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Vibrational energy distribution analysis (VEDA): Scopes and limitations



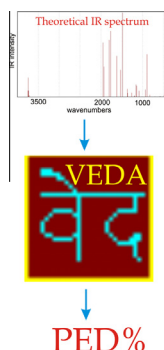
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HIGHLIGHTS

- PED analysis is indispensable in modern vibrational spectroscopy laboratories.
- VEDA program for PED analysis of theoretical vibrational spectra is described.
- VEDA generates internal coordinates based on molecular structure.
- VEDA calculates PED contributions and optimizes the set of internal coordinates.
- The art of PED interpretation using VEDA is outlined.

GRAPHICAL ABSTRACT



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ABSTRACT

The principle of operations of the VEDA program written by the author for Potential Energy Distribution (PED) analysis of theoretical vibrational spectra is described. Nowadays, the PED analysis is indispensable tool in serious analysis of the vibrational spectra. To perform the PED analysis it is necessary to define $3N-6$ linearly independent local mode coordinates. Already for 20-atomic molecules it is a difficult task. The VEDA program reads the input data automatically from the Gaussian program output files. Then, VEDA automatically proposes an introductory set of local mode coordinates. Next, the more adequate coordinates are proposed by the program and optimized to obtain maximal elements of each column (internal coordinate) of the PED matrix (the EPM parameter). The possibility for an automatic optimization of PED contributions is a unique feature of the VEDA program absent in any other programs performing PED analysis.

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Introduction

Vibrational spectroscopy is one of the oldest spectroscopies. Absorption of infra-red light by organic molecules was studied already at the end of XIX century by Abney and by Festing, while the Raman scattering was theoretically predicted and experimentally measured in 1920s by Smekal, Raman, Landsberg and Mandelstam. Nowadays, IR and Raman spectroscopies are developing dynamically and a variety of techniques such as Vibrational Circular Dichroism, Raman Optical Activity, 2D spectroscopies combining the classical spectra with the chiroptical methods, resonance

Raman techniques, and numerous Surface Enhanced Raman Spectroscopy methods are being extensively exploited. Most of these experimental measurements require a computational support. This is because numerous finger-print bands are not easily assignable based on sole experimental knowledge.

Calculation of theoretical vibrational spectra is now possible by using a variety of quantum mechanical software enabling use of a variety of quantum chemical approaches based on variational, perturbational, density functional, and coupled clusters methods. The most of vibrational spectra are still calculated within the harmonic approximation generating some systematical errors. Generally, there are two ways to interpret a theoretical vibrational spectrum of a molecule: a visualization of the atom movement, and Potential Energy Distribution (PED) analysis [1–6]. The first is simple yet

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trivial and deceptive. First of all because of overestimation of hydrogen atoms movements which are visible but often engage negligible energy of the mode. This is especially striking for large molecules in which some normal modes are extended over entire molecule. The PED analysis is more accurate and enables to quantitatively describe the contribution of movement of a given group of atoms in a normal mode. Nevertheless, the PED analysis has a limitation originating from ambiguity of the solutions discussed latter. Therefore, a correct PED interpretation requires spectroscopic knowledge and thoroughness of the interpreter.

The PED analysis results in presentation of a normal mode coordinate as a superposition of local mode coordinates. In consequence, the interpreter finds contributions of local mode energy in overall energy of the normal mode. In 1970s, a program for PED analysis was written by Balga and next modified by Lapinski [7,8]. This program requires the set of local mode coordinates to be defined by user. The coordinates must be linearly independent. This condition is difficult to be satisfied manually even for 16-atomic molecules for which 42 coordinates must be defined. Moreover, quality of the PED analysis is strongly depended on the introduced set of local coordinates. As the number of normal coordinates increases with $3N-6$, for N equal to ca. 50 atoms, the PED analysis was hardly possible. Therefore, in the end of 1990s I wrote the VEDA program which made possible automatic generation of the set of linearly independent local coordinates, first applied in analysis of 9-atomic diformate anion vibrations [9]. Since then, the VEDA program has been continuously developed and has received over 130 independent citations from laboratories all over the world. Wide interest in use of the VEDA program prompted me to describe its possibilities in more details in the present paper. Now, there are available two versions of the VEDA program enabling analysis of molecules constituted from up to 120 and (in an extended version, up to 240 atoms). The VEDA program is a freeware available from <http://www.smmg.pl/> web page.

Theory of PED analysis

Here, only a brief presentation of the theory of PED analysis is presented [10], and thus, known historical perspective of its development is skipped. Reader interested mostly in practical use of the VEDA program may omit this section on first reading.

Let us assume that Born–Oppenheimer and adiabatic approximations, separability of translation, rotation, and vibration movements, and harmonic approximation are fulfilled. Then, the molecular geometry and harmonic frequencies are obtained from quantum chemical calculations together with the kinematic \mathbf{G} and quadratic force constants \mathbf{F}_x matrix (in Cartesian coordinates). The harmonic frequencies are solutions of the following eigenvalue equation:

$$\mathbf{F}_q \mathbf{L}_q = \Lambda \mathbf{L}_q \quad (1)$$

where \mathbf{F}_q is the quadratic force constant matrix in the mass-weighted Cartesian coordinates: $q_k = m_k^{1/2} d_k$ where m is mass of k th atom and d is the atom displacement vector in Cartesian coordinates, $k = 1, \dots, N$, Λ is a diagonal eigenvalues matrix $\lambda_i = 2\pi^2 c^2 \nu_i^2$, where i indexes the modes, \mathbf{L}_q is the eigenvector matrix of normalized amplitudes.

The normal modes Q (orthogonal, in phase, collective atom displacements preserving the mass center) are related to the mass-weighted Cartesian coordinates q through the \mathbf{L}_q^{-1} matrix, while the force constant matrices \mathbf{F}_x and \mathbf{F}_q in Cartesian and Cartesian mass-weighted coordinates are related to each other through the diagonal mass matrix \mathbf{M} :

$$Q = \mathbf{L}_q^{-1} q \quad (2)$$

$$\mathbf{F}_q = \mathbf{M}^{1/2} \mathbf{F}_x \mathbf{M}^{1/2} \quad (3)$$

In this moment we can express Eq. (1) in Cartesian, mass-weighted Cartesian, and normal coordinates. However, we are interested in understanding the complex whole-molecule normal movements in terms of intuitive valence-force coordinates S (changes in bond lengths, valence angles, the out-of-plane angles, and torsional angles). They can be found from both the Q normal modes and the Cartesian X coordinates through the appropriate linear transformation matrices:

$$S = \mathbf{L}_s Q \quad (4)$$

$$S = \mathbf{B} X \quad (5)$$

The \mathbf{L}_s and \mathbf{F}_s the force constant matrix in the valence-force coordinates S can be calculated as follows:

$$\mathbf{L}_s = \mathbf{B} \mathbf{M}^{1/2} \mathbf{L}_q \quad (6)$$

$$\mathbf{F}_s = (\mathbf{B}^T)^{-1} \mathbf{F}_x \mathbf{B}^{-1} \quad (7)$$

Expressing the kinematic matrix \mathbf{G} by the \mathbf{B} and \mathbf{M} matrices:

$$\mathbf{G} = \mathbf{B} \mathbf{M}^{-1} \mathbf{B}^T \quad (8)$$

we can solve the Wilson's \mathbf{GF} problem in the valence-force coordinates:

$$\mathbf{G} \mathbf{F}_s \mathbf{L}_s = \Lambda \mathbf{L}_s \quad (9)$$

The potential energy function V of the molecule can be developed as a power series in terms of Q , and then S , in the point of equilibrium configuration. The origin can be chosen arbitrary thus the null term can be set as zero. The linear force constants vanish in the equilibrium condition as the potential function reaches minimum. Then, within the harmonic approximation, and taking into account orthogonality of Q the potential energy can be written as follows:

$$2V = (\mathbf{L}_s^{-1})^T S^T \mathbf{F}_s \mathbf{L}_s^{-1} S \quad (10)$$

$$2V = \sum_{k=1}^{3N-6(5)} \sum_{i,j}^{3N-6(5)} f_{s,ij} L_{s,ik}^{-1} L_{s,kj}^{-1} S_i S_j$$

The contribution of the i th valence-force coordinate in the k th normal mode, the percent of Potential Energy Distribution, PED(i,k)%, can be written as follows:

$$\text{PED}_{ki} = \frac{\sum_i^{3N-6(5)} f_{s,ii} L_{s,ik}^{-1} L_{s,ki}^{-1}}{\sum_{i,j}^{3N-6(5)} f_{s,ij} L_{s,ik}^{-1} L_{s,kj}^{-1}} \quad (11)$$

Calculations

DFT calculations were performed using the B3LYP functional combined with the Dunning's basis sets [11,12]. All harmonic frequencies were real for the calculated structures. The calculations were run using the programs from the Gaussian 03 package [13]. PED calculations were carried out with the aid of the VEDA program [14].

Results and discussion

Principles of operation of the VEDA program

Definitions of internal modes based on molecular structure

Let us consider a non-linear N -atomic molecule for which $3N-6$ fundamental vibrations occur. The linear molecules are rare and in each case can be considered as a specific exception for which specific mode definition can be proposed. For a non-linear N -atomic molecule we start the PED analysis by VEDA program assuming (different) $N-1$ stretching, $N-2$ bending, and $N-3$ torsion (or out-of-plane) vibrations. Such number of stretching, bending, and torsion coordinates automatically satisfies the requirement of the total number of fundamentals of the considered non-planar

molecule and makes possible to construct a set of $3N-6$ linearly independent coordinates. By stretching we understand a movement of two bonded atoms A–B in opposite directions along the bond. The bending is the movement of three bonded atoms A–B–C changing the ABC angle, whereas the torsion movements are defined for four bonded atoms A–B–C–D as either a change of angle between two A–B–C and B–C–D planes or a change of the A–D segment angle against the BCD plane (out-of-plane). For non-cyclic molecules, the number of stretching coordinates is univocal, whereas there are several possibilities for defining the bending and torsion and/or out-of-plane coordinates. For cyclic molecules there are several possibilities for choosing the stretching coordinates because of additional bond(s) closing the cycle(s). In the course of PED analysis, the starting assumption of $N-1$ stretching, $N-2$ bending, and $N-3$ torsion (or out of plane) vibrations may change and as a result one may end-up with other ratios of these three types of coordinates.

The ambiguity of coordinate definitions is the reason for which it is necessary to propose a set of coordinates alternative to the starting one. In the course of PED analysis, some of the starting coordinates can be replaced by alternative ones. It is very important that, in contrast to the set of normal coordinates, the internal coordinates cannot be assigned in a univocal way. This is the inherent feature of the PED analysis which leads to the possibility for different interpretation of the molecular movements in terms of internal coordinates.

The initial problem of PED analysis is necessity for finding the starting set of internal coordinates satisfying the linear independence condition. This is not a trivial problem particularly for molecules of high symmetry. The VEDA program automatically tests the linear independence of the starting coordinate sets and removes the problem, if necessary, by using the alternative set of coordinates. The user can decide whether to test coordinate for linear dependence automatically, one-by-one, or to change a whole subset of coordinates. The user can also do it himself, manually, or introduce the user-defined set of coordinates. In the case in which two coordinates partially describe the same mode we say that they are redundant. In this case, the VEDA program gives opportunity to replace one or both of the coordinates by non-redundant ones.

Except very simple cases, only a few normal coordinates can be simply expressed by a single stretch, a single bend, or a single torsion coordinate. On the contrary, quite a number of normal coordinates can be expressed by a combination of several stretching, several bending, or several torsion coordinates. However, usually a normal mode is a complex combination of the three types of coordinates, i.e., a combination of stretching and/or bending and/or torsion coordinates. Unfortunately such common cases have no informative and interpretative value. To understand and interpret the molecular vibrations one needs to present them as clear combinations of well defined molecular fragments separated into the three types of internal movements (pure stretchings, pure bendings, pure torsions). Moreover, from our practice we derived to the conclusion that it is desirable (but not obligatory) to separate the coordinates into those of H-atoms and those of only heavy atoms.

Different ways for optimization of PED analysis

The aim of optimization of PED analysis is to represent all normal modes by clear internal coordinates which are simultaneously as close to normal coordinates as possible. To do this, VEDA maximizes the elements of the PED matrix. In the PED matrix, the internal coordinates are in columns, the modes are in rows, and the entries denote percent contribution of the internal coordinate in the mode. The maximization routines starts either from a (linear independent) set of single coordinates (single stretches, single

bends, single torsions, or single out-of-planes) or introductory mixed coordinates based on chemical and geometrical similarity of fragments, or a user defined set of coordinates. In the course of optimization, the coordinates of introductory set are replaced by a sum or a difference coordinates (preserving the type of coordinates) formed by a trial-and-error method supported by an analysis of the PED matrix. Also, the alternative coordinates can be used.

In forming the combination or the difference coordinate, the program allows for assuming factor to be equal to 1 or to adopt a non-unit value. In the latter case, the non-unit (absolute) value can be interpreted as a significance of the particular movement in the whole complex coordinate. The diagonalization measure is expressed by the EPM parameter which is the arithmetic average of the maximal elements of each column of the PED matrix.

The other routine used in the optimization of the PED analysis is the ADM procedure which explores the Atom Displacement Matrix by selective extraction of its stretching, or bending, or torsion components. The partially optimized set of coordinates is supplemented by the ADM extracted coordinates. It is worth to mention, that the construction of introductory set of coordinates directly from the ADM matrix, in vast majority of cases, leads to very complex and knotty set of coordinates. This is connected with frequently forgotten fact, that large movement of light atoms often occur with a minimal use of potential energy.

The optimization often leads to multicomponent coordinates. Therefore, the reduction of coordinates was introduced to the VEDA options. It is the last step in given optimization course. The reduction is performed by eliminating such components of coordinates which change the EPM parameter in minimal degree.

The different optimization steps are non-commutative. Moreover, the starting points can be different from each other. As a result, one can obtain more or less different final coordinates. Therefore, the “Marriage” option of two sets of optimized coordinates was made possible. This “Marriage” option combines different coordinates obtained at independent optimization routines.

The user can edit the coordinates himself. This allows for better interpretation of the problem according to the user's needs. This can be done manually or by step-by-step routine where the user may try to force change of, for example, a torsion coordinate to a bending one. However, change of one coordinate influences the other ones and necessity of redefinition of these other coordinates usually appear. Therefore, the edited set of coordinates often requires a subsequent reoptimization. Yet, to avoid change of the coordinates that are desired by the user, it is possible to declare which of the coordinates have to be reoptimized or, alternatively, which of the coordinates have not to be reoptimized. Last but not least, the VEDA allows for repeating some optimization steps which can be important because of non-commutativity of the options. For example, after mixing the stretch, bend and torsion coordinates it is useful to return to stretch mixing. The optimization routine is interactive and options can be changed during the optimization (for example, testing for usefulness of the alternative coordinates can be switched on or off during the process).

Finally, for large molecules it happens that some modes are poorly described by internal coordinates, i.e., the PED contribution of all internal coordinates to normal mode are small. To deal with this problem, the VEDA program proposes the option “improve bad coordinates” which help to overcome the problem. Let us stress that majority of modes are describe by one, two, or three coordinates and only small number of modes are spread out on many internal coordinates.

After the optimization process, the EPM parameter reaches from 55 to 80 (%). The larger is the molecule the smaller is the EPM parameter. Remark, that some modes have, for instance, both

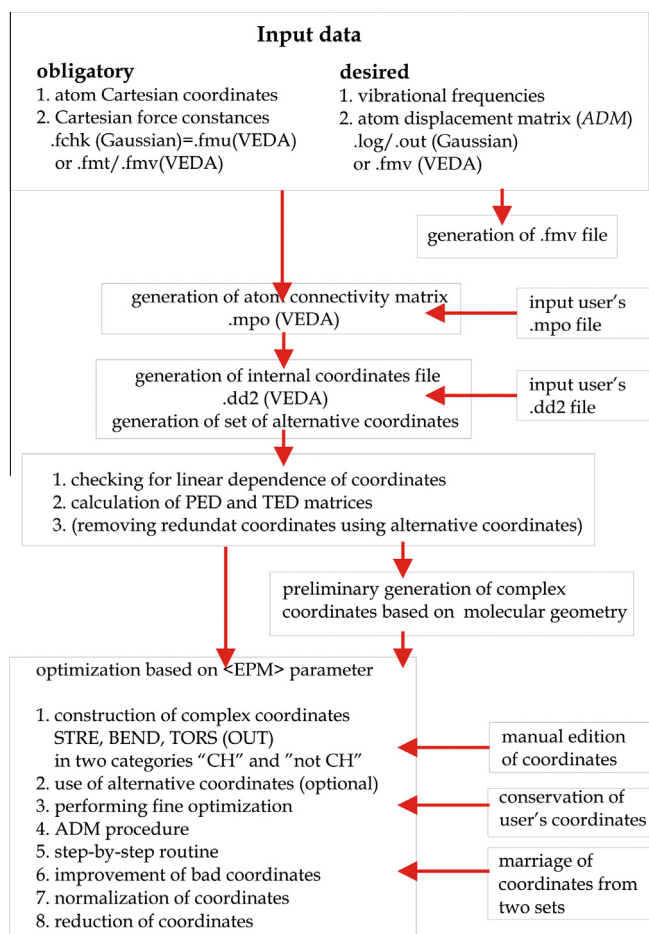


Fig. 1. Block diagram of the VEDA program.

the stretching and bending character. Therefore, they cannot be expressed by a single type of movement. Moreover, some movements can originate from both movement of light and heavy atoms and, for clarity of interpretation, we usually separate these movements in different coordinate definitions.

Block diagram

The general overview of the VEDA program is given in block diagram (Fig. 1). First, notice that there are two categories of input data: (1) obligatory (atom Cartesian coordinates, and Cartesian force-constants) and (2) desirable (calculated vibrational frequencies and atom displacement matrix (ADM)). The desirable input data are not necessary but increase the program potency in the optimization process. The two types of data can be automatically extracted from the Gaussian program [13] output files (.log file or/and .fchk file renamed as .fmu file). If the two types of input data are introduced, the VEDA program produces its own .fmv file which, from now-on, is sufficient to all further analyses. The VEDA program generates the connectivity matrix (.mpo file) and the set of initial internal coordinates (.dd2 file). Both, the .mpo file and/or .dd2 file can be replaced or edited by user to declare, for example, an additional H-bond or another intramolecular contact.

The output can be produced already at the very beginning step. The output files contain the PED and TED matrices (.ved file) and a condensed form of the output in the .vdf file. The .ved and .vdf files are generated after any course of calculations.

The next step can be an automatic mixing of the coordinates (forming linear combinations of coordinates) according to the

geometry and atom type. For example, the coordinates of diverse CH moieties are mixed with each other (according to some vicinity relations) but the CH with CC are not. Also, the CCH bending coordinates are mixed with each other but CCC with HCH are not. However, this routine can be skipped by the user.

Already at the mixing step, but also at any further step, the linear dependence of the current set of coordinates is tested and in the case of linear dependency the problem is signaled. In some cases, it can be automatically corrected by use of the alternative coordinates.

The central step for VEDA analyses is the optimization of the coordinates. The crucial optimization parameter is arithmetic average of the maximal elements of each column of the PED matrix (EPM parameter). The VEDA optimization is to maximize the EPM parameter. The optimization is performed by construction of two categories of stretching, bending, and torsion coordinates: "CH" and "not-CH" coordinates. To "CH" category, the coordinates of OH and NH moieties can be included, while the coordinates of all moieties without H-atoms are included in the "not-CH" category. User can define the "user" category which can be either non-optimized or exclusively optimized. At a given optimization step, user can be satisfied by some coordinates and their PED contribution. The "user" category allows freezing these satisfactory coordinates and reoptimize only the remaining, non-satisfactory, ones. Depend on starting point and non-commutative steps, one can end-up with some different results. The VEDA program enables one to combine the two sets of end coordinates and to form a new one in the "Marriage" routine.

Examples

Symmetric vs. asymmetric molecules

Methanol. Let us first demonstrate the PED analysis for very simple example of methanol molecule of C_s symmetry calculated at the B3LYP/aug-cc-pVQZ level. There are two kinds of modes of the C_s symmetry molecules, A' and A'' , the former of the full-symmetry and the latter breaking the symmetry of the molecule. A natural definition of coordinates reflects the symmetry of the modes (Table 1A). However, it is possible to define the local modes which do not include all of the movements in a given mode (Table 1B), yet lead to the PED analysis yielding also very good representation of the normal modes. To see this observe the s2, s6, and s9 coordinates of the modes belonging to the A'' representation presented in the two Tables 1. Remark, that for the two set of coordinates the EPM parameter, representing the quality of the analysis with respect to the maximized PED coefficients, is very high. For small symmetric molecules it seems to be not useful to represent some modes by coordinates which do not preserve all the atomic movements, but this possibility becomes extremely important as N, the number of atoms of the molecule, increases and the number of coordinates increases with $3N-6$.

The other property illustrated by the two sets of coordinates is the possibility for different interpretation of the same mode by defining it differently. Remark, that coordinate s12 in Table 1A expresses the deformation mode of the OH group, while in Table 1B the rotation of the CH_3 group with respect to the OH group. The two definition can be interchanged and placed in both set of coordinates and it is only intention of the interpreter which one to choose to illustrate the physico-chemical problem to which such an analysis is devoted.

Last but not least element of the PED analysis is the magnitude of coefficients multiplying components of the coordinates. The greater is the coefficient, the higher is the contribution of given component. In the case of methanol, the two CH distances are identical, whereas the third one, placed in symmetry plane is a bit shorter. This results in a bit larger stretch of the two distances in

Table 1A

Methanol: the final set of internal coordinates (dd2 file) obtained when symmetry of the molecule was conserved.

Average max. potential energy <EPm> = 93.362										
TED Above 100 Factor TAF = 0.003										
Average coordinate population 2.167										
Most complex coordinate No. 10, population = 4										
Not normalized 3 coordinates: 2 4 5										
s 1	1.00	STRE	5	6	OH	0.959609	f3835	100		
s 2	2.00	STRE	1	2	CH	1.087419	f3109	98		
	–1.00		1	3	CH	1.093471				
	–1.00		1	4	CH	1.093471				
s 3	1.00	STRE	1	3	CH	1.093471	f3040	100		
	–1.00		1	4	CH	1.093471				
s 4	1.00	STRE	1	2	CH	1.087419	f2994	98		
	2.00		1	3	CH	1.093471				
	2.00		1	4	CH	1.093471				
s 5	2.00	BEND	3	1	4	HCH	109.01	f1510	94	
	1.00		2	1	5	HCO	106.75			
s 6	1.00	BEND	2	1	3	HCH	108.46	f1499	94	
	–1.00		2	1	4	HCH	108.46			
s 7	1.00	BEND	2	1	3	HCH	108.46	f1480	96	
	1.00		2	1	4	HCH	108.46			
	1.00		3	1	4	HCH	109.01			
s 8	1.00	BEND	2	1	5	HCO	106.75	f1368	98	
	1.00		6	5	1	HOC	108.98			
s 9	–1.00	BEND	3	1	5	HCO	112.01	f1174	94	
	1.00		4	1	5	HCO	112.01			
k 10	1.00	BEND	2	1	5	HCO	106.75	f1078	74	f1040 22
	–1.00		3	1	5	HCO	112.01			
	–1.00		4	1	5	HCO	112.01			
	–1.00		6	5	1	HOC	108.98			
s 11	1.00	STRE	5	1	OC	1.422321	f1078	22	f1040 75	
s 12	1.00	TORS	3	1	5	6	HCOH	–61.42	f292 99	

Table 1B

Methanol: the final set of internal coordinates (dd2 file) obtained when symmetry of the molecule was ignored.

Average max. potential energy <EPm> = 94.254										
TED Above 100 Factor TAF = 0.003										
Average coordinate population 2.167										
Most complex coordinate No. 10, population = 4										
Not normalized 3 coordinates: 4 5 9										
s 1	1.00	STRE	5	6	OH	0.959609	f3835	100		
s 2	1.00	STRE	1	2	CH	1.087419	f3109	98		
s 3	1.00	STRE	1	3	CH	1.093471	f3040	100		
	–1.00		1	4	CH	1.093471				
s 4	1.00	STRE	1	2	CH	1.087419	f2994	98		
	2.00		1	3	CH	1.093471				
	2.00		1	4	CH	1.093471				
s 5	1.00	BEND	2	1	5	HCO	106.75	f1510	94	
	2.00		3	1	4	HCH	109.01			
s 6	1.00	BEND	2	1	3	HCH	108.46	f1499	99	
s 7	1.00	BEND	2	1	3	HCH	108.46	f1480	96	
	1.00		2	1	4	HCH	108.46			
	1.00		3	1	4	HCH	109.01			
s 8	1.00	BEND	2	1	5	HCO	106.75	f1368	98	
	1.00		6	5	1	HOC	108.98			
s 9	1.00	BEND	2	1	4	HCH	108.46	f1174	99	
	–2.00		3	1	5	HCO	112.01			
	2.00		4	1	5	HCO	112.01			
k 10	1.00	BEND	2	1	5	HCO	106.75	f1078	73	f1040 22
	–1.00		3	1	5	HCO	112.01			
	–1.00		4	1	5	HCO	112.01			
	–1.00		6	5	1	HOC	108.98			
s 11	1.00	STRE	5	1	OC	1.422321	f1078	22	f1040 75	
s 12	1.00	TORS	2	1	5	6	HCOH	–180.00	f292 100	
	1.00		3	1	5	6	HCOH	–61.42		
	1.00		4	1	5	6	HCOH	61.42		

the s4 mode which is represented in coefficient 2 multiplying the C1H3 and C1H4 distances, while the coefficient for the C1H5 remains equal to one. It is possible to define the s4 coordinate by using only coefficients equal to 1 but the PED coefficient of this mode is decreased by 11% and in addition another mode is then

contributing to this mode. The VEDA program enables for optimization of the coefficients too, but this makes the result of analysis more knotty. From the purely mathematical reasons of the analysis the linear independence of the coordinates is much more crucial than the magnitude of coefficients.

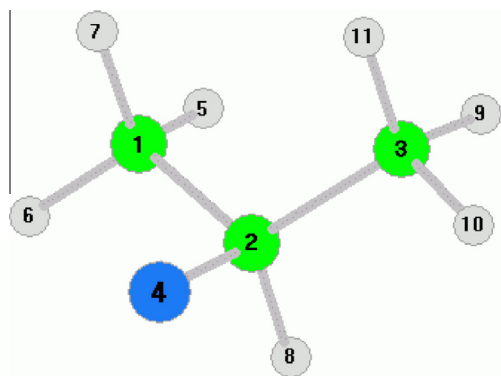


Fig. 2. The 2-fluoro propane structure.

2-Fluoro propane (2FP)

The 2FP structure (Fig. 2) consists in the CCCF skeleton, C₂H group and two CH₃ groups. The molecule exhibits 27 fundamentals. 18 vibrations originate from the two CH₃ groups (6 stretchings, 6 bendings, and 6 deformations); 3 vibrations come from the CH group (stretching, bending and a torsion); and 6 originate from the CCCF skeleton (3 stretchings, 2 bendings, and 1 deformation).

All CH₃ modes of the two methyl groups are mutually coupled. Coordinates are ordered and labeled according to decreasing wavenumbers of the 2FP modes.

The CH₃ stretchings are described by s1–s6 coordinates, where coordinates from s1 to s4 are due to four asymmetric stretching modes (3135, 3133, 3130, 3122 cm⁻¹), s5 and s6 coordinates are due to two symmetric stretching modes: 3053 cm⁻¹ (in phase) and 3049 cm⁻¹ (in counter-phase).

The HCH bendings of the CH₃ groups are labeled from s8 to s13: four of the bendings are asymmetric (1525, 1505, 1501, 1494 cm⁻¹) and two are symmetric: in phase (s12, 1432 cm⁻¹), and in counter-phase (s13, 1424 cm⁻¹).

The s16, s17, s20, s21, s26 and s27 coordinates describe deformations of the methyl groups: four of them (1205 1168 948 933 cm⁻¹) can be described either as HCCC torsions or HCC bendings. Although the movements concern all atoms of the two methyl groups, one can express the movement by selecting only two single coordinates: each representing one methyl group. The movement of other fragments either may or may not be explicitly contained in the coordinate definition. Note that mutual movements of the H-atoms within the methyl group have already been well defined by the HCH bending coordinates. Therefore it is enough to take a representative to express the movement of the whole methyl group. In term of mathematical transformations it corresponds to equivalent transformation of a matrix preserving their invariant while increasing the number of null entries. Here we describe these modes by the pair of the HCC bendings: one from the first and the other from the second CH₃ group (s16, s17, s20 and s21). The last two deformation modes (261 and 222 cm⁻¹) can be exclusively described by sum of three torsions of one and the analogous sum of torsions of the other methyl group. These two modes describe rotations of the methyl groups which in one case are in the same direction (conrotations) while in the other in diverse directions (disrotations). In contrast to the previous deformation modes they cannot be described by bending modes. (see Table 2)

Three movements of the C₂H group are CH stretching (s7, 3031 cm⁻¹), bending (s14, 1391 cm⁻¹) and deformation (s15 1384 cm⁻¹). It is important that the bending and deformation modes can be expressed in two ways. The bending mode can be ex-

pressed as HCF bending in the symmetry plane of the molecule but it can be equally well described as HCCC out of plane mode. Also, the deformation mode, occurring out of the symmetry plane, can be expressed as difference of the HC2C1 and HC2C3 modes, however it can be equally well defined as HCFC out of plane mode. Note, that bending mode can be defined by using three atoms although it can be also defined as out of plane mode which uses four atoms. In contrast, to define the deformation mode in each case, the description requires four atoms to define the movement.

There are three stretching vibrations of the CCCF skeleton: s18 (1164 cm⁻¹, CC asymmetric stretching) and s19 (963 cm⁻¹, CC symmetric stretching with in counterphase CF movement) and s22 (822 cm⁻¹ is the symmetric CC with in phase CF stretching). There are two bending vibrations: s25 (349 cm⁻¹, CCC bending) and s24 (404 cm⁻¹, CCF bending) and one FCCC out of plane s23 mode (476 cm⁻¹).

The above analysis of the simple 2FP molecule is to illustrate the following facts: (1) The description by using the bending and torsion modes can be alternative. (2) The out-of-plane mode, expressing distortion of a vector parallel to a given bond from a plane cannot be limited to description of a planar systems. (3) Only the rotations of the whole groups such as methyl groups should be necessarily defined as appropriate sum of torsion coordinates. (4) The bending which is not occurring in a plane given by its edges (bonds) can be well described by a torsion (in which the atoms are in the vertices of Y-instead of (orthodox) Z-letter).

1,1,1-Trichloro-2-fluoro propane (TCI2FP)

To illustrate the frequent problem appearing in PED analysis, we present examination of an analogous molecule in which one methyl group is replaced by the CCl₃ moiety (Fig. 3). First, presence of the CCl₃ group results in release of previous coupling between two identical CY₃ groups. Moreover, some couplings between CCl and CF modes appear and the symmetric stretching CCl₃ mode disappear. Also, the out-of-plane distortion of F atom from the CCC plane (previously at 476 cm⁻¹) was spread out over several modes and had to be replaced by a mode defined as bending. Thus, even though the 2FP and TCI2FP molecules are quite similar, the definitions of coordinates used for 2FP must be modified to well analyze the TCI2FP modes. The VEDA analysis of the TCI2FP molecule have to be performed from the beginning. Next, we would like to manually make the obtained set of coordinates as similar to that of 2FP as possible. Obviously, the newly appeared couplings must be considered. Now, the modes that have satisfying PED contributions can be fixed as USER modes, and the remaining coordinates can be optimized by using OPTIMIZATION option. Because of the specific couplings we can resign from “force normalization to unit”, which results in using a factors different from 1 in the final coordinate definition set. Although, the EPM parameter is decreased from ca. 80 to ca. 67 this is the inherent feature of the analysis of the more complex molecules.

Art of PED interpretation with VEDA

Let us first stress again that the PED analysis is not unequivocal. Nevertheless, for the most moieties the PED analysis yields clear, unquestionable, coordinates. This is especially truth for the terminal stretching modes. On the other hand, analysis of the skeleton modes is often equivocal. They can be, for example, equally well described by both bending and/or torsion coordinates. The VEDA program cannot automatically judge which type of coordinates is appropriate for the given moiety. This must be decided by a conscious user. The user must know what is the aim of the analysis. For example, if the vibrational spectra of series of conformers or isomers is analyzed, the user may be interested in comparison

Table 2
2-Fluoro propane: the final set of internal coordinates (dd2 file).

[illegible]

Table 2 (continued)

	1.00		2	3	CC						
	1.00		4	2	FC						
s 23	1.00	OUT	4	1	3	2	FCCC	f476	66	f349	13
s 24	1.00	BEND	1	2	4	CCF	f404	86			
	−1.00		3	2	4	CCF					
s 25	1.00	BEND	1	2	3	CCC	f1205	11	f476	10	f349
s 26	−1.00	TORS	5	1	2	3	HCCC	f261	98		75
	−1.00		6	1	2	3	HCCC				
	−1.00		7	1	2	3	HCCC				
	1.00		9	3	2	1	HCCC				
	1.00		10	3	2	1	HCCC				
	1.00		11	3	2	1	HCCC				
s 27	1.00	TORS	5	1	2	3	HCCC	f222	99		
	1.00		6	1	2	3	HCCC				
	1.00		7	1	2	3	HCCC				
	1.00		9	3	2	1	HCCC				
	1.00		10	3	2	1	HCCC				
	1.00		11	3	2	1	HCCC				

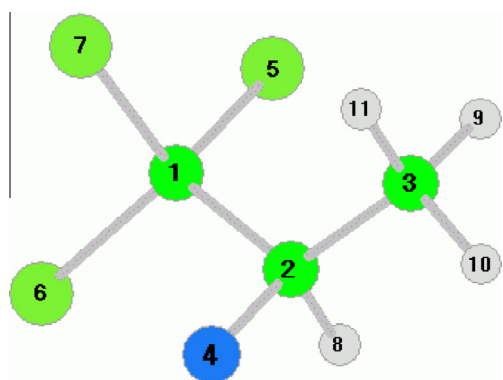


Fig. 3. The 1,1,1-trichloro-2-fluoro propane (TC12FP) structure.

and invariance of some special modes while the other modes are not so interesting. On the other hand, inadequate definition of the coordinates of non-interesting modes is often reflected in decreased quality of coordinates of the interested moiety modes. Some definition of coordinates proposed by the program may seem odd or knotty for the user. In such a case, the user can redefine them himself or run the program again by using some other parameters and optimize only the selected, odd, modes. A special case is when the user would like to replace some torsion coordinates to bending ones, or oppositely. The step-by-step routine can solve this problem. In this routine, initially the EPM parameter becomes smaller but it is gradually improved with the optimization cycles. Generally, change of one coordinate leads to EPM decrease because the coordinates are interdependent. Thus, change of one definition of coordinate must be followed by redefinition of the other coordinates.

It is worth to separately consider the movements of heavy atoms and the movements of moieties with H-atoms. Although, the VEDA program allows for PED analysis with generated mixed coordinates of both moieties with and without H-atoms, for larger molecules large part of coordinate definitions become so complex that is unclear for interpreter. We came to this conviction by analyzing theoretical IR spectra of diisopropyl naphthalenes of 102 fundamental normal modes [15]. It appeared, that by separating the “CH” and “not CH” categories of coordinates one obtains clear and understandable form of coordinates with only slight decrease of the EPM parameter. Since then, the separation of the “CH” and “not CH” coordinates has become a standard of VEDA interpretation. We observed that in many cases defining the NH or OH moieties coordinates as CH type increases clarity and quality of interpretation.

Although, we discussed possibilities of interchanging some bending and torsion coordinates we would like to stress again that this is an important element of the art of PED interpretation. Some authors believe that, for example, the CH_3 modes below 400 cm^{-1} are the only torsion modes of the methyl group. These modes are rotations of the methyl group about the CC bond. In fact, they are the best described by sum of three torsion coordinates and every other description is much worse. However, the CH_3 modes with frequencies in the range between ca. 1100 and ca. 600 cm^{-1} , can be equally well described by, e.g., a XCCH torsion or, e.g., CCH bending coordinate (see discussion of 2-fluoro propane modes in the previous section). Usually, the definitions by using bending coordinates are simpler, however, they have a rational torsion alternative.

For some ring modes, the change of angles are simultaneous with the change of bond lengths. Usually, the interpreter would not like to mix up the stretching and bending modes. For the best description of the ring modes, for example substituted, planar, six-membered ring for which 12 fundamental skeleton modes is possible, one can define either 5 stretching, 4 bending, and 3 torsion modes, or change these numbers respectively to 6, 3, and 3.

Sometimes, the most effective description of the modes is obtained by using a non-standard mode definition [16,17]. In 2000, we analyzed the IR spectra of diketene – the four-membered ring derivative [16]. It appeared, that one of the ring stretching modes is the best described by a stretching of the diagonal ring atoms [16]. In our recent paper devoted in part to alizarin vibrational spectra [17], we have used a similar approach to describe the stretching mode of the central ring of cumulated three-ring skeleton. Definitions of alizarin local coordinates for PED analysis are given in electronic supplementary information to Ref. [17].

For series of conformers it is desired to maximize the number of exactly the same modes. However, this is difficult and explanation why the modes differ requires a meticulous analysis demonstrated, for example, for lactic-acid [18], cysteine [19], β -alanine [20], and isoserine [21]. The similar problem occurs for series of analogous molecules such as halouracils [22], and isotopologues demonstrated, for example, for urea [23] and isopropanol [24]. A detailed analysis of similarities and differences of vibrational spectra and form of the modes reveals the key-structural moieties responsible for the important spectral features.

Usually, for molecules constituted by up to ca. 50-atom, the VEDA program yields PED analysis in which over half of modes is described by one (maybe complex) coordinate of PED contribution over 50%. Usually, two or three coordinates significantly contribute to the remaining modes. Only a few coordinates are poorly described and PED contributions are spread out over several coordinates. For large systems, such as triterpene xylosides constituted

by over 90 atoms [25,26], the number of modes with small PED contributions reaches 10%. Significant number of modes with small PED contributions results in bad assignments of the other modes. For these badly interpreted modes it is important to minimize their influence on the other coordinates.

Let me also mention about selected recent applications of the VEDA program, mostly published in 2011–2013, by the other users which have been continuous inspiration for the program development. Several studies were devoted to optical nonlinearity (NLO) of the studied compounds or materials [27–38]; hydrogen bond and electron donor–acceptor intermolecular interactions [39–43]; amino acids, peptides, conformational studies and interesting biomolecules [44–51]; drug molecules and herbicides [52–58]; various techniques of Raman spectroscopy: SERS [59,60], time-resolved resonance Raman spectroscopy [61–63], resonance Raman optical activity (RROA) [64], ultraviolet resonance Raman spectroscopy (UV-RR) [65]; metal complexes and organometallic compounds [66–71]; various structural studies [72–81].

Finally, we would like to stress that it is always necessary to critically verify the resulting interpretation. Thus, it is always worth to edit coordinates, check how a simplification of some coordinate definitions influences both clarity of interpretation and the EPM parameter, fix some definitions, and reoptimize the other modes. Sometimes, change of some optimization parameters is necessary. In particular, it may be worth to check how the release of normalization of coordinate coefficients to unit influences the overall quality of the analysis. Use of coordinate coefficients different from unit means that some moieties contribute to local mode more than the other moieties.

Conclusions

Nowadays computational methods of quantum chemistry are widely accessible for vibrational spectroscopists. The normal modes are clearly interpretable only for small molecules. Already for medium size molecules the way of vibrational movements become complicated. Therefore, there is a need for tools helping in interpretation of particular normal modes by means of movements of molecular fragments. These movements can be represented by changing of equilibrium coordinates such as stretchings, bendings, and torsions (out-of-plane) of bonds, angles, and dihedral angles of two-, three-, and four-atomic moieties, respectively.

The widely utilized interpretation of the normal modes by visualization of theoretical vibrational modes can provide to misleading conclusions because often large movements of light atoms are not connected with significant change of the potential energy. This is the purpose why the Potential Energy Distribution (PED) analysis should be used. The PED method is based on quantum chemically calculated kinematic \mathbf{G} , quadratic force constants \mathbf{F}_x matrix expressed in Cartesian coordinates, diagonal mass matrix \mathbf{M} , diagonal eigenvalues matrix Λ , and the eigenvector matrix of normalized amplitudes \mathbf{L}_q to yield the contributions of the i -th valence-force coordinate in the k -th normal mode, as the percent of Potential Energy Distribution, $\text{PED}(i,k)\%$. The VEDA program written by the author of this paper is calculating the PED contributions for molecules composed of 120 atoms (a basic version) and maximum 240 atoms (a non-standard version).

To find the PED contributions, VEDA needs to have the set of local coordinates defined by user or generated by the program. Usually the starting set of the coordinates leads to relatively small PED contributions which are spread out over many normal modes. The VEDA program enables to improve the PED contributions by construction of composed local coordinates. The local coordinates are composed according to two main rules: only the same type of movements (stretching, bending, or torsion) are combined, and

the movements of heavy atoms are combined separately from the movements engaging the light atoms. Although this leads to clear local mode definitions, user can ignore these rules introducing his own coordinates which mixes different types of movements. In particular, the user may decide to start the analysis based on sole atom displacements as used in mode visualizations. The possibility for an automatic optimization of PED contributions is a unique feature of the VEDA program which is absent in any other programs performing PED analysis.

The choice of local coordinates is never unequivocal and the final interpretation must be decided by user. Especially, the modes in the fingerprint region can be expressed in many different ways. The interpretation may depend on the problem which user would like to highlight. This is especially important when series of similar compounds, such as conformers or analogously substituted molecules, are analyzed.

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