base oil for different ion sources revealed exhaustive fragmentation in EI leading to the smaller fragments of homologous series of butyl (*m/z* 57), pentyl (*m/z* 71), hexyl (*m/z* 85) etc., accompanied by a set of corresponding alkenyl and alkynyl carbocations (loss of 2H or 4H, respectively) with limited or no presence of molecular ions. All the significant ions in EI spectrum were even-electron ions. In contrast, FI exclusively produced molecular ions by removing an electron from the molecule under a strong electric field. As the resulting positively charged molecular ions have little excitation, it yields to little or no further fragmentation. On the other hand, both PI and CI not only retained the molecular ions but also exhibited significant fragment ions. In PI, the absorption of photon by a gaseous molecule resulted in molecular radical cation as the primary product. Fragment ions might be generated as a result of absorption of a photon by a primary photo-dissociation product, neutral loss from the radical ions, and ionic fragmentation during photoionization step. Whereas, CI revealed the hydride abstracted ions $(M\text{-}H)^+$ and/or the protonated molecular ions $(M+H)^+$ for base oil hydrocarbons. Significantly higher fragments in CI than PI indicated that the internal energy distribution of current CI configuration lay above PI (10.8 eV) and well below EI (70 eV).

Mass spectral patterns of selected base oil components for different ion sources are presented in Figure 2 and in SI, S3 with details. A series of paraffinic compounds including *n*-paraffins (C16-C44), *iso*-paraffins (C16-C44), *iso*-prenoids (C18-C36) were detected for base oils. The fragmentation pattern for *n*-paraffins and *iso*-paraffins at 70 eV EI revealed clusters of peaks 14 mass unit apart representing loss of $(CH_2)_nCH_3$ with limited or no presence of molecular ion. For *iso*-prenoids, the cleavage of the C−C bond adjacent to the tertiary carbon resulted structurally significant odd ions as suggested by Klomp[29] and Fowler & Douglas.[30] However, such characteristic ions were significantly lower than other nonsignificant fragments of low mass alkyl chains in EI. Several early[31,32] and recent[12] works on alkanes established that by reducing the EI electron voltage from 70 to 14 or 12 eV, relative intensity of molecular ion could be increased. However, alkyl branch fragments (i.e. *m/z* 43, 57, 71, 85, 99, 127 and so forth) were still highly abundant and overlapped the structurally significant ions. In contrast, the facile fragmentation achieved by PI greatly simplified mass spectra with reduced background noise as well as enhanced molecular ions for paraffinic compounds. PI retained molecular ions as a base peak for *n*-paraffins along with several CH_2-cleaved mass fragments at lower abundances. For *iso*-paraffins, predominant ions signified the probability of cleavage at lower state of excitement, revealing the branching position. The systematic elution pattern of branched alkanes in GC×GC structured chromatogram revealed several mono-, di-, and heavily branched alkanes for base oil 2 as demonstrated in Figure 3 for C20 isomeric species with fragmentation hypothesis. Similar observation was reported earlier where 14 isomeric species of alkanes were identified in a base oil sample using PI.[11] In positive CI (methane with 5 % ammonia), alkanes were characterized by abundant $(M\text{-}H)^+$ ions, which originated from hydride abstraction. The fragmentation of the quasi molecular ion yielded in lower mass alkyl ions with moderate intensity, though such fragments provided little or no structural information, including branching position. Ions with the same *m/z* as molecular ions ($M^{+\cdot}$), were also observed and might be regarded as isotope abundant ions of the predominant $(M\text{-}H)^+$ ion and not as molecular ions. For FI, as expected, exclusively $M^{+\cdot}$ ions were observed for alkanes.

Naphthenic compounds including mono-, bi-, and polycyclic alkanes were detected in base oils (see Figure 2 and SI S3). Group-based identification of alkylcyclohexane and alkylcyclopentane series was achievable on the basis of typical EI spectra corroborated with published data.[33,34] However, the EI mass spectra lacked molecular ion information. Different analogues (i.e. alkyl-, methyl-) were dominated by fragments at *m/z* 55, 67, 83, 97, 111 respective of methyl or alkyl substitutions. Small differences in their patterns were generally considered to discriminate the probable substitution of the cyclohexane or cyclopentane ring.[35] The dominance of *m/z* 69 and 87 ions was likely due to the methyl substituted alkylcyclopentane or alkyl cyclohexane. Such differences often remained insignificant to assign the compounds in EI.[35] However, PI resulted in dominant molecular ion ($M^{+\cdot}$) and the ions at *m/z* 82 and 68 for alkylcyclohexanes and akylcyclopentanes respectively, related to the corresponding ring. Methyl-substituted isomers were tentatively identified by the presence of molecular ions and predominant ions at *m/z* 96, 110, 124 and 138 for alkylcyclohexane and at *m/z* 82, 96, 110 and 124 for alkylcyclopentane corresponding to the C-C cleavage of the alkyl chain from methyl substituted ring. In CI, hydride abstracted $(M-H)^+$ ions were observed for mono-, bi-, or polycyclic alkanes. Abundances of $(M-H)^+$ ions were significantly lower in mono-cyclic alkylcyclohexanes or alkylcyclopentanes than lower mass alkyl ion fragments. With the increase in carbon number in the alkyl chain, relative abundances of $(M-H)^+$ ions were decreased significantly (see SI, S3).

For bi-cyclic alkanes, base ion at *m/z* 137 along with $M^{+\cdot}$ ions facilitated the identification by EI. In PI, molecular ions emerged as base peak with fragment peak at *m/z* 137. The fragment ion at *m/z* 137 corresponded to a cleaved C10 decalin ion. Several tri-, tetra-, penta-, and hexa-cyclic compounds were detected in base oils. One of the tri-cyclics were characterized by $(M^{+\cdot})$ base ions and *m/z* 191 corresponding to ring fragment, identified as tricyclic terpenes consisted of a perhydrophenanthrene ring skeleton.[36] Another set of tri-cyclics was characterized by $M^{+\cdot}$ ions as base peak and peak at *m/z* 151, 177, 191 and 205 in EI, tentatively identified as methyl-, ethyl- or alkyl- substituted perhydrophenanthrene, perhydroanthracene and dodecahydrofluorene analogues.[35] With the increase in number of fused saturated cycle in the structure, the abundance of molecular ions dramatically increased with limited or no presence of fragments in EI. Like monocyclic alkanes, CI resulted hydride abstracted molecular $(M-H)^+$ ions for bi-, tri- or polycyclic alkanes. Relative abundances of molecular $(M-H)^+$ ions were gradually increased with the increase in the number of cycle in the structure. These results are in agreement with reported results on paraffinic and naphthenic compounds analyzed by CI.[37] FI yielded $M^{+\cdot}$ ions for all the naphthenic compounds. Hopanes were positively identified in base oil 1. Characteristic EI/PI fragment ions at *m/z* 191, 205, 163/177, and 123/193 for hopane, methylhopane, trisnorhopane, and secohopane, respectively enabled positive assignments of compounds corroborated with dominant $M^{+\cdot}$ ions with high mass accuracy. CI and FI resulted in hydride abstracted molecular ions $(M-H)^+$ and $M^{+\cdot}$ respectively.

Aromatic compounds, including series of monomethyl-, dimethyl-, and trimethyl- alkyl benzenes, were positively identified in base oil and corroborated by characteristic EI fragments at *m/z* 92, 105, 119 and 133 signifying cleavage of C-C bond next to benzene ring (Figure 4). Similarly, isomeric species of methyl-, ethyl-, propyl- substituted alkyl benzenes were identified in base oil. PI, however, exhibited poor peaks for such characteristic fragment ions despite higher abundance of $M^{+\cdot}$ ions. Unlike saturated acyclic and cyclic compounds, CI resulted highly abundant protonated molecular ions $(M+H)^+$ for aromatic compounds due to higher proton affinity. Fragments corresponding to methyl- or alkyl- group cleavage were also highly abundant, revealing the branching position. Steranes were characterized by higher abundance of molecular ions ($M^{+\cdot}$) along with prominent peak at *m/z* 218, 217, 259 in EI. Cholestane, ergostane and stigmastane were most abundant among those. In PI, $M^{+\cdot}$ ions emerged as base peak with significant peaks at *m/z* 218. CI resulted protonated molecular ions $(M+H)^+$ as a base peak. As expected, FI resulted exclusively $M^{+\cdot}$ ions for aromatics and steranes.

To understand ionization and/or fragmentation pattern and probabilities, theoretical vertical ionization potentials (IPv) were calculated for hydrocarbon families associated to base oil. The IPv values gradually decreased with the increasing number of fused cyclic core (Figure 5). This was true for both saturated and unsaturated hydrocarbons. In addition, the increasing carbon number in alkyl chain further decreased the IPv values. It implied that higher cyclic hydrocarbons would be more easily ionized than the lower one. On the other hand, keeping the general rules for carbocation stability (Stevenson's rule) in mind, higher stabilities would be observed in following order: most stable cyclic > allylic > tertiary > secondary > primary > least stable.

3.3 | Selectivity and sensitivity for different ion sources

Molecular ion intensity and their relative abundances are tabulated in SI, S3 for Base oil 1 and 2 belonging to Group I and II, respectively. Relative abundances of molecular ions, highlighted by color scale, revealed a large variability in sensitivity towards different chemical classes for different sources. The ionization potential of the majority of molecules is below 70 eV. So, EI at 70 eV covers a wide array of molecules to efficiently ionize and further fragment depending on the excess energy that remains within the molecule. Contour plot obtained from PI reveals that majority of the base oil chemical classes are also ionized by PI (Figure 1). Analysis of standard mix (century mix) for several chemical classes and different types of petroleum matrices revealed that EI and PI have comparable selectivity towards majority of the chemical classes analyzed; however, not exactly the same (see SI S9). Intensity of contour plot and cumulative 2nd dimension plot (2D) revealed that alkanes and naphthenic compounds are relatively more sensitive in EI than PI compared to aromatics (see SI S3). However, no drastic differences in contour plots for EI and PI was observed. Noteworthy to highlight that PI's ability to detect majority of the organics has made this technique as universal soft ionization.[38]

Facile fragmentation of the compounds in PI was observed than EI. In EI, high-energy electrons are accelerated across the source at right angles to the stream of neutral molecules in the gas phase, resulting in the ionization of suitable bonds. Furthermore, typical fragmentation and rearrangement possibilities are well classified reaction types such as alpha and inductive cleavage, retro-Diels–Alder, and the McLafferty rearrangement. Whereas, single-photon flask in PI results absorption of photon by a gaseous molecule to form a molecular radical cation as the primary product, and further fragmentation due to absorption of a photon by a primary photodissociation product, neutral loss from the radical ions, and ionic fragmentation during photoionization step.

On the other hand, under the current positive CI condition (methane+ammonia), a certain degree of selectivity was observed towards certain group of compounds in base oil 1 as visualized in Figure 1 and SI, S3. Noteworthy to mention that selectivity of CI not only depends on source condition (reagent gas, pressure, temperature, and polarity) but also the diversity of proton affinity of the compound classes resulting ions through proton transfer, hydride abstraction, electrophilic addition etc. In depth observation of contour plots of base oil 1 (see SI, S5) clearly revealed the high selectivity of CI towards two chemical classes of base oil 1, esters and benzothiophenes. Interestingly, elution zones of esters were very close to alkyl benzenes and its methyl/ethyl-substituted analogues at $^{2}t_{R}$, which is in agreement with previous reports.[11] Therefore, in other sources, particularly in EI, though the presence of esters were confirmed by extracted ion chromatograms, mass spectra was heavily shadowed by coeluting alkyl benzene fragments, rendering difficulties to successfully detect and identify esters in base oil 1. In CI, highly intense protonated quasi molecular ions $(M+H)^+$ along with low intensities of hydride-extracted molecular ions $(M-H)^+$, adduct ions $(M+C_2H_5)^+$ and $(M+C_3H_7)^+$ were also yielded. Similar fragment patterns were also reported by Aichholz and Lorbeer,[39] with positive CI (methane) analysis of saturated wax esters with highly intense protonated molecular ions. Similarly, benzothiophenes, due to their high proton affinity, were easily detected by CI, compared to other sources in base oil 1, which was well reported in several related petrochemical products.[40] The improved selectivity of heteroatom classes including sulfur containing compounds with a larger enhancement in the relative abundance of protonated molecular ions was also reported earlier by using chemical ionization of petroleum.[41,42] FI, however, exhibited almost similar profile than EI and PI for base oil 1, with a slightly higher selectivity towards steranes and aromatic compounds, as visualized in Figure 1 and SI, S4. Such ionization selectivity could be explained by the lower internal energy distribution of aromatics compared to other hydrocarbon classes, as depicted in Figure 5 in terms of IPv. Selectivity of different ionization techniques were well visualized in base oil 1 belonging to Group I because it contained saturated, aromatic and heteroatoms containing hydrocarbons. However, as expected, in base oil 2 belonging to Group II which exclusively comprised of saturated paraffinic and naphthenic hydrocarbons devoid of aromatics and heteroatoms, limited or no ionization-based selectivity was visualized (data not shown).

From the detection point of view, sensitivity of different ion–sources were also compared. Undoubtedly, the total ion current generated for any given compound through ionization is much higher for EI, followed by CI, FI and/or PI, due to their ionization efficiency, respectively, as reported elsewhere.[43] In addition, the sensitivity is also depending on the type or functional group of the compounds, due to diverse ionization selectivity of different ion sources, as discussed earlier. There is no consensus approach available to compare the sensitivity of different ion sources for mass selective detectors. This is due to the diverse fragmentation mechanisms involved in different ion sources resulting unique fragment patterns. Since, the use of total ion current (TIC) is not practically suitable for quantitative purpose due to the complexity involved in separation of the compounds in the majority of the applications, we have to select suitable ions for quantitative purpose. The selection of such quantifier ions could be completely different for different ion sources. For example, the direct comparison of sensitivities of EI and FI for saturated alkanes could not be possible due the fact that EI produces no molecular ions although FI produces exclusively molecular ions. Moreover, different variant of molecular ions, including radical, protonated, hydride abstracted or even adduct ions could emerge from different sources. Even for radical ions, generated from EI, PI and FI, it might pose different radical site with different reactivity and stability.[44] So, no common quantifier can easily be found to compare the sensitivity. Molecular ion intensities for different groups of hydrocarbons for two base oil samples presented in SI, S3 revealed only the relative abundances. Moreover, for proper visualization and to avoid overloading of the compounds, appropriately diluted base oil samples were injected and analyzed by EI (200-fold dilution in hexane), CI (25-fold), PI and FI (10-fold), thus, direct quantitative comparison is not possible. So, a more realistic approach was adopted to obtain comparative sensitivity information by constructing calibration curves for a single analyte, benzophenone (BP), under identical one-dimensional chromatographic condition (see SI, S1). It allowed the comparison of ion sources for total ion generation, molecular ion specific intensity, LOD/LOQs, linearity, as well as reproducibility. EI resulted in characteristic fragmentation, whereas, PI and FI yielded to $M^{+\cdot}$ ions, and CI generated protonated molecular ion $(M+H)^+$ (see SI, S6). In agreement with the common understanding, TIC-based calibration curves revealed higher ion generation for EI followed by CI, FI and PI (see SI, S7). However, higher sensitivity could be achieved by molecular ion-based quantification for CI than EI followed by FI and PI, due to occurrence of fragmentation in EI. Good linearity (in terms of correlation coefficient, r^2) was achieved for BP calibration curves (10 to 500 ppb) for all ion sources. However, reproducibility, evaluated through the calibration experiments (in terms of RSD%) was relatively poor for CI (6.3%), moderate for PI and FI (3.1-3.5%), and best for EI (0.4%). Realistic instrumental LODs and LOQs were determined using calibration functions.[43] In brief, instrumental LODs and LOQs were calculated as respectively 3 and 10 times the ratio of the standard deviation (SD) of signals at the lowest calibration level and the slope of the calibration curve. CI resulted in the best predicted LOD/LOQ (0.3 ppb, 1.1 ppb), followed by moderate values for EI and FI (3.1-4.6 ppb, 10.2-15.6 ppb), and relatively low for PI (10.2 ppb, 34.0 ppb). Noteworthy to mention that these comparative outcomes are extremely specific to the current detector specification used. There are several parameters that can dramatically affect such findings. For example, an increase in detector voltage from 1900 to 2100 V can increase sensitivity of a factor of 25-fold as evident for EI data (see SI, S8A). Conditions of FI emitter were also found to be affecting the detection power. By replacing the old emitter (unknown number of injections, probably >100) with a new one, a 10-fold increase in signal-to-noise ratio was achieved (see SI, S8B). The geometry of the different ion sources also affected the sensitivity. The use of a dedicated EI source increased ion intensity of about 5-fold for BP, compared to the use of the combination EI/PI source, indicating better ionization efficiency in dedicated EI source (data not shown). As in EI, the temperature of the ion source and electron energy greatly influence the sensitivity of CI along with the type of reagent gas and polarity used.

Chromatographic resolution achieved by GC×GC can further be enhanced by coupling high resolution (HR) MS. HRMS has the ability to resolve very narrow mass differences between isobars; e.g., C3 vs SH4 (0.0034 Da), CH2 vs N (0.0126 Da), and CH4 vs O (0.0364 Da), at m/z 300 have resolving power requirements of 89000, 24000, 8400 respectively, for their separation with equal peak intensity. Unlike direct infusion, in GC×GC it is highly unlikely that such isobars occupy same time domain, thus resolving power requirement would be lower. GC×GC-soft ionization-HRMS with prominent molecular ions can add several other dimensions on top of two dimensional chromatographic separation. Depending on the resolving power of the MS, added dimensions could be a) calculating elemental compositions, b) differentiating isobars with narrow mass splits, and c) mass defect based analysis, e.g., Kendrick Mass Defect (CH_2), O_2 or N_2 for improved visualization and characterization (see S9). However, isomeric separation is entirely dependent on GC×GC chromatographic separation.

4 | CONCLUSIONS

The extensive fragmentation at 70 eV EI was extremely useful for group-based identification of different hydrocarbon classes. However, molecular ions at 70 eV EI were often barely visible or absent for alkanes or mono-cyclic alkanes. On the other hand, for bi-, or poly-cyclic naphthenic, and mono-aromatic compounds, EI still remains advantageous to elucidate isomeric species. Typically, CI would not be suitable for non-targeted profiling purpose due to high selectivity, lack of universal detection criterion, and variety of fragmentation mechanisms involved. FI, being the softest ionization method, molecular ions were produced for base oil hydrocarbons, allowing direct quantitation based on the intensity of the molecular ions by obviating the need for complex matrix inversion routines. In addition, coupling to high-resolution MS, compound formulae can easily be derived from the abundant molecular ions that opens up a wide array of analysis or visualization approaches straightway. Sensitivity is still an issue for FI, however, it can be compensated by improving the detector capacity. PI has a huge potential for structural elucidation of isomeric species of wide range of functional groups particularly for saturated alkanes. Apart from ionization, photons with different energies can potentially influence the chirality of isomers by switching the helicity, known as photoisomerization. Thus, by tandem MS, chiral isomer specific fragment ions can be monitored. Although the PI D_2 lamp itself cannot vary the energy, lamp with different gases like Ar, Kr, Xe, etc. emit different energy making the ionization selective towards certain application. Another important aspect is that current combination EI/PI source allows several tailor-made approaches including simultaneous hybridization of electron/photon ionization. Preliminary investigation indicated that this approach can be a powerful tool for cross section-based application to unravel structure of isomeric species of methyl/alkyl aromatic compounds or other similar compounds where PI yielded exclusively molecular ions. Additional research is currently being conducted to further verify the concept.

SUPPORTING INFORMATION

S1. Chromatographic and ion source conditions; S2. Extracted ion channels for EI, PI, CI, and FI; S3. Identification of base oil hydrocarbons and molecular ion abundances; S4. Contour plots and cumulative 2nd dimension plots for EI and PI; S5. Selectivity of ion sources; S6. Mass spectra and s/n ratios for different ion sources; S7. Sensitivity of different ion sources; S8. Impact of detector voltages and probe condition; S9. Utility of high-resolution MS coupled to GC×GC-TOF.

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CONFLICT OF INTEREST

No conflict of interest is declared for the present work.

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FIGURE 1

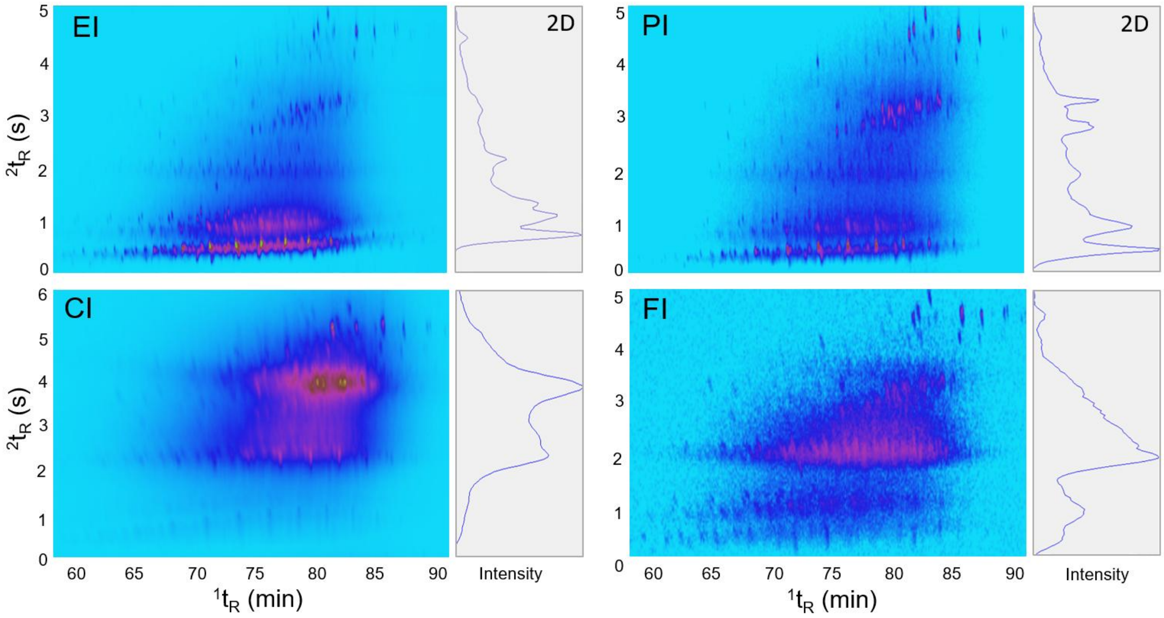

FIGURE 1. GC×GC-TOF/MS contour plots of base oil sample 1 (Gr. I) for EI, PI, CI, and FI, revealing elution patterns of hydrocarbon classes and selectivity towards different ion sources as visualised by 2D plots (^1t_R: First dimension retention time; ^2t_R: second dimension retention time) .

FIGURE 2

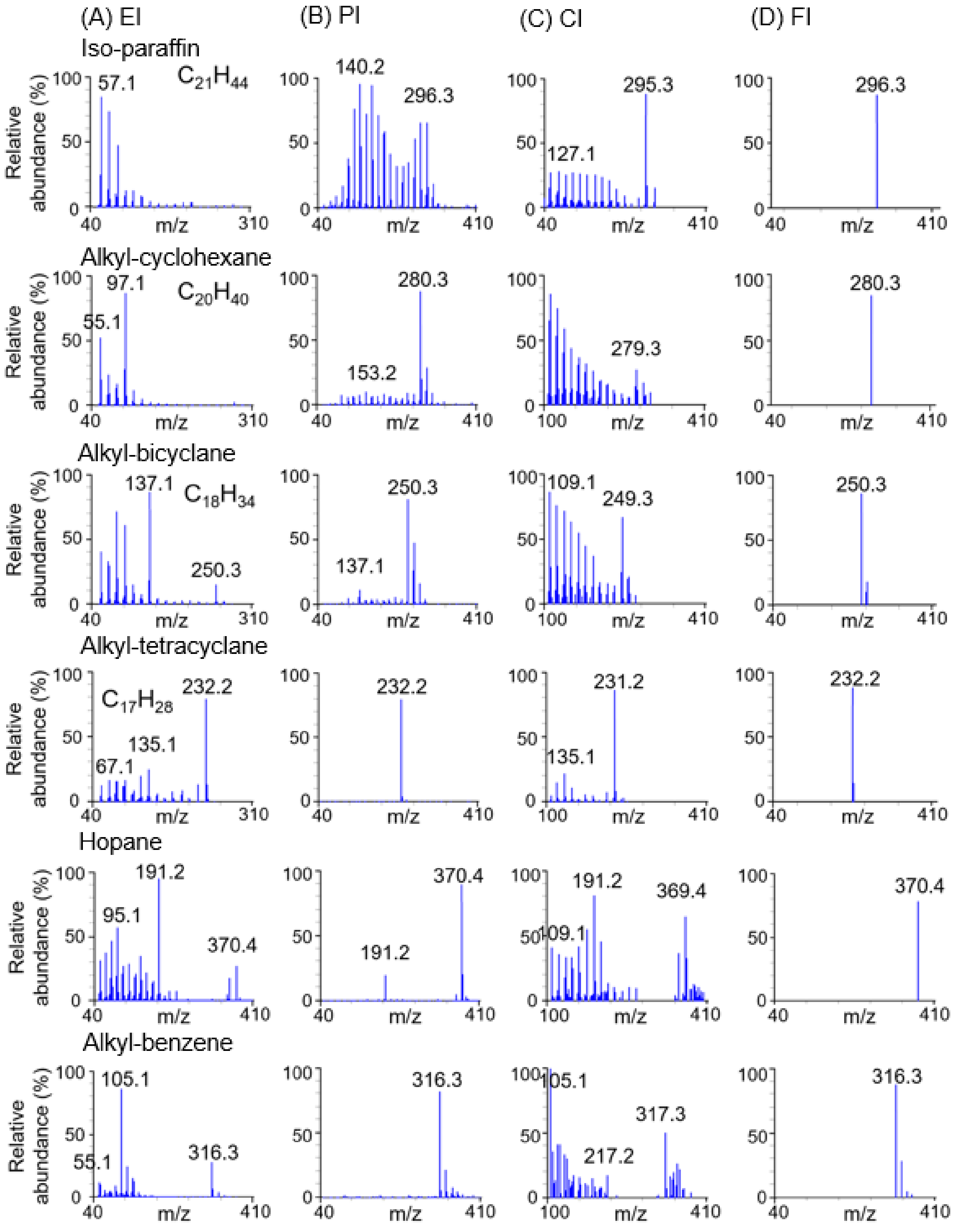

FIGURE 2. EI, PI, CI, and FI mass spectra for selected hydrocarbon classes eluted by GC×GC-TOF/MS.

FIGURE 3

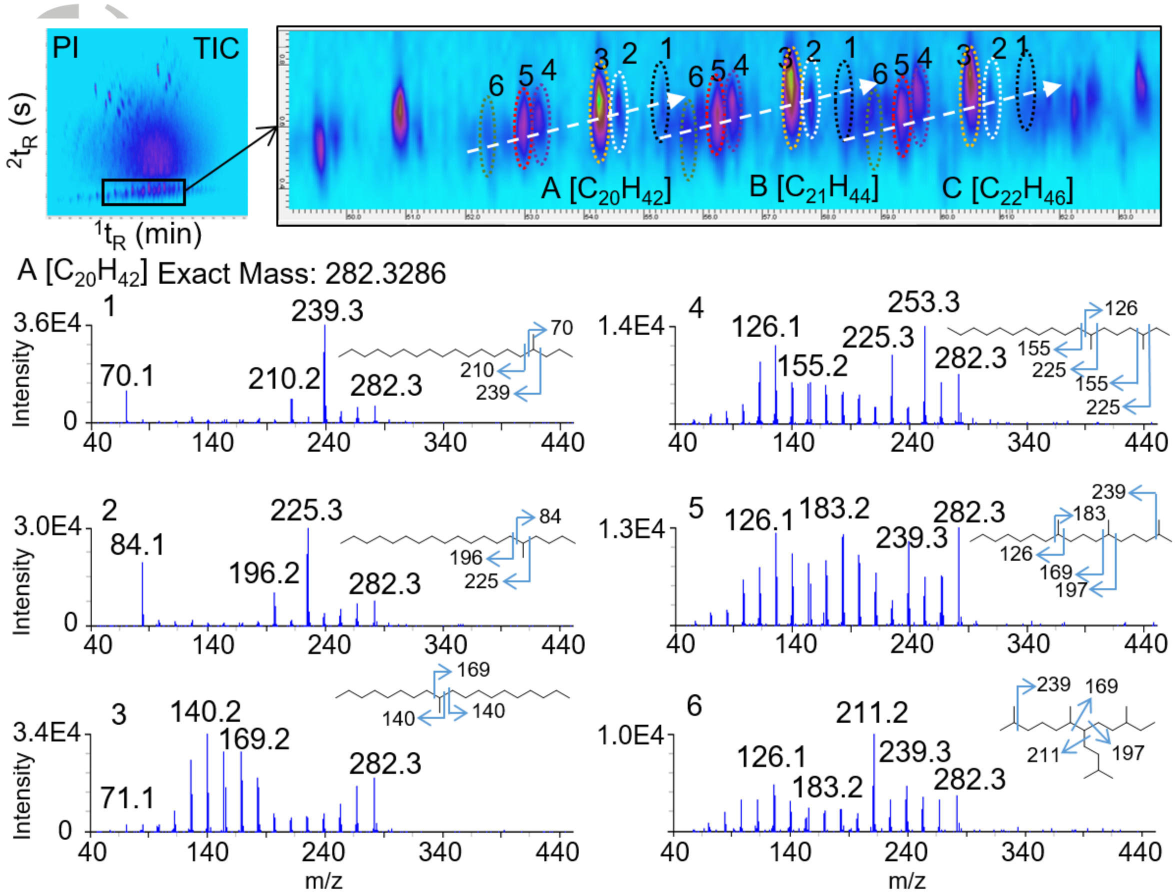

FIGURE 3. GC×GC-PI-TOF/MS plot of a base oil sample 2 (Gr. II), revealing structural elution pattern of isomeric isoparaffins (C20, C21, C22). Fragmentation hypothesis along with mass spectra for six (1-6) isomeric species of C20 is presented below.

FIGURE 4

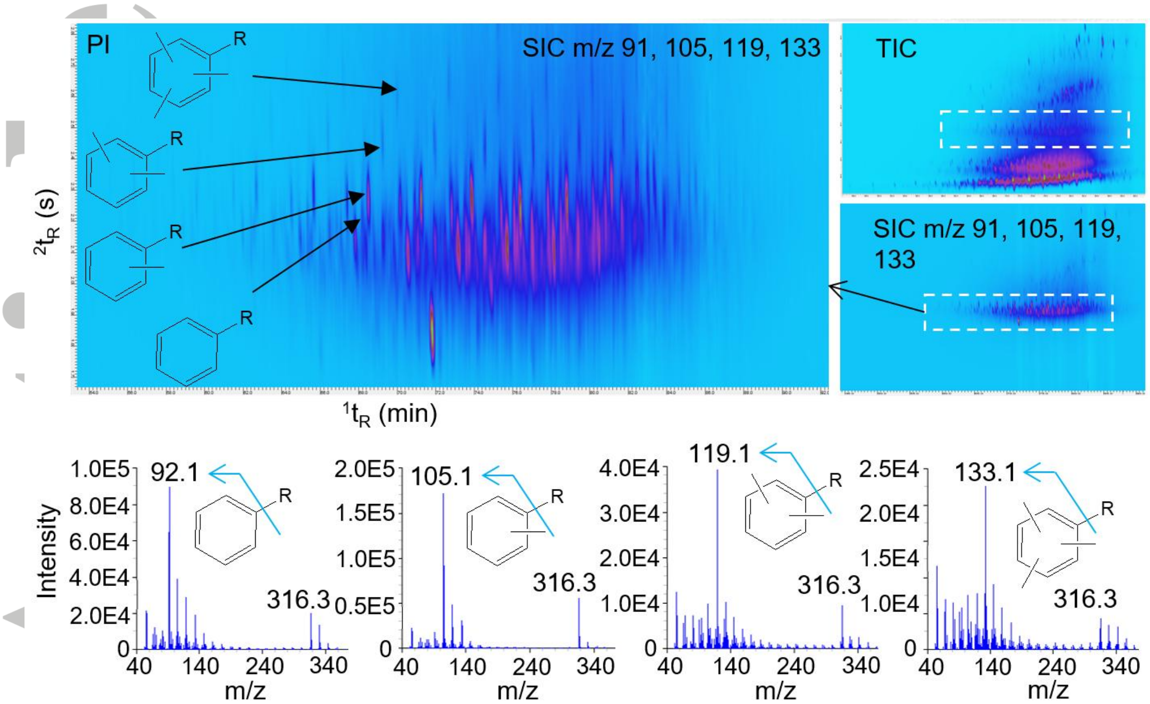

FIGURE 4. GC×GC-EI-TOF/MS plot of a base oil sample 1 (Gr. I), revealing elution pattern of methylalkyl isomeric species of monoaromatic compounds. Mass spectra and fragmentation hypothesis of is presented below. Elution pattern of ethly-, propyl-, butyl- substituted isomeric species of alkylbenzenes are included in supporting information.

FIGURE 5

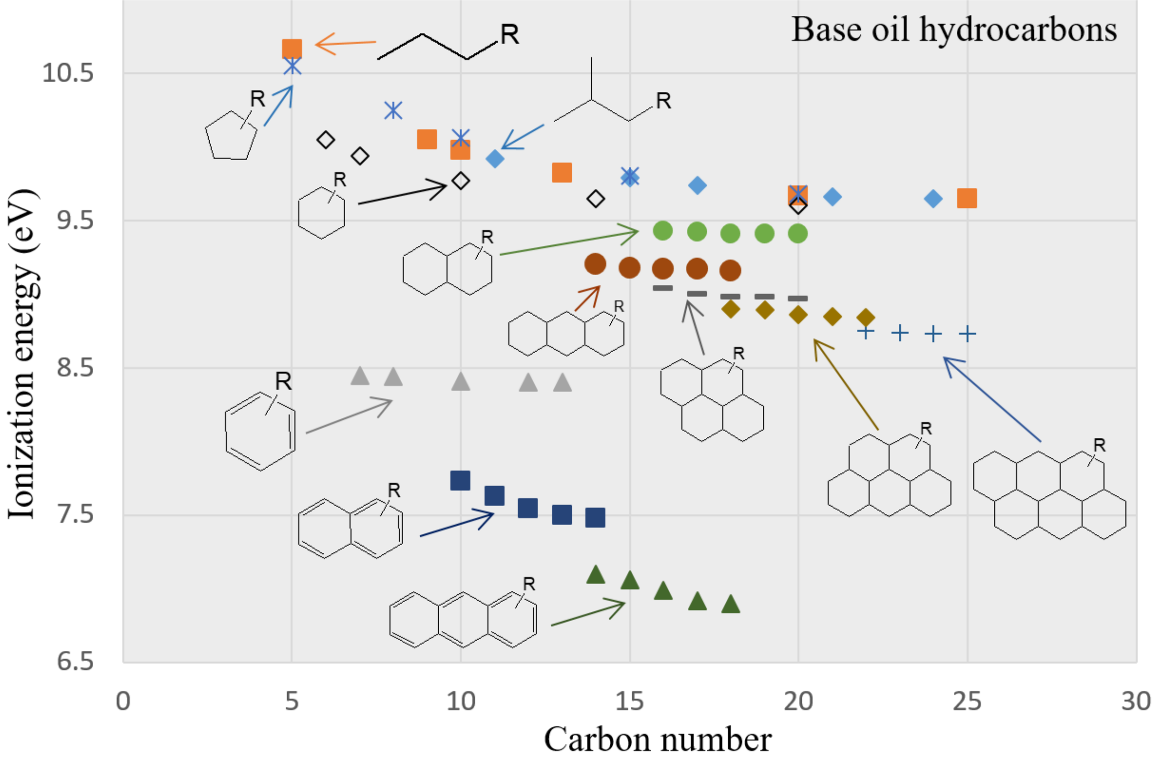

FIGURE 5. *Ab initio* computations of the vertical ionization potential (IP_V) for alkyl series of several parafennic, naphthenic, and aromatic hydrocarbons.