

On Scalability of DFT-Calculated IR Spectra for Spectrum-Feature Extraction and Estimation of Dielectric Response

SAMUEL G. LAMBRAKOS

*Center for Materials Physics & Technology Branch
Materials Science & Technology Division*

ANDREW R. SHABAEV

*Materials and Sensors Branch
Materials Science & Technology Division*

SONJAE WALLACE

*Lehman College, CUNY
New York, NY*

LOU, MASSA

*Hunter College, CUNY
New York, NY*

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14. ABSTRACT Extraction of spectrum features for target molecules from measured spectra, for purpose of their detection, can be achieved by comparison to template spectra within a spectrum database, which are sufficient approximations of dominant spectral features. This study continues presentation of the concept of using Density Functional Theory (DFT) to calculate template spectra for practical detection of target substances, by comparison with spectra within databases. DFTcalculated spectra are well posed for comparison to measured spectra, as template spectra, to the extent of their scalability to larger space-time scales. Specifically, the focus of this study is scalability of DFT-calculated IR spectra with respect to meso and macro scales, characteristic of dielectric response as measured using different IR spectroscopies. A case study analysis concerning scalability of IR spectra for caffeine is described.					
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1. Introduction

Infrared (IR) spectra provide identification of molecules for practical detection of target substances. In practice, identification of target molecules can be made by comparison of measured spectra, of initially unknown molecules, with reference or template spectra contained within a database of spectra corresponding to known molecular structures [1-6]. As emphasized previously, database spectra for use as templates are presently almost entirely composed of experimentally measured spectra [7,8]. Accordingly, previous studies [9-13] presented the relatively new idea of using IR spectra calculated by means of density functional theory (DFT) to complement experimentally measured IR spectra contained within a database of template spectra. The use of what are reliable calculated IR spectra will enhance the detection of target molecules, e.g., contaminants in water environment [9-13]. The concept of extending experimental IR databases with complementary DFT-calculated IR spectra, remains relatively new, and not yet widely considered. This important observation is discussed in references [9-13]. Extending IR-spectral databases using DFT calculations has two aspects, which are: using DFT-calculated spectra for physical interpretation, a perspective of theoretical chemistry; and using DFT-calculated IR spectra for comparison with measured spectra, a relatively new perspective for practical IR-spectral database extension.

This study continues presentation of the concept of using density functional theory (DFT) for complementary extension of IR-spectral databases. Specifically, this study examines the scalability of DFT-calculated spectra with respect to the macroscale applications of constructing template spectra for spectrum-feature extraction and of estimating dielectric response. Using DFT-calculated spectra as templates for the purpose of spectrum-feature extraction is described by Figure 1. Referring to Figure 1, an IR-spectrum database should be constructed with respect to a specific class of target molecules and detection scenarios, where DFT-calculated spectra provide a complementary extension of experimentally measured IR-spectra, and where both DFT-calculated and experimental spectra are considered equally useful. As emphasized previously, in many cases, calculation of IR-spectra using DFT may be more convenient than laboratory measurements.

Algorithms for comparison of DFT-calculated and measured IR spectra (see Figure 1) remains for continuing development. DFT-calculated spectra are essentially distributions of delta functions, which must be enhanced, as well as scaled, to be used as templates for spectrum-feature extraction from measured spectrum, which are on the macroscale. Further, comparison of DFT-calculated spectral templates and measured spectra must consider their inherent difference in nature. DFT calculated IR spectra are to be considered the result of independent computational experiments, and not spectra to be validated by reproducing measurements. Spectrum-feature enhancement operations can be applied to DFT calculated spectra in the same spirit that feature enhancement operations are applied to experimentally measured spectra (see reference [14-17] and references therein). Accordingly, DFT calculated spectra, measured spectra, and their spectrum-feature enhancements, can be used to construct ensembles of template spectra. The concept of comparing extracted features to those of spectrum templates, is motivated by algorithms applied in signal processing [18].

Presented in reference [12] are comparisons of synthetically broadened DFT-calculated and measured spectra. These comparisons are significant in demonstrating scalability of DFT spectra with respect to feature extraction on the macroscale. This scalability motivates development of spectrum-feature enhancement operations of DFT-calculated and measured spectra, for both their comparison and construction of template-spectrum database consisting of enhanced spectral features (see Figure 1). This study demonstrates a set of such operations.

Before proceeding, to be noted is that fundamentally spectrum-feature extraction defines an inverse problem, where as with all methods of inverse analysis [19,20], operations for feature extraction are not unique and characterized by sensitivity with respect to levels of spectrum-feature details to be extracted.

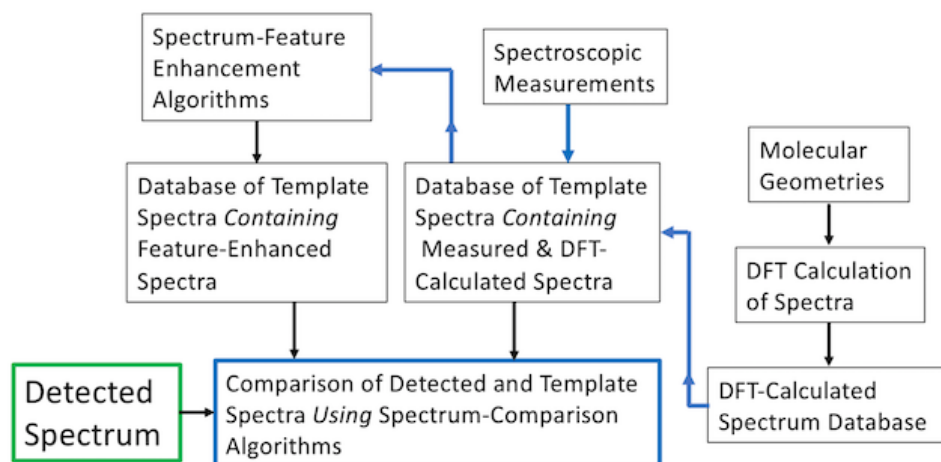


Figure 1. Ontology of computational framework for using DFT-calculated and measured spectra as templates, for spectrum-feature extraction.

The ability of DFT-calculated IR spectra, feature enhanced by transformations to continuous-function representations, to have very high correlation with measured IR-spectra, which are on the macroscale, establishes foundation for estimation of dielectric functions of materials. This new procedure further extends the concept of using DFT for complementary extension of IR-spectral databases, but more specifically in terms of a more basic material property, the dielectric function. The general procedure for estimation of dielectric functions, using DFT-calculated IR-spectra, is described by Figure 2, and presented in the next section. In contrast to using DFT-calculated spectra for feature extraction, which defines an inverse problem [19,20], estimation of dielectric functions using DFT defines a “direct” modeling problem, which is based on fundamental electromagnetic theory [21,22].

Emphasized in previous studies [9-13] is that an important application of spectrum-feature extraction is for the monitoring of toxic materials, representing environmental contaminants. Emphasized in this study is that spectral-feature extraction is equivalently important for the quality control of foods. A contribution of this study, resulting from prototype analysis demonstrating the functional character of DFT-calculated spectra for construction of template spectra, is an ensemble of template spectra for caffeine IR spectra, which can be applied for spectral-feature extraction associated with practical quality control of coffee, a global problem of importance (see references [23-26] and references therein).

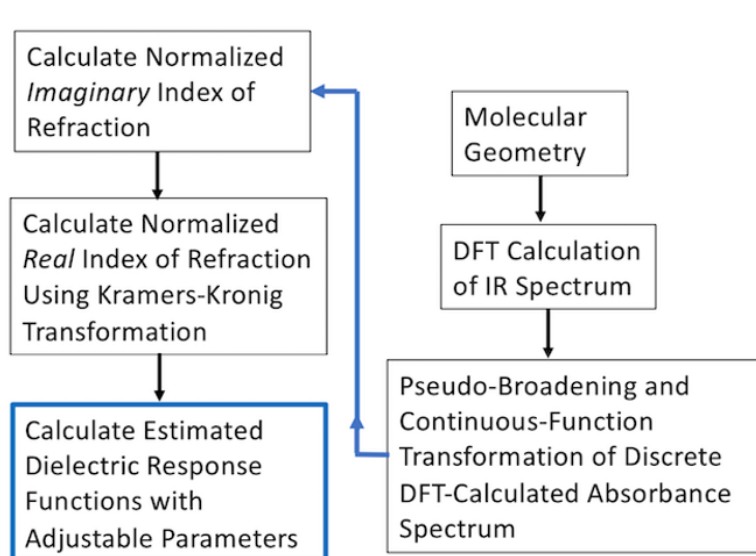


Figure 2. Ontology of computational framework for using DFT-calculated IR spectra to estimate dielectric response.

In what follows, methods for DFT calculation of IR spectra, and estimation of dielectric, transmission and reflectance functions using these spectra, are described. Next, DFT calculations of energy-minimized geometries and IR spectra for isolated molecules of caffeine within different solvent backgrounds are presented. Next, prototype constructions of spectrum templates are presented. Next, an estimate of the dielectric, transmission and reflectance functions for caffeine, obtained using DFT calculated spectra is presented. Next, a discussion is given concerning spectral-feature extraction and estimation of dielectric, transmission and reflectance functions, using DFT calculations. Finally, a conclusion is presented.

2. Methods of Calculation

DFT-Calculation of IR Spectra.

As in previous studies, the DFT models and associated software used for quantum-mechanics based calculation of IR spectra are briefly described for completeness. The commercial computer program GAUSSIAN16 (G16) and associated post-processing software was used for DFT-calculation of IR spectra [27-29]. Using this program one can simulate the effect on IR spectra due to continuous solvent backgrounds, where IR spectra are calculated using the Born-Oppenheimer approximation. The equations of motion which underlie the calculations are the Kohn-Sham (KS) equations for implementation of density functional theory [30-36]. The results of solving the KS equations yield the KS orbitals which deliver the formally “exact” electron density, the molecular equilibrium structure, and the IR spectra, the details of which are discussed in references [29] and [35]. Equilibrium structures of molecules are obtained by energy minimization. Using Gaussian, the IR spectra are calculated including frequency and intensity of each spectral line. These are harmonic frequencies calculated, which is a good approximation for the case of strong bonds, the focus we assume here. DFT calculations in this study employed the DFT chemical model B3LYP/6-311++g(3df,3pd) (see [36-39]), which is a reasonably large basis set, including a set of diffuse functions, and polarization functions on heavy atom. All of these basis functions designate the 6-311G basis set supplemented by diffuse functions, indicated by the sign ++, and polarization functions (df), having a set of d and f functions on heavy atoms [40]. The chemical models

indicated above, used in the calculations of this paper, have been used extensively, and have provided accurate energy-optimized molecular structures and IR spectra.

Construction of Spectrum Templates using DFT-Calculated IR Spectra.

The purpose of spectrum templates is target-molecule feature extraction, by their comparison with measured (or detected) spectra, where features of a target molecule are “buried” within a spectral background. In principle, template spectra are “feature-enhanced” spectra, constructed for convenient comparison with measured spectra. In that DFT calculated spectra are essentially distributions of delta functions, specific procedures for construction of template spectra should be considered. In principle, procedures for construction of template spectra, which are feature-enhanced spectra, can include continuous-function transformations of DFT calculated spectra, entailing interpolation and pseudo-broadening. Other procedures can include discrete-function transformation of measured spectra, for comparison with DFT calculated spectra, entailing discrete sampling of continuous measured spectra. Procedures for feature enhancement of DFT-calculated spectra, for the purpose of constructing template spectra, are in principle not unique. Among these procedures, as described below, are pseudo-broadening of DFT calculated spectra.

Estimation of Dielectric Functions, Reflectance and Transmission.

This study introduces procedures for estimation of dielectric functions, reflectance and transmission, based on the ability of pseudo-broadened DFT-calculated IR spectra to have very high correlation with measured IR-spectra, on the macroscale. Pseudo broadening of DFT spectra for estimation of dielectric functions is not in the same spirit as in the case of spectrum template construction. For the case of dielectric-function estimation, one seeks by means of pseudo broadening, a best or most reasonable approximation of macroscale absorbance spectra using DFT spectra.

One procedure for pseudo broadening of DFT spectra are linear combinations of Lorentz line-shape functions, given by,

$$\alpha_c(\omega) = \sum_{k=1}^{N_k} \frac{A_k \gamma_k^2}{(\omega - \omega_k)^2 + \gamma_k^2} \quad (1)$$

where A_k and ω_k , $k=1-N_k$, are DFT-calculated IR intensities and frequencies, and γ_k^2 are pseudo-broadening parameters. Although the functional form Eq.(1) is physically motivated, and provides for the calculation of dielectric response using analytical functions, its purpose is that of parameterized interpolation, for best-fit of experimentally measured spectra. Examples of using Lorentz functions for spectral-line fitting are given in references [41,42]. Pseudo-broadening parameter sensitivity should be an issue for parametric modeling of spectra.

Given an assumed reasonable estimate of the absorbance function $\alpha_c(\omega)$, e.g., Eq. (1), a procedure for estimating the dielectric function begins with the normalized imaginary index of refraction, given by

$$k_N(\omega) = \frac{k(\omega)}{\max[k(\omega)]} \quad (2)$$

where

$$k(\omega) = \frac{\alpha_c(\omega)}{\omega}, \quad (3)$$

Next, using the Kramers-Kronig relation [22], the normalized real index-of-refraction change is estimated by

$$\Delta n_N(\omega) = \frac{2}{\pi} P \int_0^{\infty} \frac{\Omega k_N(\Omega) d\Omega}{\Omega^2 - \omega^2} \quad (4)$$

where P denotes the Cauchy principal value [22]. Given the absorbance function $\alpha_C(\omega)$ expressed by Eqs. (1), it can be shown that

$$\Delta n_N(\omega) = \sum_{k=1}^{N_k} \frac{1}{\omega} \frac{A_k(\gamma_k/2)(\omega_k - \omega)}{(\omega_k - \omega)^2 + (\gamma_k/2)^2} \quad (5)$$

For purpose of comparison, adjustable parameters are introduced, based on the understanding that dielectric functions on the macroscale depend on “scatterer” density [22], condensed-phase coupling characteristics, and that the transformation Eq.(4), with respect to integration range, can be incomplete, when applied to experimental measurements [43-45]. Accordingly, DFT-calculated spectra are adopted as an estimated model-ansatz, to be combined with parameters, for construction of parametric models to fit experimental measurements. For comparison with dielectric functions obtained from measurements, a parametric model is given by

$$k_s(\omega) = A_s k_N(\omega) \quad (6)$$

and

$$n_s(\omega) = n_0 + B_s \Delta n_N(\omega), \quad (7)$$

where A_s and B_s are scaling coefficients of the normalized quantities defined by Eqs. (2) and (4), and the constant component n_0 of the real index, with A_s and B_s , compensate for approximations underlying Eq.(4), applied to measurements. For comparison with measured reflectance and transmission, respectively, parametric models are given by

$$R_M(\omega) = \exp(-C_s \alpha_s(\omega)) \quad (8)$$

and

$$T_M(\omega) = \exp(-D_s \alpha_s(\omega)), \quad (9)$$

where C_s and D_s are adjustable path-length parameters.

3. Prototype IR-Spectrum Templates for Caffeine Molecules

Examined in this section is the functional character of DFT-calculated spectra, for their inclusion within template-spectrum databases, and their ability to show very good correlation with measured spectra, i.e., their scalability from micro to macro scale with respect to IR-spectral structure. The procedure for continuous-function transformation of DFT spectra and their pseudo broadening considered here is spectrum modeling using Lorentzians, similar to the procedure used by GaussView [27], which entails constructing the slope field [46] of DFT-calculated spectra [28]. As demonstrated, and continuing observations of previous studies, the functional character of DFT-calculated spectra, providing good correlation with measured spectra, establishes foundation for using DFT spectra as template spectra and to estimate dielectric functions, examined in the next section.

For this study, IR spectra for a caffeine molecule within different solvent backgrounds, and in vacuum (characteristic of gas phase), have been calculated using the Kohn Sham equation implementation of DFT. As indicated, the commercial computer program Gaussian 16 [28, 29], and procedure as described above, were used to effect the calculations. For each molecule and background, the minimized ground state energy for each molecule is indicated Table 1, and the spectral IR intensity corresponding to each calculated frequency is listed in Tables 2. Shown in Figs. (3)-(5) are DFT-calculated spectra for a single caffeine molecule, as isolated and within water and chloroform solvent backgrounds, respectively. These figures, showing the basic form of DFT-calculated spectra, provide a delta-function representation of IR spectra. Shown in Fig. (3) is an example of a caffeine molecule having an equilibrated minimum-energy structure.

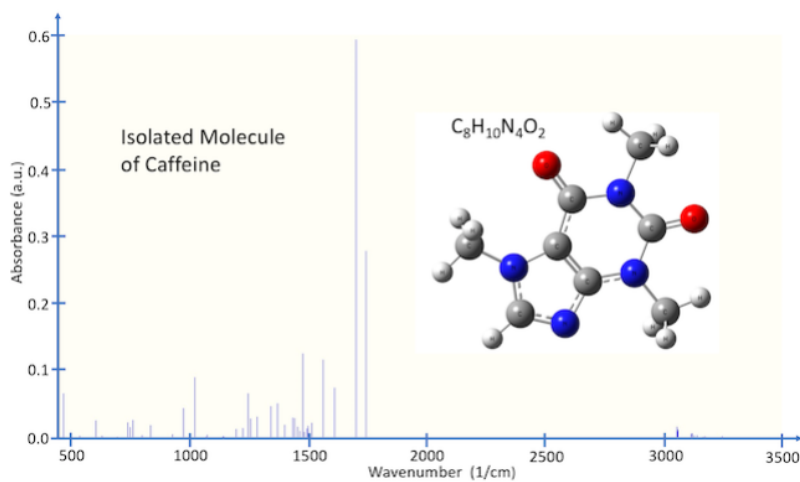


Figure 3. DFT-calculated IR spectra and molecular structure for isolated caffeine molecule. Energy of equilibrated molecular structure -680.615395 Hartree.

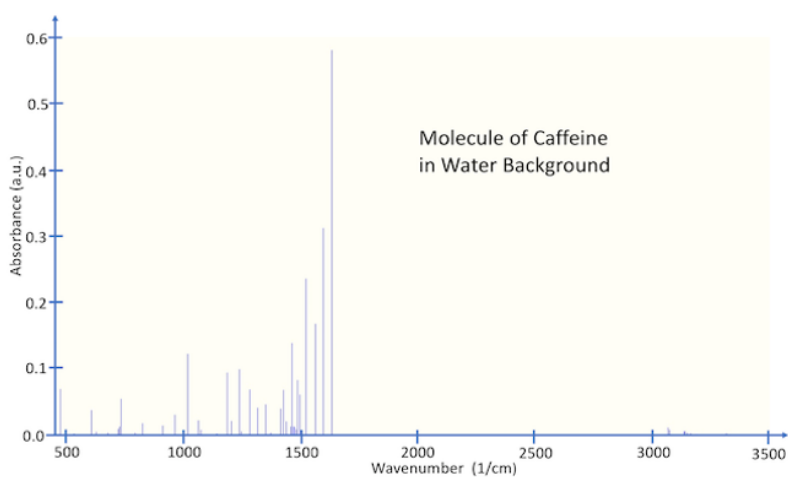


Figure 4. DFT-calculated IR spectra for caffeine molecule in water background. Energy of equilibrated molecular structure -680.379863 Hartree.

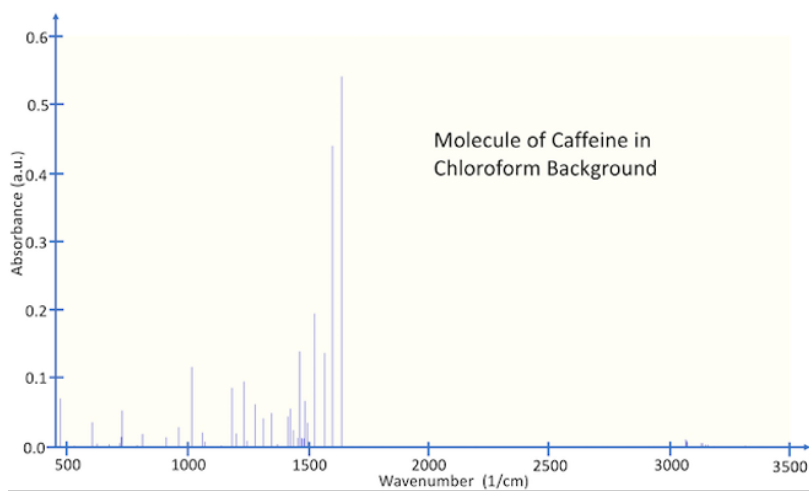


Figure 5. DFT-calculated IR spectra for caffeine molecule in chloroform background. Energy of equilibrated molecular structure -680.374694 Hartree.

Table 1. Energies of Equilibrated Molecular Structures

Solvent	Energy (Hartree)
Acetone	-680.378811
CCl ₄	-680.370069
Cyclohexane	-680.369283
Chloroform	-680.374694
THF	-680.376529
Water	-680.379863
Methanol	-680.379333
Vacuum	-680.615395

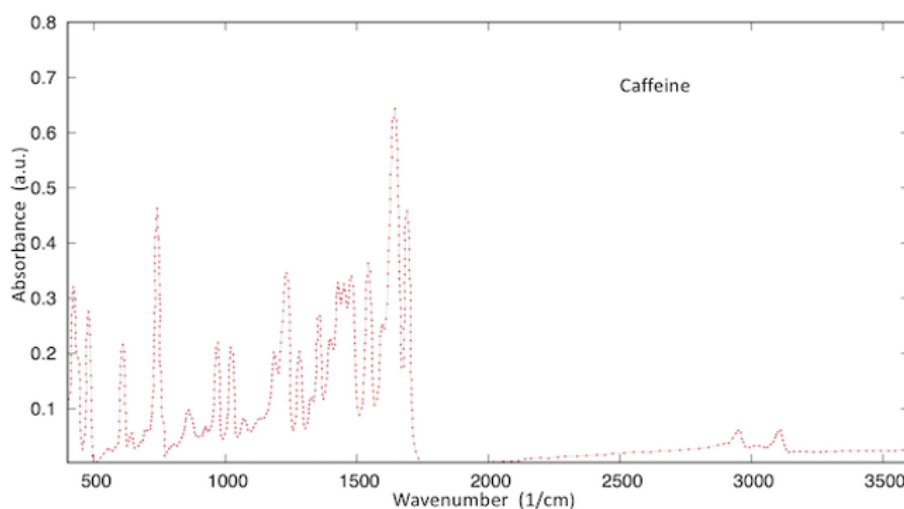


Figure 6. Measured absorbance function of caffeine [23].

Our analysis first examines scalability of DFT-calculated spectra for a caffeine molecule, within different solvent backgrounds, by their comparison to the measured IR spectrum shown in Fig. (6). Shown in Figs. (7) and (8) are two different transformations of the measured IR spectrum Fig. (6), representing spectral-feature enhancements, for the purpose spectrum-feature extraction by comparison to spectrum templates.

Next, we examine interpolation and pseudo-broadening of DFT-calculated IR spectra, with respect to construction of template spectra, which are non-unique procedures for spectrum feature enhancement. Shown in Figs. (9)-(16) are the DFT-calculated spectra of Table 2 that have been pseudo-broadened using linear combination of Lorentz line-shape functions Eq. (1). To be noted is that trend features of DFT-calculated spectra are preserved with respect to continuous-function interpolation and pseudo broadening. This property and ability of DFT-calculated spectra to have good correlation with measured spectra, thus demonstrating scalability from micro to macro scale, provides foundation for using DFT to calculate estimates of dielectric, transmission and reflectance functions, which are macroscopic material properties.

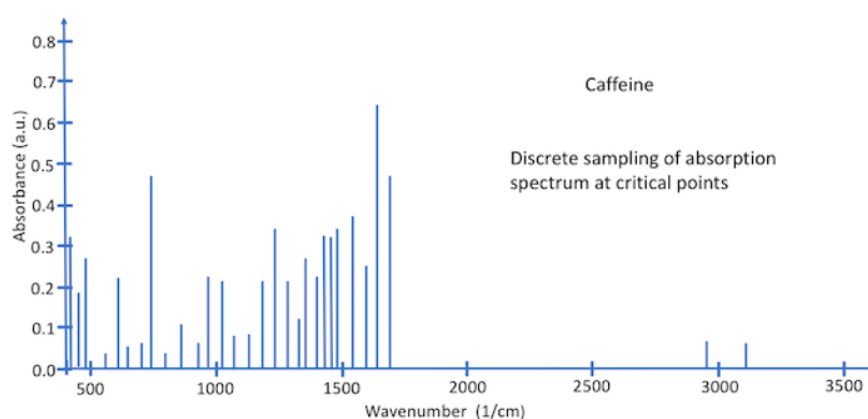


Figure 7. Discrete-function approximation of absorption function (Fig. 6) for caffeine.

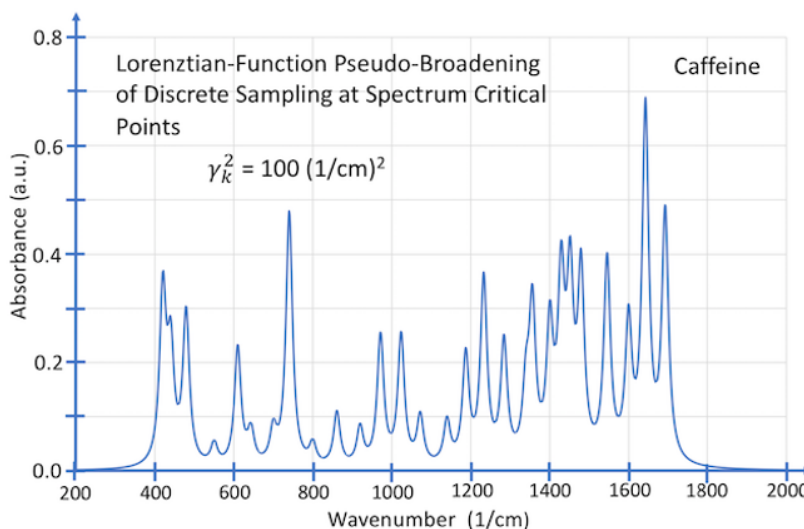


Figure 8. Pseudo-broadening of discrete-function approximation (Fig.7) of absorbance spectrum (Fig. 6).

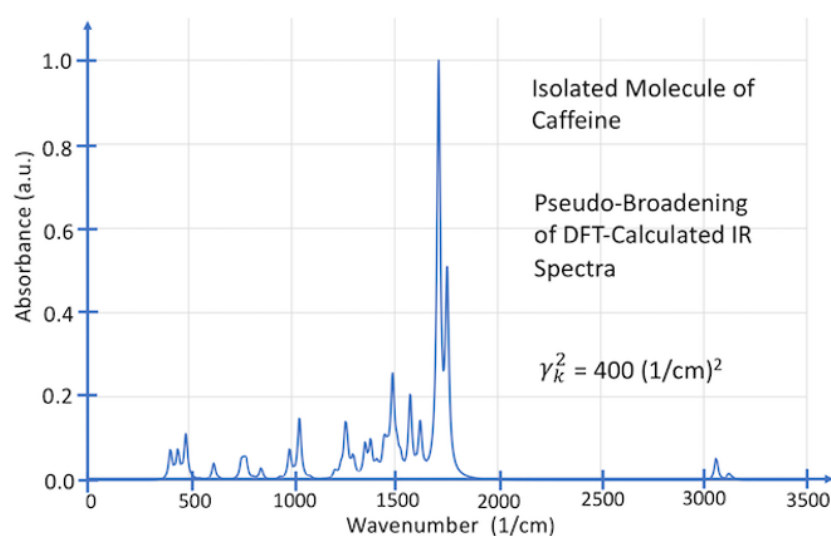


Figure 9. Interpolation of DFT-calculated IR spectra using model Eq.(1) for isolated caffeine molecule (Figure 3).

Referring to the ontology shown in Fig. (1), to be noted is that the different types of spectra and their functional representations, Figs. (3)-(11), consisting of DFT-calculated and measured spectra, and their spectrum-feature enhancements, can be adopted as an ensemble of template spectra. The comparisons shown in Figs. (3)-(11) continues support of previous experience indicating that the DFT-calculated IR spectra of this paper are expected to deliver reasonable correspondence to the analogous experimental IR spectra.

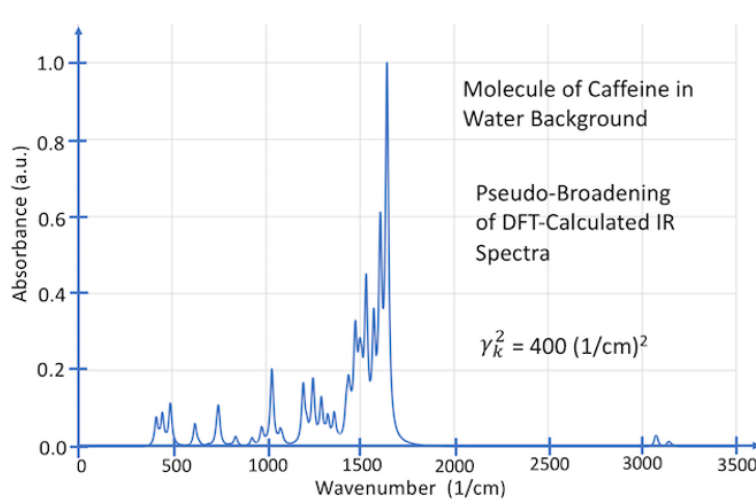


Figure 10. Interpolation of DFT-calculated IR spectra using model Eq.(1) for caffeine molecule in water background (Figure 4).

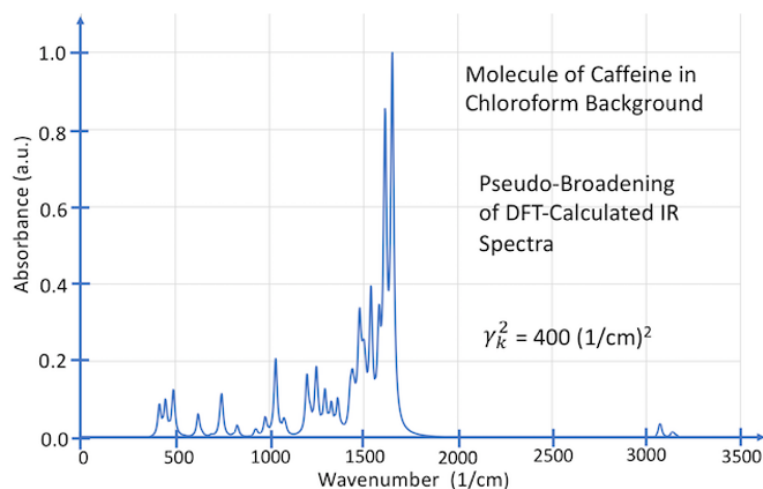


Figure 11. Interpolation of DFT-calculated IR spectra using model Eq.(1) for caffeine molecule in chloroform background (Figure 5).

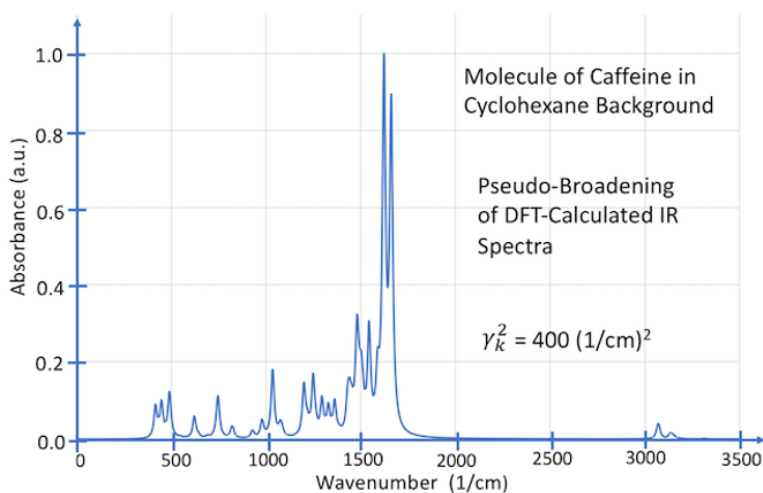


Figure 12. Interpolation of DFT-calculated IR spectra using model Eq.(1) for caffeine molecule in cyclohexane background (Table 2).

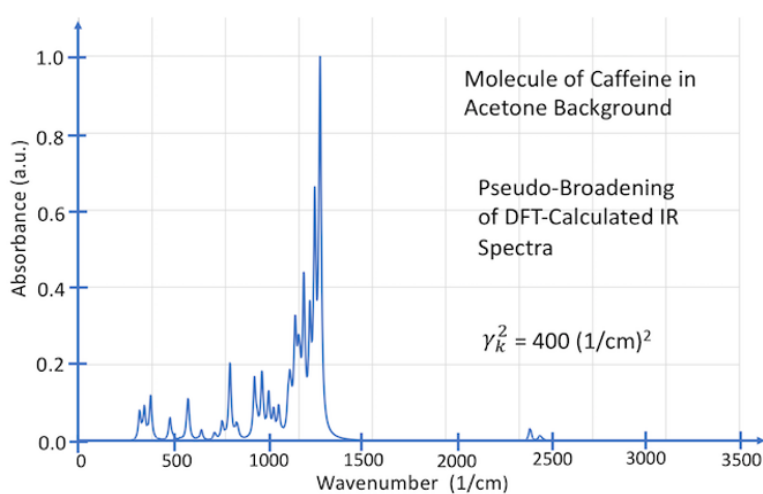


Figure 13. Interpolation of DFT-calculated IR spectra using model Eq.(1) for caffeine molecule in acetone background (Table 2).

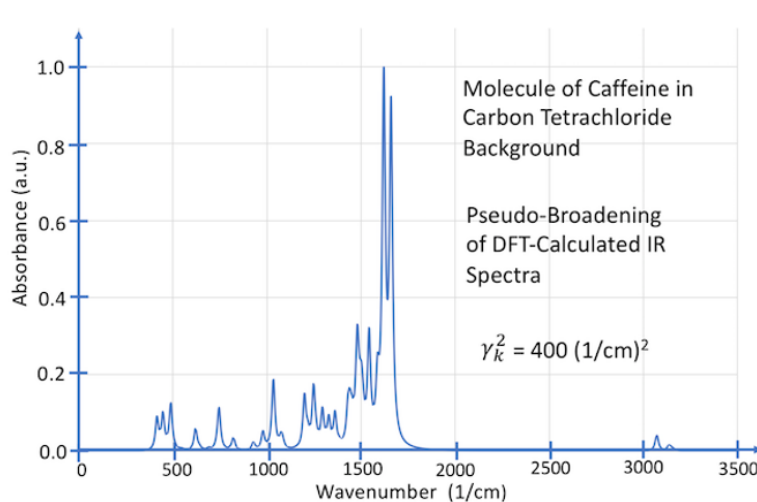


Figure 14. Interpolation of DFT-calculated IR spectra using model Eq.(1) for caffeine molecule in carbon tetrachloride background (Table 2).

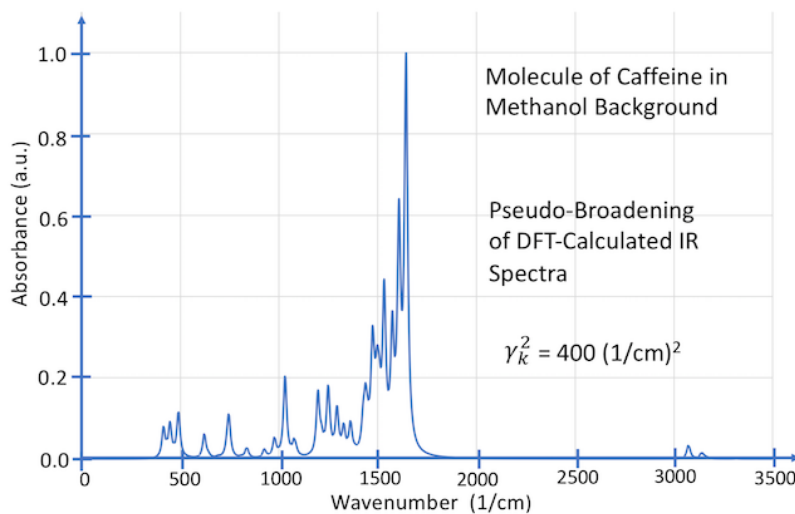


Figure 15. Interpolation of DFT-calculated IR spectra using model Eq.(1) for caffeine molecule in methanol background (Table 2).

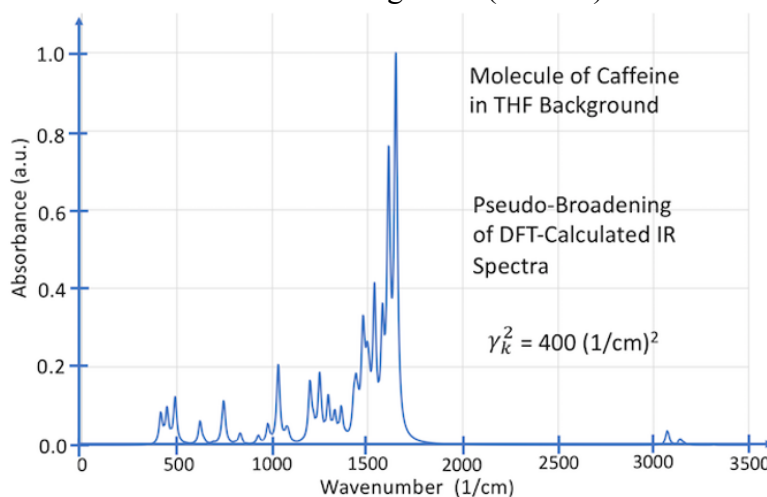


Figure 16. Interpolation of DFT-calculated IR spectra using model Eq.(1) for caffeine molecule in THF background (Table 2).

Table 2. DFT-calculated spectra

isolated molecule		in water		in chloroform		in acetone	
Frequency (cm ⁻¹)	Intensity (M ⁻¹ cm ⁻¹)	Frequency (cm ⁻¹)	Intensity (M ⁻¹ cm ⁻¹)	Frequency (cm ⁻¹)	Intensity (M ⁻¹ cm ⁻¹)	Frequency (cm ⁻¹)	Intensity (M ⁻¹ cm ⁻¹)
69.16	1.29	74.48	33.10	48.77	27.77	69.68	34.67
80.54	88.43	81.40	254.90	50.59	8.77	83.94	198.15
90.02	49.24	88.04	11.89	86.60	64.83	88.08	15.90
95.75	1.19	116.09	124.09	94.07	53.27	114.84	90.02
118.92	48.06	126.83	654.44	112.95	52.22	126.38	678.20
127.15	220.69	170.63	157.82	125.96	646.84	169.86	151.41
160.12	125.25	206.31	335.76	167.23	133.81	206.29	326.67
208.74	172.64	242.49	9.95	205.83	294.30	242.02	9.82
214.13	4.03	300.76	6.13	240.04	9.02	300.24	5.92
276.56	3.39	301.93	45.14	298.39	4.91	302.01	43.13
297.99	31.98	361.03	198.36	301.50	35.98	360.89	191.74
355.65	5.00	392.32	305.22	360.11	166.17	392.25	294.87
356.77	94.65	397.33	0.22	391.92	253.69	396.88	0.26
396.05	138.95	415.05	221.94	394.98	0.36	415.02	215.05
410.68	142.91	447.81	243.19	415.03	192.95	447.69	237.29
446.23	131.88	490.67	340.29	447.27	213.32	490.48	328.85
485.54	216.16	547.46	2.43	489.66	288.90	547.39	2.66
553.76	5.11	621.44	182.13	546.93	3.67	621.39	172.67
620.85	81.50	641.72	18.64	620.93	143.58	641.66	17.48
647.88	4.93	692.00	11.16	641.39	14.50	691.84	11.36
710.78	0.28	735.39	40.07	691.36	11.64	735.24	33.24
754.60	71.39	741.20	58.43	734.73	16.92	741.33	58.10
765.05	47.81	746.28	266.65	742.01	56.17	746.12	254.78
777.40	82.64	807.05	9.01	745.67	214.80	807.24	8.37
816.01	8.11	838.06	82.16	808.05	6.09	836.05	80.40
851.30	57.76	925.67	64.73	829.07	74.52	925.91	61.00
942.47	10.71	977.09	143.83	926.81	51.79	977.21	136.59
989.51	141.92	1030.59	607.39	977.80	115.75	1030.98	580.37
1037.00	294.38	1076.45	103.70	1032.39	481.90	1076.45	99.17
1083.59	0.36	1086.53	30.89	1076.09	83.32	1086.48	29.81
1088.16	9.47	1152.82	0.14	1085.94	26.39	1152.65	0.04
1153.19	0.02	1153.14	1.92	1152.04	0.03	1153.48	2.10
1156.87	2.05	1155.57	0.16	1154.70	2.22	1155.91	0.16
1158.03	0.25	1197.18	465.46	1157.08	0.22	1197.49	439.40

Table 2 (cont.)

isolated molecule		in water		in chloroform		in acetone	
Frequency (cm ⁻¹)	Intensity (M ⁻¹ cm ⁻¹)	Frequency (cm ⁻¹)	Intensity (M ⁻¹ cm ⁻¹)	Frequency (cm ⁻¹)	Intensity (M ⁻¹ cm ⁻¹)	Frequency (cm ⁻¹)	Intensity (M ⁻¹ cm ⁻¹)
1209.32	37.34	1215.55	99.67	1198.47	353.90	1215.57	94.11
1238.59	42.92	1249.20	490.37	1216.14	77.10	1248.89	468.25
1260.45	215.17	1258.66	21.23	1248.40	393.77	1258.82	24.80
1268.96	88.98	1293.50	338.09	1259.85	31.22	1293.77	321.85
1298.47	98.15	1327.94	197.33	1294.34	252.91	1327.87	189.85
1355.81	151.89	1362.45	223.79	1328.02	169.16	1362.36	220.04
1382.74	165.50	1384.26	10.54	1361.92	201.45	1384.39	10.20
1413.54	59.93	1426.12	192.25	1384.77	11.47	1426.70	192.36
1446.51	94.34	1438.22	334.09	1428.58	181.69	1438.66	308.24
1454.26	91.88	1448.59	97.01	1439.96	227.55	1449.00	96.92
1466.36	49.52	1468.82	55.71	1450.84	96.51	1468.97	54.31
1477.93	29.15	1473.52	689.18	1469.85	49.28	1474.47	658.68
1489.19	413.14	1481.08	58.14	1477.61	576.51	1482.20	56.01
1489.59	22.57	1482.90	54.05	1486.10	50.07	1484.14	52.21
1495.87	23.32	1490.28	36.97	1488.04	45.20	1491.03	40.35
1507.77	41.26	1497.01	408.68	1494.24	46.26	1497.71	375.27
1511.81	55.55	1507.53	296.47	1500.09	274.03	1507.94	252.09
1527.31	68.65	1532.05	1173.77	1509.36	141.89	1533.44	1086.42
1574.88	383.45	1572.70	834.68	1538.40	805.70	1574.72	793.08
1623.16	243.24	1607.23	1555.18	1581.28	566.28	1608.23	1629.63
1712.85	1977.52	1642.77	2900.67	1613.32	1828.91	1644.35	2754.78
1754.12	924.52	3071.39	48.25	1651.50	2251.88	3071.13	46.85
3058.67	50.74	3075.82	33.38	3070.00	42.50	3075.75	33.06
3059.89	27.05	3077.31	27.90	3075.17	32.35	3077.11	27.33
3062.65	35.94	3137.46	21.01	3075.76	24.72	3137.10	20.09
3118.64	14.23	3142.35	22.64	3135.45	17.62	3142.21	21.73
3121.71	16.54	3153.21	11.35	3141.28	18.94	3153.10	10.63
3131.10	6.65	3167.04	8.47	3152.13	8.51	3166.35	8.28
3142.97	7.76	3190.22	1.39	3162.91	7.61	3190.14	1.37
3167.56	0.33	3190.78	0.71	3188.28	0.81	3190.52	0.77
3176.53	1.20	3317.52	5.43	3188.37	1.31	3317.64	5.12
3248.29	2.18			3316.84	4.03		

Table 2 (cont.)

ccl4		in methanol		in cyclohexane		in THF	
Frequency (cm ⁻¹)	Intensity (M ⁻¹ cm ⁻¹)	Frequency (cm ⁻¹)	Intensity (M ⁻¹ cm ⁻¹)	Frequency (cm ⁻¹)	Intensity (M ⁻¹ cm ⁻¹)	Frequency (cm ⁻¹)	Intensity (M ⁻¹ cm ⁻¹)
24.04	58.05	72.03	35.13	16.69	82.64	40.91	10.88
49.09	2.74	82.76	225.69	46.41	2.72	59.14	28.47
86.36	46.73	87.86	10.49	86.35	43.85	86.35	87.47
98.51	19.35	115.38	101.98	98.76	17.67	91.10	63.91
112.85	37.71	126.57	672.75	112.43	32.94	113.34	60.04
126.23	579.84	170.22	154.28	126.33	569.35	125.98	671.25
164.97	120.97	206.30	331.06	164.70	119.50	168.40	140.65
204.97	258.72	242.30	9.91	204.83	252.42	206.11	308.36
238.24	7.99	300.49	6.03	238.01	7.83	240.88	9.38
296.71	3.73	301.98	44.11	296.47	3.55	299.18	5.38
300.34	29.40	360.96	195.08	300.18	28.51	301.86	39.04
358.84	139.89	392.28	300.14	358.56	135.70	360.51	177.39
391.52	210.95	397.12	0.24	391.45	204.19	392.08	271.86
393.12	0.32	415.02	218.44	392.81	0.30	395.82	0.33
415.18	171.15	447.75	240.30	415.25	167.20	415.03	201.95
446.91	186.95	490.58	334.22	446.88	182.62	447.45	224.05
488.81	248.94	547.43	2.56	488.67	242.70	490.03	306.20
546.42	5.06	621.43	177.25	546.37	5.30	547.16	3.18
620.36	120.87	641.71	17.93	620.25	117.68	621.16	155.19
641.20	11.80	691.92	11.25	641.18	11.37	641.50	15.72
691.11	11.17	735.31	36.72	691.11	11.04	691.56	11.62
734.44	10.01	741.25	58.29	734.44	9.38	734.94	22.30
742.90	52.63	746.20	260.34	743.08	51.80	741.71	57.11
745.46	179.55	807.14	8.71	745.48	174.49	745.85	231.66
808.93	4.18	836.99	81.26	809.06	3.91	807.70	7.03
822.31	69.39	925.79	62.33	821.39	68.57	832.12	76.97
927.81	43.06	977.14	139.35	927.99	41.62	926.41	55.62
978.70	96.10	1030.82	593.41	978.88	93.54	977.54	124.89
1034.07	381.62	1076.47	101.66	1034.31	365.77	1031.73	524.68
1075.51	70.37	1086.52	30.31	1075.40	68.41	1076.29	89.70
1085.08	23.14	1152.76	0.06	1084.93	22.50	1086.23	27.78
1151.80	0.05	1153.32	2.05	1151.85	0.05	1152.28	0.03
1156.03	2.18	1155.75	0.16	1156.28	2.16	1154.18	2.20
1158.44	0.26	1197.36	451.92	1158.69	0.25	1156.58	0.19

Table 2 (cont.)

ccl4		in methanol		in cyclohexane		in THF	
Frequency	Intensity	Frequency	Intensity	Frequency	Intensity	Frequency	Intensity
(cm ⁻¹)	(M ⁻¹ cm ⁻¹)	(cm ⁻¹)	(M ⁻¹ cm ⁻¹)	(cm ⁻¹)	(M ⁻¹ cm ⁻¹)	(cm ⁻¹)	(M ⁻¹ cm ⁻¹)
1199.25	281.22	1215.50	96.28	1199.34	271.05	1198.01	389.41
1217.10	60.23	1248.98	478.59	1217.34	57.67	1215.88	84.69
1248.08	321.04	1258.71	23.76	1248.07	308.93	1248.56	425.36
1261.04	34.64	1293.70	332.07	1261.18	35.63	1259.34	28.80
1294.91	195.21	1327.86	192.54	1294.97	186.87	1294.10	281.27
1328.50	149.05	1362.43	222.20	1328.64	146.32	1327.92	178.41
1361.63	178.19	1384.35	10.10	1361.63	173.74	1362.09	209.89
1385.33	13.42	1426.42	193.12	1385.53	13.73	1384.56	10.87
1430.14	161.35	1438.44	319.97	1430.40	156.89	1427.82	187.59
1440.95	164.59	1448.75	96.91	1441.13	157.28	1439.47	260.98
1452.64	95.45	1468.90	54.99	1452.91	95.06	1450.04	96.77
1471.41	44.13	1473.99	671.51	1471.78	43.28	1469.42	51.44
1480.16	506.11	1481.65	57.03	1480.52	494.49	1476.31	609.44
1489.61	45.58	1483.55	53.12	1490.13	44.81	1484.48	52.35
1491.45	38.22	1490.64	38.70	1492.01	37.25	1486.47	48.27
1497.63	48.74	1497.36	391.55	1498.12	49.26	1492.79	44.90
1502.12	197.50	1507.74	273.93	1502.43	187.96	1499.12	314.22
1510.80	86.41	1532.75	1124.56	1511.05	80.91	1508.75	180.46
1542.83	570.86	1573.88	813.44	1543.45	538.07	1536.26	923.22
1587.73	300.24	1607.67	1602.58	1588.79	267.31	1578.40	679.51
1620.78	1926.00	1643.44	2824.18	1622.32	1920.59	1610.92	1744.61
1659.16	1779.25	3071.25	47.50	1660.34	1708.28	1648.31	2466.35
3068.47	38.74	3075.80	33.19	3068.22	38.16	3070.53	44.29
3073.69	27.36	3077.23	27.60	3073.38	26.77	3075.48	32.50
3074.35	26.04	3137.28	20.52	3074.24	25.99	3076.43	26.08
3133.35	16.11	3142.30	22.16	3132.98	15.94	3136.23	18.55
3140.13	16.64	3153.15	10.97	3139.96	16.30	3141.77	20.08
3150.25	6.96	3166.79	8.38	3149.85	6.76	3152.67	9.35
3159.00	7.22	3190.35	1.38	3158.48	7.22	3164.42	7.88
3185.50	0.59	3190.78	0.75	3185.20	0.60	3189.15	1.23
3185.94	1.41	3317.68	5.27	3185.79	1.39	3189.34	0.91
3314.77	3.06			3314.35	2.91	3317.28	4.49

4. Prototype Estimation of Dielectric, Transmission and Reflectance Functions

Demonstrated in this section are estimations of dielectric, transmission and reflectance functions, based on the observed scalability of DFT-calculated spectra, as shown above for the case of caffeine, and for other substances in previous studies (see [9-13]). Estimation of these functions are calculated using the parametric models defined by Eqs. (1)-(9).

An example of comparing DFT-calculated dielectric functions to spectroscopic measurements, concerning caffeine on the macroscale, considers the work of reference [47], which presents a detailed analysis, using various spectroscopic methods, of caffeine dielectric response for the macroscopic condensed-phase. A comparison of the DFT-calculated estimates of dielectric functions shown in Figs. (17)-(19) to spectral measurements of [47] shows good correlation. A specific case of this correlation is described by comparison of Figs. (17)-(19) to the imaginary and real indices of refraction shown in Figs. (20) and (21), respectively, obtained from measurement. As discussed above, this comparison is with respect to the adjustable parameters defined by Eqs. (6) and (7). Comparison of the dielectric functions shown in Figs. (17)-(19) demonstrates an insensitivity to small variations of spectral features associated with coupling to the different background environments considered.

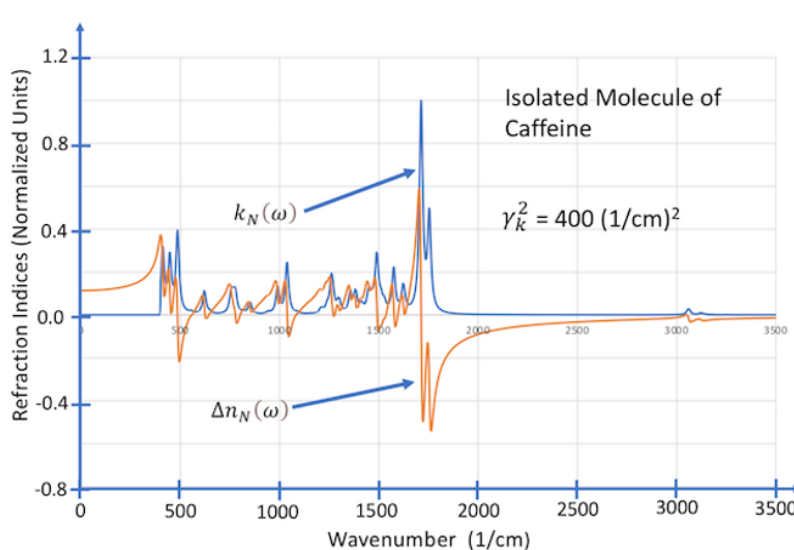


Figure 17. Normalized imaginary index of refraction and real index of refraction change calculated using absorbance function Figure 9.

An aspect of the comparisons, Figs (17)-(21), is that the imaginary and real indices of refraction obtained by measurement, Figs. (20) and (21), respectively, are given as a function of frequency on a logarithmic scale. This is significant within the context of our general analysis, which is to demonstrate scalability of DFT-calculated spectra by their correlation with measured spectra. Accordingly, the logarithmic function representations shown in Figs. (20) and (21) specify a procedure for “feature-narrowing” of measured spectra for comparison to spectra based on DFT calculation.

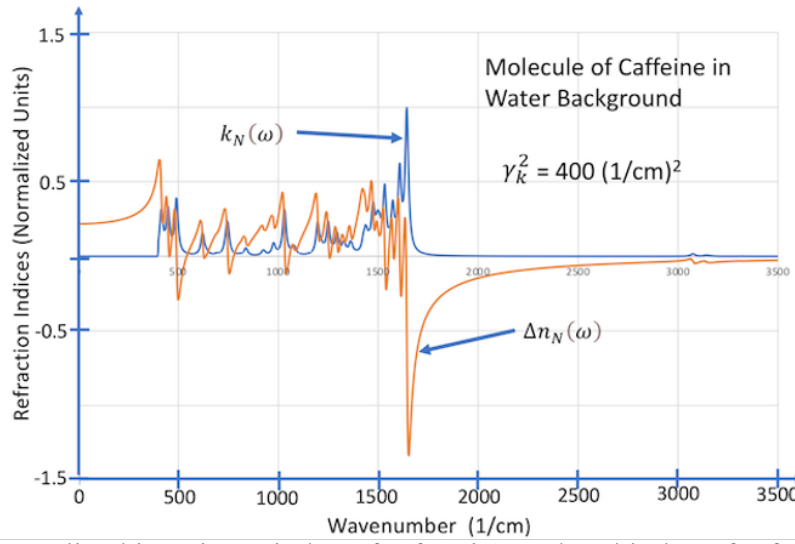


Figure 18. Normalized imaginary index of refraction and real index of refraction change calculated using absorbance function Figure 10.

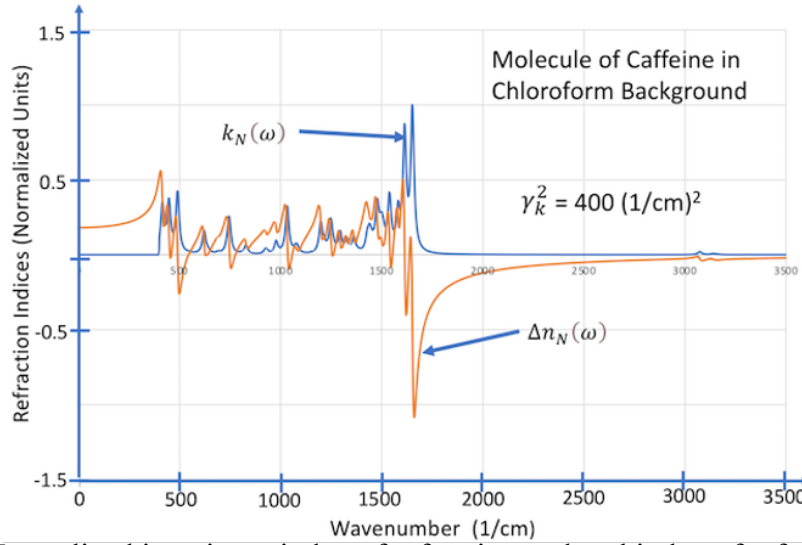


Figure 19. Normalized imaginary index of refraction and real index of refraction change calculated using absorbance function Figure 11.

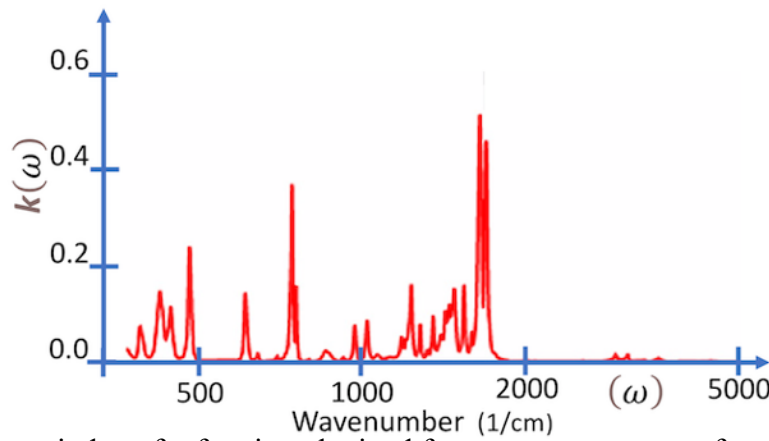


Figure 20. Imaginary index of refraction obtained from measurement, as function of frequency on a logarithmic scale [47].

Another example of comparing DFT-calculated dielectric functions to spectroscopic measurements, concerning caffeine on the macroscale, considers the IR spectrum shown in Fig. (22) (see reference [48]), which is of a slight variant of the caffeine molecule, i.e., $C_8H_9ClN_4O_2$, Caffeine, 8-chloro. A comparison of DFT-calculated estimates of transmission functions, Figs. (18), obtained using parametric model Eq. (9), to transmission measurements of [48], Fig. (22), show good correlation. Emphasized is that this comparison is within the adjustable pseudo-broadening parameter γ_k^2 , where the best fit to the spectrum of Fig. (22) is shown in Fig. (23). Comparison of Figs. (22) and (23), demonstrate that a change in one functional group produces a small change in an overall family of IR spectra. Functional groups in a molecule generally have only one identifying stretch and maybe an overtone. Hence, not much should be different between spectra of Figs. (22) and (23), since only a small functional group was changed.

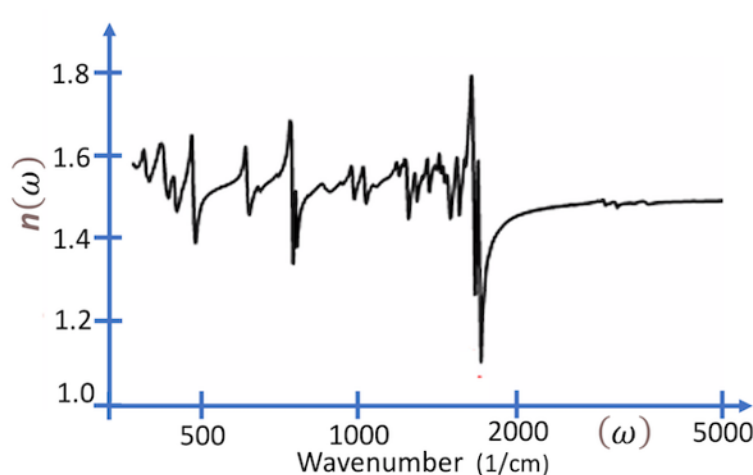


Figure 21. Real index of refraction obtained from measurement, as function of frequency on a logarithmic scale [47].

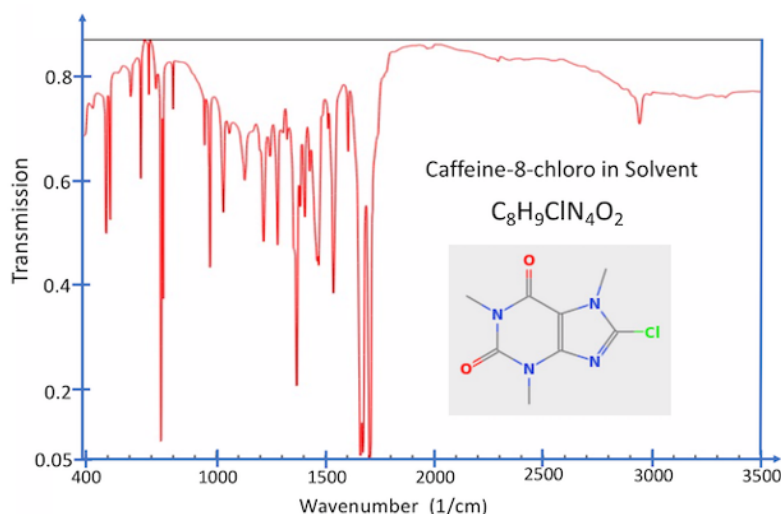


Figure 22. Transmission spectrum obtained from measurement [48].

For our next comparison, noted is that parametric modeling of transmission and reflectance, for the purpose of spectrum comparison, are formally the same, i.e., Eqs. (8) and (9), and are both defined in terms of adjustable pseudo-broadening and path-length parameters. This comparison considers the measured reflectance spectrum shown in Fig. (19), which is of caffeine on a rough aluminum surface [47]. Referring to Fig. (24), noted is that the measured spectrum, given as a function of frequency on a logarithmic scale, is characterized by relatively broad and smoothed-out features, relative to those shown in Fig. (22), associated with transmission. A comparison of DFT-calculated estimates of reflectance functions, Figs. (25) and (26), obtained using parametric model Eq. (8), to measured reflectance [48], Fig. (24), shows good correlation. This comparison combines both pseudo-broadening, via parametric model Eq. (8), and feature-narrowing, via frequency dependence on a logarithmic scale, and is within the adjustable pseudo-broadening parameter γ_k^2 , which is varied for comparison, Comparison of Figs. (25) and (26) demonstrates that the procedure of pseudo-broadening also is that of smoothing spectral features, for purpose of comparison.

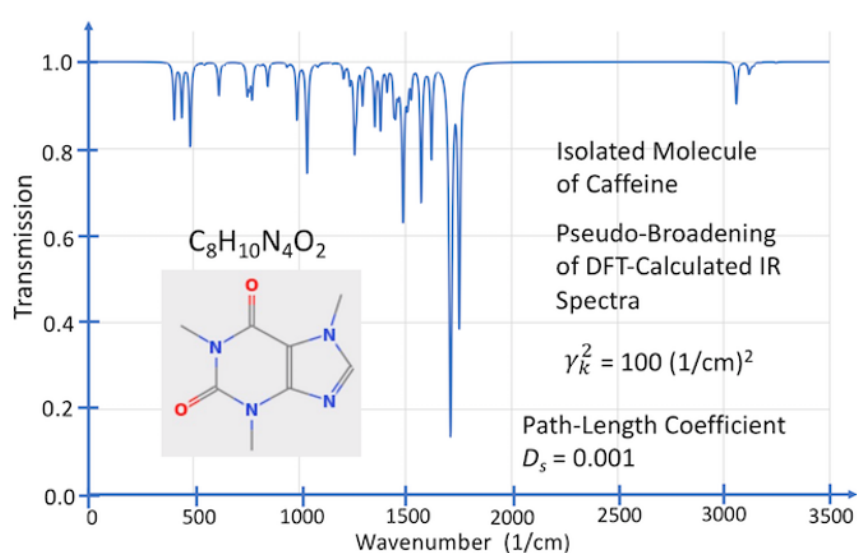


Figure 23. Estimate of transmission spectrum using DFT-calculated IR spectrum of isolated molecule of caffeine (Fig. 3), showing relatively good correlation with measured spectrum Fig. (17).

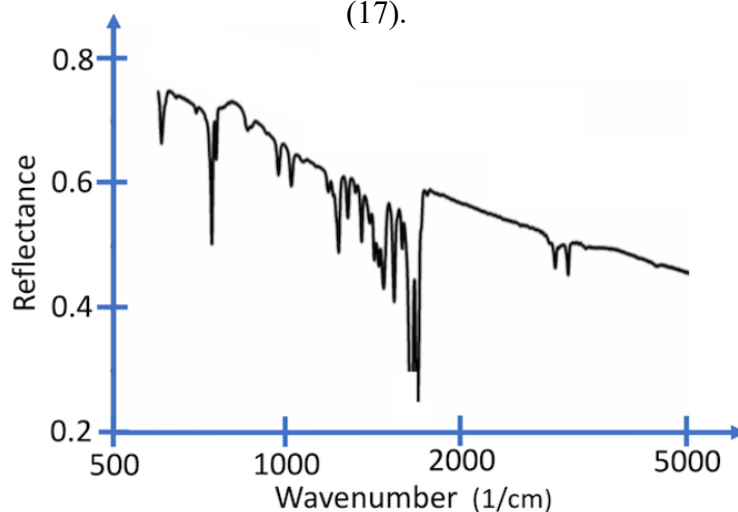


Figure 24. Reflectance spectrum obtained from measurement [47].

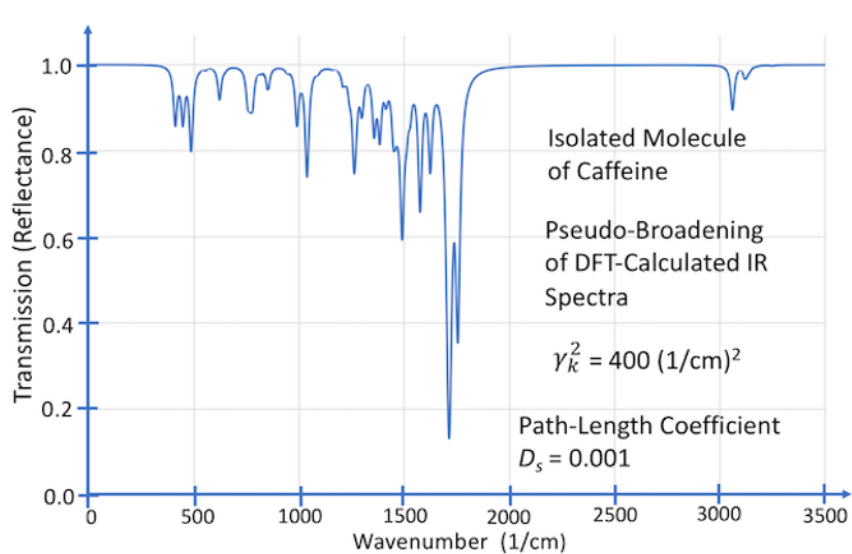


Figure 25. Estimate of transmission or reflectance spectrum using DFT-calculated IR spectrum of isolated molecule of caffeine (Fig. 3), where parameter $\gamma_k^2 = 400 (1/\text{cm})^2$.

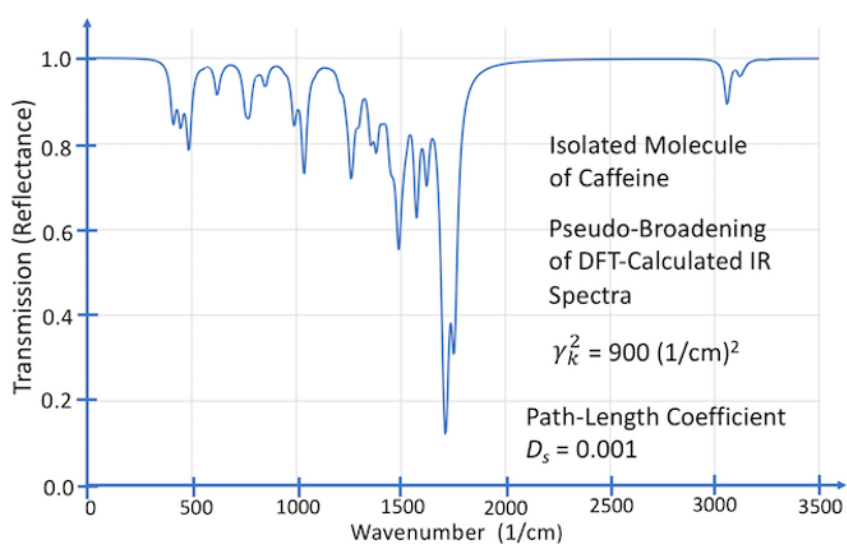


Figure 26. Estimate of transmission or reflectance spectrum using DFT-calculated IR spectrum of isolated molecule of caffeine (Fig. 3), where parameter $\gamma_k^2 = 900 (1/\text{cm})^2$.

5. Discussion

This study demonstrates that DFT-calculated spectra are sufficiently robust with respect to micro-to-macro scalability, which is in terms good correlation with measured IR spectra and insensitivity to variations of spectral features associated with coupling to different background environments. The DFT calculation of IR spectra for a caffeine molecule in different solvent backgrounds, and small variation of molecular structure, e.g., Fig. (22), represent a computational experiment demonstrating that average spectral features are insensitive to ambient-background coupling at the molecular level. This insensitivity is also demonstrated by comparing DFT-

calculated spectra, with various spectrum-feature enhancements, to IR spectra obtained from measurements. The DFT-calculated spectra, given in Table 2, should provide useful estimates for analysis and modeling of substances containing caffeine. Comparisons of DFT calculated dielectric, transmission and reflectance functions to experimental measurements demonstrate their scalability. Beyond the scope of this study, it should be noted that the modeling of mixtures of materials (say for example, coffee blends) requires dielectric functions as input to effective-medium models [22].

The results of this study further support the concept spectrum database enhancement using DFT-calculated spectra, as described by Fig. (1). Specifically, if DFT-calculated spectra are to a practical complement to experimental measurements, within a spectrum-template database, they must be scalable to meso and macro scales, within reasonable levels of approximation.

6. Conclusion

DFT-calculated IR spectra of a caffeine molecule in different solvent backgrounds, and their spectral-feature enhancements using interpolation and pseudo-broadening procedures, can be utilized as template spectra for feature extraction related analysis of substances containing caffeine, especially quality control of different varieties of coffee [23-26]. This work presents a collection of DFT calculated IR spectra for caffeine, representing a prototype database of IR spectrum templates for its identification (and quantification). It is of significance that DFT-calculated IR spectra contain features associated with isolated molecules, allowing their separation from signatures related to experimental artifacts and intermolecular interactions. In addition, this work presents a set of methods for comparison of DFT-calculated and measured IR spectra. These methods remain an open area of investigation.

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References

- [1] Haaland D. M., "Multivariate Calibration Methods Applied to Quantitative FT-IR Analyses", Chapter 8, Practical Fourier Transform Infrared Spectroscopy, Editors: Ferraro J.R. and Krishnan K., Academic Press, Inc., San Diego, CA (1990).
- [2] Lam R.B., "On the Relationship of Least Squares to Cross-Correlation Quantitative Spectral Analysis," Appl. Spectros., 37 pp. 567-569 (1983).
- [3] Brown S.D., "The Kalman Filter in Analytical Chemistry," Anal. Chem. Acta 181 pp. 1-26 (1986).
- [4] Cooper W.S., "Use of Optimal Estimation Theory-in particular the Kalman Filter-in Data Analysis and Signal processing," Rev. Sci. Instrum. 57, No. 11, pp. 2862-2869 (1986).
- [5] Mann C.K., Goleniewski J.R., Sismanidis C.A., "Spectrophotometric Analysis by Cross-Correlation," Appl. Spectros., 36, pp. 223-227 (1982).
- [6] Mann C.K. and Vickers T.J., "Signal Enhancement by Data Domain Averaging," Appl. Spectros., 40, 4, pp. 525-531 (1986).
- [7] Harrick N.J., Internal Reflection Spectroscopy, Interscience Publishers, New York (1967).
- [8] Griffiths P.R. and Christopher C.C., Handbook of Vibrational Spectroscopy, John Wiley & Sons, New York (2002).
- [9] Huang L., Lambrakos S.G., Massa L., "IR Absorption Spectra for Chlorinated Ethanes in Water Using Density Functional Theory," Multiscale and Multidisciplinary Modeling, Experiments and Design, Volume 2, Issue 3, September 2019, pp. 175-183 (2019).
- [10] Wallace, S., Lambrakos, S.G., Massa, L., "Density Function Theory (DFT) Calculated Infrared Absorption Spectra for Nitrosamines," Water Science and Technology, Volume 80, Issue 10, pp. 1967-1974 (2019).
- [11] Wallace, S., Lambrakos, S.G., Shabaev, A., Massa, L., "Calculated IR Absorption Spectra for Perfluoroalkyl and Polyfluoroalkyl (PFAS) Molecules," Structural Chemistry, (2021) 32, pp. 899-901.
- [12] Wallace S., Lambrakos S.G., Shabaev A., Massa L., "On Using DFT to Construct an IR-Spectrum Database for PFAS Molecules," Structural Chemistry, 33, pp. 247-256 (2022),
- [13] Lambrakos, S.G., Shabaev, A., Wallace, S., Massa, L., "IR Absorption Spectra for PFAS Molecules Calculated Using Density Functional Theory," Naval Research Laboratory Memorandum Report, Naval Research Laboratory, Washington, DC, NRL/MR/6394--19-10, 116, July 24, 2020.
- [14] Zhao B.B.H., Zhang L., Zhang X., Liu J., Wu T., Wang S., "Hyperspectral Feature Extraction Based on the Reference Spectral Background Removal Method," IEEE Journal of Selected Topics in Applied Earth Observations and Remote Sensing," Vol. 8, Issue 6 (2015), pp. 1-27.
- [15] Mazet V., Carteret C., Brie D., Idier J., Humbert B., "Background removal from spectra by designing and minimizing a non-quadratic cost function," *Chemom. Intell. Lab. Syst.* 76 (2005) pp. 121-133.
- [16] Schulze G., A. Jirasek A., Yu M.M., Lim A., Turner R.F., Blades M.W., Investigation of selected baseline removal techniques as candidates for automated implementation, *Appl. Spectrosc.* 59 (2005) pp. 545-574.
- [17] Lasch P., "Spectral Pre-Processing for Biomedical Vibrational Spectroscopy and Microspectroscopic Imaging," Chemometrics and Intelligent Laboratory systems, Vol. 117 (2012), pp. 100-114.

- [18] Smith, S. W., *The Scientist and Engineer's Guide to Digital Signal Processing*, Chapter 3: "The Sampling theorem," and Chapter 7: "Properties of Convolution, Correlation," California Technical Publishing, San Diego, CA (1997).
- [19] Kirsch, A., "An Introduction to the Mathematical Theory of Inverse Problems" Springer-Verlag, New York, 1996.
- [20] Tarantola A., "Inverse Problem Theory and Methods for Model Parameter Estimation," SIAM, Philadelphia, PA, 2005.
- [21] Kortum, G. *Reflectance Spectroscopy*, Springer-Verlag, Berlin (1969).
- [22] Bohren C. F., and Huffman, D. R., *Absorption and Scattering of Light by Small Particles*, Wiley-VCH, 2004.
- [23] Abdalla, M. A., "Determination of Caffeine, the Active Ingredient in Different Coffee Drinks and Its Characterization by FTIR/ATR and TGA/DTA," *International Journal of Engineering and Applied Sciences*, Vol.2, Issue 12, (2015), pp. 85-89.
- [24] Collazos-Escobar G.A., Gutierrez-Guzman N., Vaquiro-Herrera H.A., Amoroch-Cruz C. M., "Moisture Dynamic Sorption Isotherms and Thermodynamic Properties of Parchment Specialty Coffee (*Coffea Arabica* L.)," *Coffee Science*, 15:e151684 (2020).
- [25] Craig A.P., Franca A.S., Oliveira L.S., Evaluation of the Potential of FTIR and Chemometrics for Separation Between Defective and Non-Defective Coffees," *Food Chemistry*, 132 (2012), pp. 1368-1374.
- [26] Monje A. F. B., Parrado L. X., Gutierrez-Guzman N., "ATIR-FTIR for Discrimination of Espresso and Americano Coffee Pods," *Coffee Science*, v. 13. n.4 (2018), pp. 550-558. DOI:10.25186/cs.v13i4.1499.
- [27] Dennington R., Keith, T. and Millam J., GaussView, Semichem Inc., Shawnee Mission, KS, 2019
- [28] Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.
- [29] Frisch A., Frisch M. J., Clemente F. R., and Trucks G. W., Gaussian 09 User's Reference, Gaussian Inc., p, 105-106 (2009), online: www.gaussian.com/g_tech/g_ur/g09help.htm. [accessed 2021 Jun 22]
- [30] Hohenberg P. and Kohn W., "Inhomogeneous Electron Gas," *Phys. Rev.* **136**, B864, (1964).
- [31] Kohn W. and Sham L. J., "Self-Consistent Equations Including Exchange and Correlation Effects," *Phys. Rev.* **140**, A1133 (1965).
- [32] Jones R. O., and Gunnarsson O., "The density functional formalism, its applications and prospects," *Rev. Mod. Phys.* **61**, 689 (1989).

- [33] Martin R.M., Electronic Structures Basic Theory and Practical Methods, Cambridge University Press, Cambridge, p. 2 (2004).
- [34] Wilson, E. B., Decius, J.C., and Cross P.C., Molecular Vibrations, McGraw-Hill, New York (1955).
- [35] Ochterski J.W., “Vibrational Analysis in Gaussian,” help@gaussian.com, (1999).
- [36] Becke A. D., “Density-functional Thermochemistry. III. The Role of Exact Exchange,” *J. Chem. Phys.*, **98**, pp. 5648-5652 (1993).
- [37] Miehlich B., Savin A., Stoll H., and Preuss H., “Results Obtained with the Correlation Energy Density Functionals of Becke and Lee, Yang and Parr”, *Chem. Phys. Lett.*, **157**, pp. 200-206 (1989).
- [38] McLean A.D. and Chandler G.S., “Contracted Gaussian-basis sets for molecular calculations. 1. 2nd row atoms, Z=11-18,” *J. Chem. Phys.*, **72**, pp. 5639-48 (1980).
- [39] Clark T., Chandrasekhar J., Spitznagel G.W., and Schleyer P.V.R., “Efficient diffuse function-augmented basis-sets for anion calculations, 3., the 3-21+G basis set for 1st-row elements, Li-F,” *J. Comp. Chem.*, **4**, pp. 294-301, (1983).
- [40] Frisch M.J., Pople J.A., and Binkley J.S., “Self-Consistent Molecular Orbital Methods Supplementary Functions for Gaussian Basis Sets,” *J. Chem. Phys.*, **80**, pp. 3265-69 (1984).
- [41] Ordal, M. A., Long L. L., Bell, R. J., Bell, S. E., Bell, R. R., Alexander, R. W. and Ward, C. A., “Optical properties of the metals Al, Co, Cu, Au, Fe, Pb, Ni, Pd, Pt, Ag, Ti, and W in the infrared and far infrared,” *Applied Optics* **22**, pp. 1099-1119 (1983).
- [42] Rakić, A. D., Djurišić, A. B., Elazar, J. M. and Majewski, M. L., “Optical properties of metallic films for vertical-cavity optoelectronic devices,” *Applied Optics* **37**, pp. 5271-5283 (1998).
- [43] King, F. W., “Numerical evaluation of truncated Kramers-Kronig transforms,” *J. Opt. Soc. Am. B* **24**, pp. 1589-1595 (2007).
- [44] M. Bakry and L. Klinkenbusch, “Using the Kramers-Kronig transforms to retrieve the conductivity from the effective complex permittivity,” *Adv. Radio Sci.*, **16**, pp. 23-28 (2018).
- [45] Ohta, K. and Ishida, H. , “Comparison Among Several Numerical Integration Methods for Kramers-Kronig Transformation,” *Applied Spec.*, Vol. 42, No. 8 (1988), pp. 952-957.
- [46] Polyanin A.D., Manzhirov A.V., *Handbook of Mathematics for Engineers and Scientists*, CRC Press (2006). p. 453.
- [47] Bernacki B.E., Johnson T.J., Myers, T.L., “Modeling Thin Layers of Analytes on Substrates for Spectral Analysis: Use of Soli/Liquid n and k Values to Model Reflectance Spectra,” *Opt. Eng.* 59(9), 092005 (2020), doi: 10.1117/1.OE.59.9.092005.
- [48] NIST Standard Reference Database 69: NIST Chemistry WebBook, U.S. Secretary of Commerce on behalf of the U.S.A. IR spectrum of Caffeine, 8-chloro from Smith, A.L., The Coblenz Society Desk Book of Infrared Spectra in Carver, C.D., editor, The Coblenz Society Desk Book of Infrared Spectra, Second Edition, The Coblenz Society:Kirkwood, MO, 1982, pp 1-24.