Analysis of the ab-initio force-fields of the polyatomic molecules followed by solution of the inverse spectral problem

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Abstract

An effective technique of ab-initio force constant correction to fit theoretical vibrational frequencies to experimental ones was proposed. For CH_3X (X = F,Cl, Br, I) molecules, refined force constants were obtained and analyzed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The application of force-fields (FF) of polyatomic molecules currently has two main trends: (i) construction of the FF of structurally similar molecules in order to calculate unknown normal vibrational frequencies; (ii) application of force constants (separate elements of the FF) as constants which characterize specific properties of the molecules, such as the energy of homolytic bond cleavage, etc.

It is due to these applications of FFs that attention has been paid in the last years to the problem of the correct solution of the inverse spectral problem (ISP) for calculations of the FF of complex molecules [1–8]. Most of this work has been devoted to the question of stability of

the mathematical solution of the ISP in reference to the variation of input data. Analysis of the possible ensemble of solutions has been performed far less frequently. A new mathematical approach has been proposed by one of us which enables one to obtain a stable solution, which is the only solution in reference to the input FF (U_0) [7]. However, with the choice of a somewhat different U_0, one will obtain different resulting FFs (U_f). Therefore, with the application of this algorithm, the problem arises of finding the uniform, mathematically and physically substantiated methodology of formation of the U_0 matrix. If such precautions are not taken, the results of the ISP solution performed by different authors may vary markedly, even with an equivalent choice of internal coordinates for the same molecule.

Although methods for calculation of U_0 are built into all modern quantum mechanical soft-

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ware, all of these packages use a **Z** matrix [9] for the representation of the internal coordinates. These matrices do not include all bonds and angles as dependent coordinates, but rather a set of independent orthogonal parameters, bonds, and some simple and dihedral angles. In calculation of the normal vibrational frequencies, this makes it difficult to assign frequencies and, particularly, to compare the results with the ones obtained by a traditional solution of the ISP.

In this paper, we have tried to answer the following questions. (1) How acceptable are the results of ab-initio calculations of the normal vibrational frequencies with utilization of different basis sets? (2) How necessary are the calculations of the FF by the solution of the ISP? Upon which set of conditions do they become efficient? (3) Which are the conditions, possibilities and problems connected to ab-initio calculations of the U_0 and for the following solution of the ISP?

We analyze them by carrying out the analysis of several relatively simple molecules — the mono halogen-substituted methanes CH_3X (X = F, Cl, Br, I).

2. Model and computational details

The electronic structure of the CH_3X molecules and the derived physical parameters were calculated by the ab-initio method using computational package Gaussian94 revision D [10], on the SGI Power Challenge with IRIX 6.2 operating system. In order to choose the optimum basis set for the normal vibrational frequency calculations STO-3G, 3-21G, 6-31G, 6-31G*, 6-311G*, 6-311 + G**, 6-311G(2df,p), and 6-311 + G(3df,2p) and LANL1DZ basis sets were used. Along with the non-empirical methods, semi-empirical methods, such as INDO and MINDO3 were used to calculate the normal vibrational frequencies of the molecules discussed. The corresponding calculations were performed with MOPAC 7 software package on

PPro 200 computer with the Linux 2.1.35 operating system.

Since all the force constants in the programs are calculated in Hartree–Bohr radian units, we used the following conversion equations to transform them to the 10^6 cm^{-2} unit system, which is used by the ISP programs: K_q, $K_{q_{ij}}$ (10^6 cm^{-2}) = 24.2879 K_q H/B^2, K_α, $K_{\alpha\alpha}$ (10^6 cm^{-2}) = 5.71136, 0.71136 H/R^2, $K_{q\alpha}$ (10^6 cm^{-2}) = 11.78156 $K_{q\alpha}$ H/BR.

Vibrational equation in internal coordinates taking into account intermolecular forces was considered and all the solutions were obtained as follows:

$$\mathbf{U} = \mathbf{T}^{1/2} \sum \lambda_i H_i \mathbf{T}^{1/2} + \theta_1 V + V\theta_1 - \theta_1 V\theta_1,$$

(1)

Here, **U** is the required matrix of force constants, $\mathbf{T}^{-1}$ is the matrix of kinematics coefficients, fully determined by the geometry of equilibrium configuration and atomic masses, $\mathbf{T}^{1/2}$ is the generalized inverse matrix to $\mathbf{T}^{-1/2}$ in the terms of Penrose, V is the arbitrary symmetrical appropriate order matrix, $\lambda_i = \omega_i^{-2}$, ω_i are the experimental frequencies, H_i are the orthogonal projectors with the following properties: (1) $\sum H_i = \mathbf{I}$, where **I** is the unit matrix, (2) $H_i H_j = 0$, if $i \neq j$, (3) $H_1 = \theta_1$, θ_1 is the spectral projector associated with a kernel of a matrix $\mathbf{T}^{-1}$.

The full system of internal coordinates can contain one or more linearly-dependent ones. The obtained representation (1) enables one to separate the elements of the matrix connected with redundant coordinates $\theta_1 V + V\theta_1 - \theta_1 V\theta_1$. There are no sufficient experimental frequencies for calculation of a unique matrix **U**. An additional a priori information is necessary.

Let us consider the simplest case, when the vibrational spectrum of a single molecule is known. The matrix of kinematics coefficients **T** and the initial matrix of force constants U_0 are supposed to be known. It is required to build the matrix **U**, reproducing with definite assignment on the forms of normal vibrations in the point

$\mathbf{U}_0$ (i.e., to order till i pairs $\lambda_i^{\exp}$ and H_i^0) and having the least deviation from $\mathbf{U}_0$ in the Euclidean norm. Here, H_i^0 represents the spectral projectors in expansion $\mathbf{T}^{-1/2}\mathbf{U}_0\mathbf{T}^{-1/2} = \sum \lambda_i^0 H_i^0$. Within this statement, widely spread in the condition of shortage of other information, the problem has an analytical solution. Thus, $\mathbf{U}$ permits the unique representation:

$$\mathbf{U} = \mathbf{T}^{-1/2}\sum\lambda_i^{\exp}H_i^0\mathbf{T}^{1/2} + \theta_1\mathbf{U}_0 + \mathbf{U}_0\theta_1$$
$$- \theta_1\mathbf{U}_0\theta_1, \qquad (2)$$

The method was realized in our VIBR program. VIBR software uses the final $\mathbf{Z}$ matrix optimized by Gaussian94 and final FF matrix in internal coordinates as input data.

3. Results and discussion

The comparison of the calculated and experimental vibrational frequencies of CH_3X is presented in Tables 1 and 2. One can see that the STO-3G basis set produces the least reliable values of λ_i. The extension of the basis set to 3-21G and 6-31G enables one to substantially diminish the deviation between the theoretical and the experimental values. As can be seen from Table 1, for different frequencies the minimum deviation is achieved at different basis sets. Moreover, with the best LANL1DZ basis sets deviations from experimental frequencies do not diminish to less than 200 cm^{-1}. The calculation of vibrational frequencies by semi-empirical methods also gives poor agreement. Moreover, the deviation for various deformational vibrations has different signs.

It is obvious that the force constants that correspond to these frequencies are far from being accurate. This calls for a different approach to the calculation of the force constants.

Let us examine the properties of the FF obtained by ab-initio calculations (Table 3). The analysis of the FF obtained by the Gaussian94 program and converted to corresponding units shows that similar force constants obtained by

Table 1
The normal vibrational frequencies of CH_3F calculated with the different basis sets and semi-empirical methods

Basis set	Frequencies (cm^{-1})					
	A_1	E	A_1	E	A_1	E
Experiment	1048	1207	1464	1514	3054	3164
STO–3G	1355	1329	1784	1807	3512	3685
321G	1141	1277	1623	1686	3229	3294
631G	1098	1267	1633	1659	3245	3344
631G*	1185	1311	1651	1653	3236	3316
6311G**	1168	1300	1624	1613	3193	3275
6311+G**	1156	1296	1611	1614	3196	3280
6311G(2df,p)	1181	1309	1623	1619	3181	3257
6311+G(3df,2p)	1165	1308	1617	1619	3182	3259
LANL1DZ	1130	1273	1650	1666	3230	3316
MNDO	1416	1279	1416	1481	3224	3224
MINDO-3	709	1016	1370	1446	3471	3521

the same basis set change monotonically in the row of F, Cl, Br, I. Some deviation is observed for the force constants $\mathbf{U}_{XCH-HCH}$, which differ only slightly by absolute value in the row of F, Cl, Br and I. These values can be practically considered to be constant. For example, in the $\mathbf{U}_f$ obtained at an arbitrary random set of $\mathbf{U}_0$ [8], the most drastic changes in the FF (in most cases — a decrease in the force constants) is observed with F- to Cl-substituted derivatives. Therefore, the postulate of the monotonic change of all kinds of FF in the row of halogen-substituted methanes [8] is confirmed by independent ab-initio calculations.

The force constants presented in Table 3 are the first ones obtained by an ab-initio calculation using a basis set of wave functions, which is equally efficient for all molecules. These force constants have been refined further by solution of the ISP using the adapted algorithm described in Ref. [7]. The results obtained are also presented in Table 3 as an array of $\mathbf{U}_f$.

One can see that the precise solution of the ISP for all the vibrational frequencies with the given $\mathbf{U}_0$ leads to a substantial increase of $\mathbf{U}_{CX}$ and $\mathbf{U}_{CH}$, making them comparable with the values obtained in Ref. [8]. The force constants $\mathbf{U}_{CH-CH}$ and $\mathbf{U}_{CH-XCH}$ also drastically change. Nevertheless, the essential feature of the $\mathbf{U}_0$ —

Table 2
The normal vibrational frequencies of CH_3X in LANL1DZ basis set and experimental frequencies

Type	CH_3F		CH_3Cl		CH_3Br		CH_3I	
	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental
A_1	1130	1048	684	709	580	611	529	533
E	1273	1207	1120	1016	1058	954	1011	883
A_1	1650	1464	1521	1370	1448	1305	1454	1251
E	1666	1514	1631	1446	1618	1444	1614	1438
A_1	3230	3054	2399	2955	3282	2925	3273	2915
E	3316	3164	3406	3034	3421	3062	3411	3062

the monotonic change of all the force constants in the row of F, Cl, Br and I — is preserved in U_f. This proves that the algorithm [7], as mentioned above, allows one to obtain the elements of U_f, which have main features similar to the ones of the input matrix U_0.

There is no other known algorithm for the solution of the ISP that guarantees the conservation of the main features of U_0 in U_f. Therefore, the other existing algorithms are less suitable for the improvement of the force constants obtained by ab-initio calculations of U_0. Our other important finding can be seen by comparison of U_f obtained by us and in Ref. [8] in the row of F, Cl, Br and I when different sets of basis are

used. It is the first time, we believe, that several complete sets of force constants have been obtained for each molecule that allow one to accurately reproduce all the frequencies. In this way, we have demonstrated the presence of multiple solutions to the ISP, which was theoretically predicted. It was shown by analysis of the matrices of the forms of vibration obtained by the solutions of the ISP, that there are differences of the corresponding matrix elements in the present paper and in Ref. [8], although they do not change the assignment of the frequencies and do not exceed the accuracy of modern spectroscopic methods of measuring the electrooptical parameters of complex molecules.

Table 3
The force-fields of CH_3X obtained with the LANL1DZ basis set and corrected to fit the experimental spectra

Force constants	F		Cl		Br		I	
	U_0	U_f	U_0	U_f	U_0	U_f	U_0	U_f
CX	9.917	8.525	4.875	5.120	4.217	4.557	3.714	3.688
CH	9.299	8.413	9.715	7.770	9.775	7.810	9.723	7.743
XCH	1.680	1.418	1.435	1.171	1.341	1.072	1.280	0.976
HCH	1.252	1.039	1.217	0.961	1.197	0.957	1.185	0.941
CX–CH	0.243	0.211	0.048	0.063	0.013	0.015	−0.027	−0.006
CX–XCH	0.786	0.654	0.704	0.619	0.640	0.559	0.573	0.471
CX–HCH	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
CH–CH	0.038	0.018	0.032	0.087	0.074	0.016	0.005	−0.036
CH–XCH	−0.093	−0.079	−0.152	−0.119	−0.160	−0.125	−0.169	−0.136
CH–XCH	−0.077	−0.067	−0.079	−0.065	−0.086	−0.067	−0.096	−0.074
CH–HCH	0.233	0.209	0.207	0.165	0.202	0.162	0.202	0.162
CH–HCH	−0.233	−0.208	−0.207	−0.165	−0.202	−0.162	−0.202	−0.162
XCH–XCH	0.255	0.161	0.221	0.162	0.220	0.164	0.219	0.153
XCH–HCH	−0.300	−0.235	−0.295	−0.227	−0.295	−0.234	−0.305	−0.246
XCH–HCH	0.300	0.235	0.295	0.227	0.295	0.234	0.305	0.246
HCH–HCH	0.626	−0.520	−0.608	−0.480	−0.598	−0.459	−0.592	−0.471

It is obvious that, for the analysis of the changes of particular force constants such as U_{CX} and U_{CH} or the corresponding molecular properties (which is important for the second application of the FF, see above), it is necessary to compare FF obtained with the same basis sets.

It is noteworthy that the U_{CH} obtained by solution of ISP problem correlate with the values of bond energies for corresponding molecules: CH_3F — 103.3 kcal/mol, CH_3Cl — 102.7 kcal/mol and CH_3Br — 102.7 kcal/mol.

The results obtained allow us to demonstrate that the corrected derivation of the elements of the U_0 matrix with unknown spectral properties and the following calculation by the solution of the direct spectral problem (DSP) enable one to determine the normal vibrational frequencies much more accurately than it can be achieved by the direct ab-initio calculations. This can be performed on the condition that all the methodological precautions are taken in the choice of the molecules and the computational programs.

4. Conclusion

Direct estimations of the normal vibrational frequencies of halogen-substituted methanes by ab-initio calculations are not efficient since they cannot provide the required accuracy of 20–30 cm^{-1}.

Calculation of the frequencies, with the use of the corrected force constants set, provides the required accuracy. In this case, the force constants are refined by the solution of the ISP for corresponding molecules with the known experimental spectral data. Such molecules should form a row with monotonic changes in the properties with an increase in the atomic number of the atom that is varied. The U_0 of such molecules can be found by ab-initio calculations on the optimum basis.

In order to implement the above methodology for obtaining the corrected force constants, one can use Gaussian94 and VIBR programs.

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