


Simulation of Vacuum Ultraviolet Absorption Spectra: Paraffin, Isoparaffin, Olefin, Naphthene, and Aromatic Hydrocarbon Class Compounds

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Abstract

The advent of a new vacuum ultraviolet (VUV) spectroscopic absorption detector for gas chromatography has enabled applications in many areas. Theoretical simulations of VUV spectra using computational chemistry can aid the new technique in situations where experimental spectra are unavailable. In this study, VUV spectral simulations of paraffin, isoparaffin, olefin, naphthene, and aromatic (PIONA) compounds using time-dependent density functional theory (TDDFT) methods were investigated. Important factors for the simulations, such as functionals/basis sets and formalism of oscillator strength calculations, were examined and parameters for future PIONA compound simulations were obtained by fitting computational results to experimental spectra. The simulations produced satisfactory correlations between experimental observations and theoretical calculations, and enabled potential analysis applications for complex higher distillate fuels, such as diesel fuel. Further improvement of the methods was proposed.

Keywords

Vacuum ultraviolet, VUV, time-dependent density functional theory, TDDFT, paraffin, isoparaffin, olefin, naphthene, and aromatic compounds, PIONA analysis

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Introduction

Recently, a new bench-top vacuum ultraviolet (VUV) spectroscopic detector has been developed for gas chromatography applications.^{1,2} It has been applied successfully in a variety of applications areas, including pesticide,³ fragrance,⁴ fatty acid,^{5,6} permanent gas,⁷ petrochemical,^{8–13} forensic,^{14–16} and environmental analysis.¹⁷ Compared with other electron absorption instrumentation, the VUV detector has several notable advantages. Foremost, it can conveniently acquire electronic absorption spectra in the range of 125–240 nm, a range that reaches the energy level of $\sigma \rightarrow \sigma^*$ excitation. Measurements in this range of absorption were previously relegated to bright source synchrotron facilities. For traditional UV–Vis detectors, molecules must possess suitable light absorbing functional groups to be measurable in the UV–Vis range (~200–720 nm). As a result, many molecules which lack these functional groups are transparent in the UV–Vis range. On the contrary, virtually every molecule absorbs strongly in the 125–240 nm VUV–UV region. This

advantage has been exploited heavily to advance measurements of alkanes, alkenes, and other low functionality molecules.^{1,4,7,9}

As it is combined with gas chromatography, the VUV detector acquires absorption spectra in the gas phase. Consequently, complicated solvent effects are avoided and the interactions between molecules are minimized. In the past, electron absorption spectra of molecules were primarily measured in condensed phases, introducing complicated environmental effects. The various intermolecular interactions due to environmental effects have been a major source of deviation between experimental observation and theoretical predictions.^{18,19} The new VUV

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detector has afforded easier access to electron absorption spectra for a wide variety of molecules under a universal and simple gas-phase environment.

As a traditional analytical spectroscopy method, a successful qualitative analysis normally requires the pre-existence of pure analyte spectra in a searchable database library. Although it is a new tool, the VUV spectra library is developing quickly (approximately 2000 compounds currently). However, there are situations where the spectra for some molecules have not been measured, and are therefore unavailable in the library. In many cases, it may be a matter of obtaining suitable samples and/or standards. However, there are also situations where obtaining pure compound spectra may be impractical. As a solution, we are exploring the possibility of generating reliable theoretical spectra using computational chemistry and substituting these spectra in analysis for molecules whose experimental spectra are not yet available. Several of our reported works showed the method to be a promising one.^{8,16,20}

Computational chemistry can be a very useful and complementary tool for VUV chemical analysis. Although almost every molecule is active in the VUV range and measurable, there will be cases where it is impossible to measure VUV spectra for all the chemical compounds contained in a complex sample. For example, in paraffin, isoparaffin, olefin, naphthene, aromatic (PIONA) analysis,^{4,21–23} which is extremely important in petroleum industry for the classification of fuel content, the number of possible hydrocarbon structures increases dramatically when the number of carbon atoms increases (more than one million structures are possible when the number of carbon atoms reaches 20). It will be impossible to obtain standards and measure the spectra for all of these structures. It is under these situations, where the possibility of using computational chemistry as a complementary tool to simulate spectra is being investigated. Reasonable correlation between theoretical computations and measured VUV spectra have been shown previously in a few instances, especially for characterizing general trends in wavelength shifts or where the differentiation of isomers was desired.^{1,8,16}

The gold standard for modern petroleomics is analysis using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS), as exemplified by the extensive body of work from Marshall and Rodgers²⁴ and Hur et al.²⁵ FT-ICR-MS and its analysis of petroleum hydrocarbons has advanced over many years to its current status of having availability of a 22 T magnet to achieve resolution between species whose weights differ by less than the mass of an electron. That said, mass spectrometry will always have issues differentiating isobaric species having identical elemental formula. The complementarity of VUV–UV absorption spectroscopy to mass spectrometry has been demonstrated in numerous studies, including those that combine both VUV and MS analysis for more

complete coverage and confidence in assigning identities to components in complex mixtures.^{26,27} Whereas FT-ICR-MS can be hardly matched in terms of its ability to speciate the most complex petroleum mixtures, including crude oil, gas chromatography–VUV (GC-VUV) has become an established method for routine day-to-day fuels classification; two ASTM methods are now established using GC-VUV methodology for gasoline and jet fuel analysis, respectively.^{28,29} Efforts are still needed to advance GC-VUV methodology for analysis of higher fuels, and the incorporation of theoretical computations is expected to be of benefit for this development.

The aim of the current work is to evaluate VUV spectral simulation for PIONA compounds. The process of simulating VUV spectra using computational results from quantum mechanical calculations has been explored. The influence of the important choice of functionals, basis sets, and formalism of oscillator strength calculation were investigated. With suitable functional and basis set, the theoretical calculation data were then fit to experimental spectra to optimize the parameters for spectral simulation of each PIONA group. These parameters can then be used for future spectral simulations of PIONA compounds having higher carbon numbers in future work.

Computational Chemistry Background

Given a molecular structure, quantum mechanical calculations can be used to compute its electronic excitation energies, which correspond to expected wavelengths of absorption in an electron absorption spectrum, as well as corresponding oscillator strengths,³⁰ which correspond to the intensity of absorption. A theoretical VUV spectrum then can be generated by broadening each excitation with a Gaussian shape and summing them up.¹⁹ The centers of Gaussian functions are the positions of calculated excitation energies, and the integrated areas of the Gaussian functions are proportional to calculated oscillator strengths. The widths of Gaussian shapes are normally adjusted to best match the experimental spectra. While there are various computational chemistry methods to calculate excitation energies and oscillator strengths, at present for medium and large molecules, time-dependent density functional theory (TDDFT)³¹ is essentially the only choice which adequately balances computational cost and accuracy:³² the technique usually provides excitation energies accurate to within 0.25 eV^{33,34} and has been applied to molecules with hundreds of atoms. Indeed, in a recently reported VUV spectra simulation study,³⁵ it was shown that the simulated VUV spectra by TDDFT method outperform the ones simulated by a more expensive symmetry adapted cluster/configuration Interaction method.³⁶ Therefore, in this study, all spectra were simulated using results from TDDFT calculations.

Several limits must be acknowledged when simulating an electron absorption spectrum using excitation energy and oscillator strengths calculated using the TDDFT method. The excitation energy calculated from TDDFT is a vertical absorption energy under the Franck–Condon approximation, namely that the geometry of the molecule is considered unchanged during the electronic excitation. Additionally, every experimental electronic absorption spectrum is a vibronic spectrum because nuclear vibrations are always coupled together with electronic excitations. In principle, wavelengths of maximum absorption from experimental spectra do not fully correspond to calculated vertical absorption energies. It has been shown that a simulation of vibrationally resolved electron absorption spectra does provide a much better match with experimental spectra, both in terms of the wavelengths of maximum absorption and the shape of absorption bands.³⁷ However, to simulate vibrationally resolved spectra, a gradient of an excited state's potential energy surface around its equilibrium geometry must be calculated to obtain the vibrational information of the excited state, and this must be performed for every excited state. Although the VUV instrument is very suitable for vibration–excitation coupling study of specific excitations, a topic which will be reported in our future work, it is impractical to consider simulations including the vibration–excitation coupling for the entire 125–240 nm range, throughout which it is not unusual that several hundred excited states exist.

Another simplification one must keep in mind is that spectra were always simulated from a single optimized geometry of a molecule. Neither interactions between molecules nor molecular conformational changes were considered for the simulations. Although the effects from these considerations are usually small, it is reported that a flexible conformation could influence band positions and strengths.³⁸

Bearing these limits in mind, our goal was mainly of practical purpose: To explore simulations of electronic absorption spectra between 125 and 240 nm. This is very different from numerous benchmarking works which focused on only several low-lying excited states or specific types of excitations. There are usually several hundred excited states in the wavelength range of interest which might include various types of excitations (valence, Rydberg, local, and charge-transfer). To simulate the spectra in the whole range, all the excitation energies and corresponding oscillator strengths within the range were calculated using the TDDFT method. Each excitation was converted to a Gaussian shape. A universal scaling factor of Gaussian centers (excitation energies) and full width at half-maximum (FWHM) of Gaussian shape for all excitations were optimized to obtain best match of simulated and experimental spectra by minimizing sum of squared residuals (SSR) between the two spectra.

Methods and Materials

Computational Details

All VUV spectra were simulated using TDDFT³¹ implemented in Gaussian 09 (version A.02) program.³⁹ Molecular structures were optimized using B3LYP functionals^{40–43} and 6-31+G(d,p) basis set,^{44,45} followed by frequency calculations to confirm they are energy minima. All calculations were performed at the High Performance Computing Center at The University of Texas at Arlington.

Experimental Details

Experimental absorbance spectra were obtained using VGA-100 VUV absorption spectroscopy gas chromatography detectors (VUV Analytics, Inc.). Of the experimental spectra considered in Tables I and II, most were obtained via measurement of a PIONA standard kit (Supelco), except for 2,2-dimethylbutane and 2-methyl-3-ethylpentane, which were obtained from well-characterized gasoline-range fuel samples. In each case, a GC-VUV experiment was performed and the absorbance spectrum associated with the peak belonging to the relevant compound recorded to the VUV spectra library. Experimental spectra used to perform the optimizations in Tables S1–S5 (Supplemental Material) were obtained similarly, either from the PIONA standard or via measurements of well-characterized fuel samples. Additional experimental details regarding GC-VUV-based PIONA measurements can be found in a previous study.⁹

Results and Discussion

Functionals and Basis Sets

Over the past several decades, many excellent functionals were designed for DFT calculations and some of them were proposed specifically for TDDFT excited state calculations. For example, range-separated functionals were designed to correct the incorrect asymptotic behavior of the exchange–correlation kernel of TDDFT for long-range excitation.⁴⁶ As for basis sets, to correctly describe Rydberg excitations in which one or more electrons are distant from the nucleus, diffuse functions are considered to be important since they are responsible for the “tail” portion of atomic orbitals. For most molecules, the first several low-lying excitations usually do not correspond to Rydberg excitation. It is reasonable to use a basis set without diffuse function if these states are the goal of the study, as indicated in prior literature.⁴⁷ However, as mentioned above, our goal is to simulate spectra for the entire 125–240 nm range. Depending on molecular structures, various types of excitations (local excitation, charge-transfer excitation, Rydberg excitation) could co-exist in this range. The simulation of spectra can be reasonable only when the functional/basis set are chosen wisely.

Table I. SSR (sum of squared residuals) between simulated and experimental spectra by various choices of TDDFT functionals and basis sets.

	PBE0 cc-pVDZ	LC-wPBE cc-pVDZ	M06-2X cc-pVDZ	PBE0 aug-cc-pVDZ	LC-wPBE aug-cc-pVDZ	M06-2X aug-cc-pVDZ
Hexane	3.3	16.7	8.9	5.0	2.3	2.1
2,2-Dimethylbutane	2.0	2.2	2.1	1.3	2.1	1.6
Benzene	15.2	17.1	16.8	12.4	13.3	12.3
Cyclohexane	8.3	8.3	8.2	0.4	10.6	1.2
1-Hexene	103.0	324.7	271.1	52.1	34.1	30.0
Octane	1.9	3.2	2.3	1.3	1.8	1.2
2-Methyl-3-ethylpentane	1.6	1.9	1.7	0.7	1.6	2.0
Ethylbenzene	29.8	31.8	29.7	9.4	16.7	10.1
cis-1,2-Dimethylcyclohexane	4.2	3.0	2.7	4.0	8.3	1.9
cis-2-Octene	137.0	280.8	206.3	66.3	65.2	72.7
	B3LYP 6-31G**	CAM-B3LYP 6-31G**	wB97x 6-31G**	B3LYP 6-31+G**	CAM-B3LYP 6-31+G**	wB97x 6-31+G**
Hexane	14.6	8.5	38.0	2.2	2.4	2.4
2,2-Dimethylbutane	2.0	2.0	2.1	1.8	2.1	2.1
Benzene	17.3	17.1	15.8	12.5	14.4	13.4
Cyclohexane	8.1	8.2	13.5	5.5	20.3	12.3
1-Hexene	330.1	306.9	312.6	12.8	19.4	27.9
Octane	1.9	4.5	10.6	1.1	1.9	1.9
2-Methyl-3-ethylpentane	1.7	1.8	2.0	0.5	1.6	1.7
Ethylbenzene	29.7	34.2	35.2	18.3	15.0	18.1
cis-1,2-Dimethylcyclohexane	2.9	2.9	3.3	1.4	4.8	4.4
cis-2-Octene	250.1	281.2	300.6	31.4	12.6	12.5

Table II. Percent differences between calculated oscillator strengths using length or velocity formalisms by various choices of TDDFT functionals and basis sets.

	PBE0 cc-pVDZ	LC-wPBE cc-pVDZ	M06-2X cc-pVDZ	PBE0 aug-cc-pVDZ	LC-wPBE aug-cc-pVDZ	M06-2X aug-cc-pVDZ
Hexane	4%	3%	13%	0%	0%	9%
2,2-Dimethylbutane	5%	4%	14%	-1%	-1%	8%
Benzene	1%	-1%	8%	-1%	-1%	7%
Cyclohexane	4%	3%	13%	-1%	-1%	8%
1-Hexene	3%	2%	11%	-1%	-1%	8%
Octane	3%	2%	12%	-1%	-1%	8%
2-Methyl-3-ethylpentane	5%	4%	15%	-1%	-1%	8%
Ethylbenzene	2%	1%	11%	-1%	-1%	7%
cis-1,2-Dimethylcyclohexane	3%	4%	13%	-1%	-1%	8%
cis-2-Octene	3%	3%	12%	-1%	-1%	8%
	B3LYP 6-31G**	CAM-B3LYP 6-31G**	wB97x 6-31G**	B3LYP 6-31+G**	CAM-B3LYP 6-31+G**	wB97x 6-31+G**
Hexane	3%	4%	2%	-3%	-3%	-3%
2,2-Dimethylbutane	5%	5%	3%	-3%	-3%	-3%

(continued)

Table II. Continued.

	B3LYP 6-31G**	CAM-B3LYP 6-31G**	wB97x 6-31G**	B3LYP 6-31+G**	CAM-B3LYP 6-31+G**	wB97x 6-31+G**
Benzene	3%	2%	2%	-2%	-2%	-2%
Cyclohexane	5%	5%	3%	-4%	-4%	-4%
1-Hexene	2%	3%	2%	-5%	-4%	-4%
Octane	2%	2%	2%	-3%	-3%	-3%
2-Methyl-3-ethylpentane	4%	5%	4%	-2%	-2%	-2%
Ethylbenzene	1%	2%	1%	-4%	-3%	-3%
cis-1,2-Dimethylcyclohexane	2%	4%	3%	-2%	-3%	-3%
cis-2-Octene	2%	2%	2%	-4%	-4%	-3%

To evaluate the choice of functional/basis set, spectra were first simulated for two groups of PIONA compounds: one group with six carbon atoms (hexane, 2,2-dimethylbutane, hexene, cyclohexane, and benzene) and another group with eight carbon atoms (octane, 2-methyl-3-ethylpentane, cis-2-octene, cis-1,2-dimethylcyclohexane, and ethylbenzene). Six functionals which perform best in previously reported benchmarking works^{33,34} were used and among them two popular range-separated functionals, LC-wPBE⁴⁸ and CAM-B3LYP,⁴⁹ were included. Both Pople^{44,45} and Dunning's correlation consistent basis sets,⁵⁰ with and without diffuse function were tested. SSR between simulated spectra and experimental spectra were calculated to evaluate the choice of each functional/basis set (Table I).

The data in Table I clearly show that basis sets with diffuse function included must be used. In cases where basis sets without diffuse function (cc-pVDZ and 6-31G**) were used, the Rydberg excitations at short wavelengths were missed in simulated spectra, resulting in a very poor match with the experimental spectra and exhibiting a very large SSR value. This is clearly shown in Fig. 1 as an example. Only with basis sets including diffuse functions, such as aug-cc-pVDZ or 6-31+G**, were more appropriate spectral shapes produced.

As shown in Table I and Fig. 2, using range-separated functionals (LC-wPBE⁴⁸ and CAM-B3LYP⁴⁹) did not produce general better SSRs than using standard functionals (PBE0⁵¹ and B3LYP⁴⁰⁻⁴³). This is understandable, since little long-range charge-transfer excitation from the PIONA compounds studied in this work were expected.

From Table I, the choice of either PBE0/aug-cc-pVDZ or B3LYP/6-31+G** functionals/basis set produced quite good matches between simulated spectra and experimental spectra for all five PIONA groups. The latter was chosen for all other spectral simulations in this study for the reason that 6-31+G** is a slightly smaller basis set compared with aug-cc-pVDZ. For future simulations of large PIONA molecules with high carbon number, the reduction of computational cost due to size of basis set can be significant.

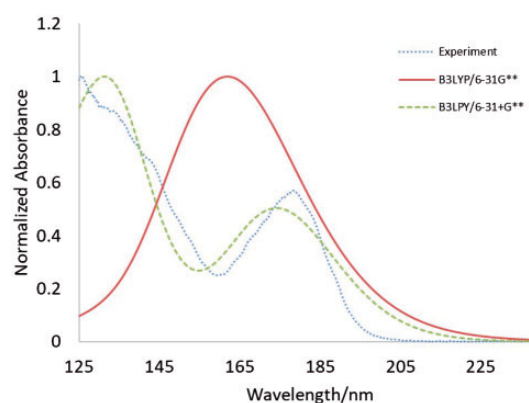


Figure 1. Experimental and TDDFT simulated VUV spectra for 1-hexene. The Rydberg excitations at short wavelengths were missed in simulated spectrum when a basis set without diffuse function (6-31G**) was used.

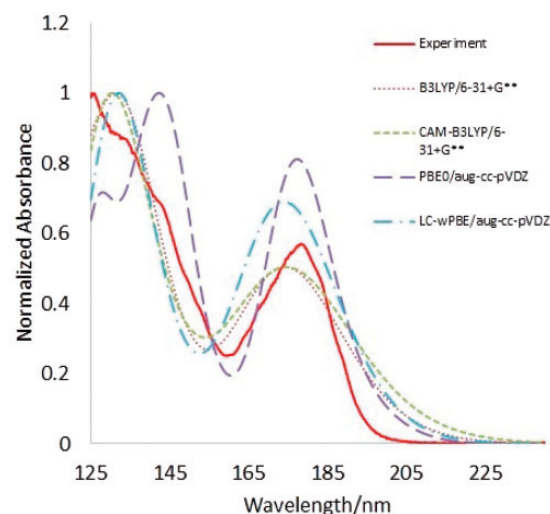


Figure 2. Experimental and TDDFT simulated VUV spectra for 1-hexene. The benefit of using range-separated functionals is minimal.

Oscillator Strength

The position of absorption bands are determined by calculated excitation energies, while the strengths of band are determined by oscillator strengths.³⁰ There exist two different ways to calculate oscillator strength, namely length formalism or velocity formalism.⁵² While they are identical when the system's wavefunction is exact and rarely differ from each other by a factor of more than two in computations, for some cases they can differ from each other as much as by a factor of 20.⁵³ Which of the two formalisms is better has been long debated.^{54–62} It is therefore interesting to investigate the influence of these two formalisms over the entire VUV region for PIONA compounds.

The sum of all computed oscillator strengths in the range of 125–240 nm using the two formalisms was

calculated and their percent differences are listed in Table II. One can see that for the functional/basis sets we chose in this study (B3LYP/6-31+G^{**}), the resulting difference from the two formalisms is around 3%. The difference can be up to 15% for other functional/basis sets as shown in Table II.

PIONA VUV Spectral Simulation

The VUV spectra were simulated for a total of 198 PIONA compounds (26 paraffin compounds, 44 isoparaffin compounds, 49 olefin compounds, 36 naphthene compounds, and 43 aromatic compounds). The optimized scaling factors, FWHMs, and SSR are listed in Tables S1–S5 in supporting information. Comparisons of simulated and experimental spectra for a group of PIONA compounds with eight carbon atoms (octane, 2-methyl-3-ethylpentane,

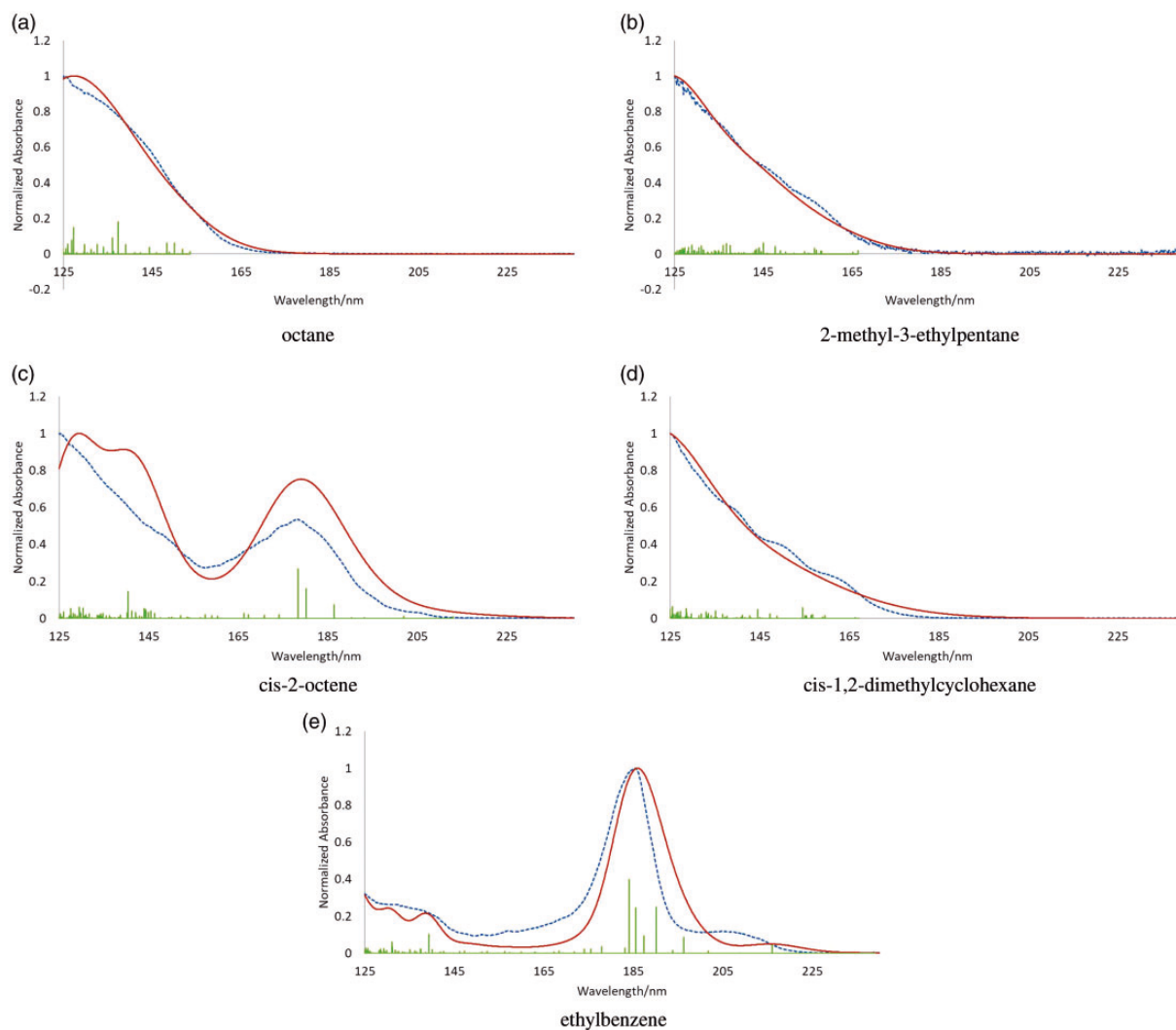


Figure 3. Experimental (dotted blue) and theoretical (solid red) VUV spectra for a group of PIONA compounds with eight carbon atoms. The theoretical spectra were simulated using TDDFT (B3LYP/6-31+G^{**}) method. (a) octane, (b) 2-methyl-3-ethylpentane, (c) cis-2-octene, (d) cis-1,2-dimethylcyclohexane, and (e) ethylbenzene.

cis-2-octene, *cis*-1,2-dimethylcyclohexane, ethylbenzene) are shown in Fig. 3a to 3e as an example.

Although oscillator strengths calculated using length formalism or velocity formalism can be very different for some excitations,^{53,60} and their total strengths differ by around 3% in the VUV range, as was shown in Table II, it turns out the simulated spectra were almost identical regardless of which set of oscillator strengths was used. The velocity formalism is slightly better for olefin and aromatic compounds, while the length formalism is better for alkanes (paraffins, isoparaffins, and naphthenes). However, the overall improvements are not significant. All scaling factors were within 0.98 to 1.02, indicating very good peak position predictions using the chosen functional/basis set of B3LYP/6-31+G**.

Alkanes contain only σ bonds within their structures and it is known that their excitations are only of the Rydberg type.⁶³ The lack of band structure results in a large FWHM value when matching experimental spectra. Since the optimization of FWHM is purely for practical purposes to best match experimental spectral shape, one should not seek much physical meaning to these large FWHM values.

For olefin and aromatic compounds, the most important feature of their spectra is the set of strong bands associated with $\pi \rightarrow \pi^*$ excitation of double bond and benzene structures. The position of this peak will shift more or less according to details of the structures. The almost equivalent optimized scaling factors obtained for the various olefin or aromatic compounds indicate that the simulation is capable of correctly predicting the experimental peak positions for different structures.

Within the same type of compounds, very similar optimized scaling factors and FWHMs were obtained. This is encouraging, indicating that these same parameters should apply to PIONA compounds whose experimental spectra are unavailable. The use of TDDFT calculations, together with the fitted scaling factor and FWHM from this work, are expected to generate VUV spectra that exhibit similar agreement to the experimental spectra for PIONA compounds with higher carbon number.

Conclusion

Vacuum ultraviolet absorption spectra between 125 and 240 nm were simulated using TDDFT methods for various PIONA compounds. Functionals, basis sets, and formalism for calculating oscillator strengths were investigated to determine the best combination for VUV simulation. Optimized parameters of scaling factor and FWHM were found to be quite stable for a wide range of PIONA group compounds investigated in this study. They are proposed to be used for future simulations for PIONA compounds with higher carbon number whose experimental spectra are difficult to obtain. We expect the ability of simulating these spectra will be helpful in analysis of complex higher distillate fuels like diesel.

As we mentioned, a single optimized geometry of molecules was used for spectral simulation in this work. Although overall the comparison between experimental spectra and theoretical simulation are satisfied by simulating spectra on a single structure, we realized many PIONA compounds possess quite flexible structures. We are exploring simulations including more structures for flexible molecules and expect a further improvement of VUV spectral simulation as this work develops. Importantly, the readily available means of acquiring experimental spectra for a wide range of chemical compounds will allow for more efficient refinement of computational methods for simulating spectra.

Conflict of Interest

KAS is a member of the Scientific Advisory Board for VUV Analytics, Inc.

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Supplemental material

The supplemental material mentioned in the text, consisting of the optimized scaling factors, FWHMs, and SSRs, is available in the online version of the journal.

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