An single program multiple data strategy for calculation of anharmonic vibrations

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This paper presents a general perturbational and variational scheme to calculate solutions of the spectral problem for the vibrational molecular Hamiltonian. A parallel strategy in the ongoing development of our software P_Anhar is presented, in order to calculate the vibrational spectrum of medium sized molecules. The efficiency of this approach is checked on ethylene oxide.

KEY WORDS: SPMD strategy, anharmonic frequencies, variational method, ethylene oxide

1.   Introduction

Nowadays, the help of computers in science is invaluable [1]. Computers are widely used in a spectrum of activities from geology to mathematics, from biology to quantum chemistry. In this last field, parallel computing is for sure one of the greatest challenges. While parallel computing was at first not very popular in computational chemistry, it is already and clearly will continue, contributing to the solution of problems that stretch current computer hardware and algorithms to their limits.

First steps in parallel computing are not easy: indeed, there is a wide variety of computer types, which can do parallel computing: massively parallel processors (MPP) like the Cray-T3E, scalable shared memory systems like the SGI-Origin, or clusters of PCs running under a Unix-like operating systems. Moreover, there are different ways to control parallel execution, mainly single instruction multiple data (SIMD), where the machine has a single control unit with many processors, which acts on different data sets, multiple instruction multiple data (MIMD), where each processor is controlled independently, which makes this way more flexible but also more complex, and single program multiple data

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(SPMD). This is now the most common way to organize a parallel program, especially on MPP computers. The idea is that a single program is written and loaded onto each node of a parallel computer. Each copy of the single program runs independently (aside from coordination events), so the instruction streams executed on each node can be completely different, though all are particular paths through the code. Tasks within the code and data are allotted to processors as part of the parallel algorithm, the specific path through the code being determined by the processor's rank in the parallel machine. Parallelization of a code can be achieved with the help of standard libraries for message passing like PVM [2] and MPI [3], or using compilers like high performance Fortran (HPF) [4]. Although optimal parallelization may benefit from a detailed knowledge of the architecture of the computer and the libraries and compilers available for the hardware, portable, efficient codes can be written with the help of the tools mentioned.

Quantum chemistry software is increasingly designed to be used with massively parallel computers or PC clusters: Gaussian [5], GAMESS(US) [6], GAMESS-UK [7], NWChem [8], Columbus [9,10], MPQC [11] ... to mention a few, thus enabling users to reach larger systems than were accessible before, or to study smaller ones at higher levels theory. This was possible thanks to a lot of successful efforts in parallelizing first the self-consistent field method (SCF) [12,13], then electron correlation methods such as Møller–Plesset perturbation theory (MPn) [14,15], coupled-cluster methods [16–18] and also configurational interaction (CI) [19]. Besides these established softwares, many of which were not first designed to work with a parallel approach, there are more and more attempts from independent groups to develop parallel applications to compute a specific property. In the field of vibrational spectroscopy for example, P_Anhar [20, 21] was recently developed. Admittedly, reference software is still actively developed in this area (Multimode [22], MCTDH [23], Spectro [24] ...). However, considering the huge computational and memory needs for a full vibrational calculation, earlier codes were limited, e.g. most theoretical studies of anharmonicity never exceeded molecules of over five atoms [25]. Both bench scientists'needs and computational programs make the development of VQC methods (vibrational quantum chemistry) attractive, with an aim to study larger systems [21,26–30].

The purpose of the present paper is the continuation of our previous work on our software P_Anhar [20]. Some upgrades have been done on this code (i.e. for example, the Coriolis contribution was added in agreement with the two previous works [31, 32]), and we have checked it through the calculation of the spectrum of a medium sized molecule: ethylene oxide (C_2H_4O).

2. Overall structure

Parallel programming needs first to make several choices related to the problem one wants to treat and to the desired performance for the developed

software. In the field of vibrational chemistry, the goal is either to increase the size and complexity of chemical systems that can be treated with quantum chemistry or to enhance the accuracy of calculations for small molecules for which the mathematical solution is not always sufficient. The main choices made during the development of the P_Anhar software [20,21] are described below.

2.1. Workstation

Nowadays, PC clusters are increasingly adopted as a cheaper alternative to mainframe parallel supercomputers for running large scale numerical simulations. The floating point performance offered by the latest generations of Pentium and AMD processors, as well as the availability of high-speed interconnection networks, have led to the setting up of powerful PC clusters.

The system that was used to carry out the calculations reported in this paper has the following configuration:

- 8×1 GHz Intel Pentium III processors on dual-processor motherboards with 512 MB RAM per motherboard.

- 2×2 GHz Intel Xeon processors on dual-processor motherboard with 4 Go RAM.

- 100 Mbit/s fast Ethernet for network communications.

- Linux O/S (Red Hat Linux release 7.1 for the PIII and 7.2 for the Xeon; Kernel 2.4.xx).

- Intel fortran compiler Version 7.1.

Several reasons explain this choice:

- Since heterogeneous clusters are increasingly common and powerful [33], P_Anhar was developed and tested on the configuration described above in order to obtain the most portable code.

- The Fortran Intel compiler is the most natural optimized choice for the Pentium processor, leading to well tuned executables.

- As reference [21], the number of nodes of the cluster has been adapted to perform efficient calculations of the vibrational spectra of systems up to 10 atoms.

2.2. Performances

During the last decade, performance prediction has been repeatedly quoted as a key factor to developing parallel systems [34–36]. Predicting the behaviour

of a program performance as a function of the number of processors and of the problem size is essential to users in order to choose the right implementation method, to manage execution of processes in shared supercomputer systems or in non-dedicated networks of workstations/PC and finally for tuning optimizations in parallelizing compilers. Theoretical performance analysis of parallel algorithm on the case of a heterogeneous cluster is a much more difficult task than on homogeneous systems. While some efforts in this direction have been made [33,37], there is no adequate and practical model of heterogeneous networks of computers yet, to predict the execution time with satisfactory accuracy. Thus, another concept has to be found besides the usual measure of speed-up. As shown in [21], the concept of efficiency is certainly the most pertinent in our case. For example, the "average efficiency" $S''_M = \frac{t_1}{M\langle t_i \rangle}$ (where t_1 represents the time taken by the program to run on one processor and M the number of processors in the cluster) enables us to directly appreciate the average yield of the whole cluster of PC's with slow and fast processors to better distribute the tasks over the cluster and then, in each parallel section, to optimize the number of PC's to put in communication with each other, depending on the available power and memory.

2.3. Message passing

The MPI message passing library (LAM-MPI Version 0.4) was chosen in our code, as this is currently the most efficient portable parallelization model and implementations are available for clusters node of personal computers as well as for mainframes.

2.4. Diagonalization

A most useful solution for diagonalization is the (P)DSYEVX routine from the (Sca)LAPACK package [38,39], which is well optimized and quite efficient. (P)DSYEVX enables the user to obtain all eigenvalues or eigenvalues in a selected window. DSYEVX's major drawback is that the full matrix has to be stored on every processor, which restricts the size of problem that can be handled. In order to avoid putting the entire matrix in memory, the Davidson algorithm [40] is also implemented. In this scheme, one only needs to have a limited matrix and a vector in RAM. Only the nth-first eigenvalues can be computed, and the method is slower than the (Sca)LAPACK's routine, as the multiplication between a vector and a matrix is very CPU consuming.

3. Vibrational calculation

Whatever the size of the molecule, the study of vibrational spectra (wavenumbers and intensities) always implies:

– determining an anharmonic potential function (paragraph 3.1)

– solving the Schrödinger vibrational equation, which gives the eigenvalues of fundamentals, harmonic and combination bands in the mid-IR (paragraphs 3.2 and 3.3)

The main theoretical issue of this method comes with the fact that these two steps are vibrator size-dependant. Consequently, a study of medium sized molecules (6–20 atoms) is always faced with the difficulty to reach the same accuracy as for small systems (see for example [41,42]). Below is shown how the use of parallelism can go beyond these constraints.

3.1. Potential energy surface

Regardless of the size of the system, calculations of molecular vibrations first require analytical expressions for the potential function. In order to express all anharmonic force constants in the same units as the harmonic terms (in cm^{-1}), it is convenient to write this function in terms of dimensionless normal coordinates q_i [43]:

$$\frac{V}{hc} = \frac{1}{2!} \sum_i \omega_i q_{i,\sigma_i}^2 + \sum_{i \leqslant j \leqslant k} k_{ijk} q_{i,\sigma_i} q_{j,\sigma_j} q_{k,\sigma_k}$$
$$+ \sum_{i \leqslant j \leqslant k \leqslant l} k_{ijkl} q_{i,\sigma_i} q_{j,\sigma_j} q_{k,\sigma_k} q_{l,\sigma_l} + \cdots, \tag{1}$$

where the indices σ are used to label the different partners of degenerate vibrations.

In our procedure, quadratic, cubic (k_{ijk}) and quartic (k_{ijkl}) force constants are obtained by fitting data from *ab-initio* calculations of the electronic energy for several nuclear configurations in order to deduce the analytical potential function. Unfortunately, the number of force constants increases quickly with the size of the molecule, leading to problems of data acquisition for the polynomial expansion coefficients to be determined for systems over four atoms. Thus, the *ab initio* data has to be acquired another way in order to study larger systems. There are several possibilities. First, molecular symmetry puts some restrictions on the general expression (1). The invariance of the potential energy under all symmetry operations of the point group requires that all cubic and quartic terms vanish unless the direct product of the representation spanned by the normal coordinates is totally symmetric. In the case of ethylene oxide, the numbers of unique symmetry force constants is 37 (quadratic), 181 (cubic) and 1019 (quartic), i.e. a total of 1237 non-vanishing constants out of the total 3860 (68% saving). The second idea is to obtain a potential function by using jointly the energy (E) and gradient (G) data arising from calculations of the electronic wave function. As shown in [44], the gain increases rapidly with the size of the molecule,

yet, for larger systems, this is still not sufficient. Third, it is then profitable to couple the both strategies with parallel programming. Indeed, each *ab initio* calculation is independant of the results for other points on the grid; thus, the use of *n* processors divides the wall time needed to compute the potential energy surface (PES) by a factor of almost *n*. For example, if ten processors are used in parallel to compute the (C_2H_4O) PES, only 70 $(E + G)$ calculations per processor are needed, which is equivalent to the CPU time necessary for the classical PES calculation of a four atoms system without parallelizm.

In this paper, all the *ab initio* calculations on the PES of the ethylene oxide were carried out with the 6–31G(d,p) basis set [45] and the Becke [46] three-parameter exchange functional (B3) in combination with the Lee Yang and Parr [47] (LYP) correlation functional developed in the GAUSSIAN 03 suit of programs [5]. Although such conditions are unusual for an accurate vibrational treatment, they are sufficient and well-suited to this study. First, because the very recent study already quoted [29] reveals that this basis set performs a very good job for harmonic frequency calculations and that B3LYP anharmonicities generally agree closely with the best ones usually calculated at the CCSD(T) level of theory. Second, the aim of this paper is not a benchmark calculation on C_2H_4O but to show how parallelisation can help to take into account the anharmonicity and consequently, help to obtain the most detailed vibrational data for molecules over five atoms. Two ways can be considered to solve this problem: the perturbational (paragraph 3.2) and the variational (paragraph 3.3) methods.

3.2. Solution of the vibrational Schrödinger equation – perturbational approach

If the potential function (1) is introduced into Schrödinger equation, an exact solution of the type obtained for the harmonic oscillator cannot be found. However, one can take advantage of the fact that for finite but small displacements of the nuclei the quadratic part of *V* is much larger than the contribution of cubic terms, which is in turn larger than the quartic part. The vibrational Hamiltonian may thus be divided into orders of magnitude and perturbation theory used to calculate the corrections to the harmonic vibrational energy due to the various terms:

$$V/hc = V^{(0)} + \lambda V^{(1)} + \lambda^2 V^{(2)} + \cdots,$$
$$E/hc = \sum_{i=s,t} \omega_i \left(v_i + \frac{d_i}{2} \right) + \lambda E^{(1)} + \lambda^2 E^{(2)} + \cdots, \quad (2)$$

where [48]

$$V^{(0)} = \frac{1}{2} \sum_{i=s,t} \omega_i q_{i,\sigma_i}^2,$$
$$V^{(1)} = \sum_{ijk=s,t} k_{ijk} q_{i,\sigma_i} q_{j,\sigma_j} q_{k,\sigma_k}, \quad (3)$$
$$V^{(2)} = \sum_{ijkl=s,t} k_{ijkl} q_{i,\sigma_i} q_{j,\sigma_j} q_{k,\sigma_k} q_{l,\sigma_l}$$

and where λ is a parameter defining the order of magnitude of the various terms, the subscripts s and t refer, respectively, to the non-degenerate and doubly degenerate modes, and ℓ is the vibrational angular momentum quantum number. The corresponding corrections to the energy to first and second-order are given by, respectively:

$$E^{(1)} = \sum_m \langle v, \ell | V^{(1)} | v, \ell \rangle = 0,$$

$$E^{(2)} = \sum_{v,\ell} \left[\langle v, \ell | V^{(2)} | v, \ell \rangle + \sum_{\substack{v, \ell \neq v', \ell' \\ v \neq v'}} \frac{\langle v,\ell|V^{(1)}|v',\ell'\rangle \langle v',\ell'|V^{(1)}|v,\ell \rangle}{E_v^0 - E_{v'}^0} \right]. \tag{4}$$

In these expression $\langle v, \ell |$ and $\langle v', \ell' |$ indicate the complete zero-order vibrational wavefunctions corresponding to the vibrational zero-order energies E_v^0 and $E_{v'}^0$, respectively. If we take into account both the fact that each matrix element of the vibrational Hamiltonian can be directly evaluated with respect to the vibrational wavefunction and that the potential is expanded in a basis of $(q_t^\pm = q_{t1} \pm i q_{t2})$, the vibrational energy of a state $E_{v,\ell}$ is given by:

$$\begin{aligned}
E_{v,\ell} &= \sum_s \omega_s \langle v_s | q_s^2 | v_s \rangle + \sum_t \omega_t \sum_\ell \langle v_t, \ell | q_t^2 | v_t, \ell \rangle \\
&+ \sum_{s \neq s'} k_{sss's'} \langle v_s | q_s^2 | v_s \rangle \langle v_{s'} | q_{s'}^2 | v_{s'} \rangle + \sum_{s=s'} k_{ssss} \langle v_s | q_s^4 | v_s \rangle \\
&+ \sum_{s,t} k_{sstt} \langle v_s | q_s^2 | v_s \rangle \left(\sum_\ell \langle v_t, \ell | q_{t_+} q_{t_-} | v_t, \ell \rangle \right) \\
&+ \sum_{t \neq t'} k_{ttt't'} \left(\sum_\ell \langle v_t, \ell | q_{t_+} q_{t_-} | v_t, \ell \rangle \right) \left(\sum_{\ell'} \langle v_{t'}, \ell' | q_{t'_+} q_{t'_-} | v_{t'}, \ell' \rangle \right) \\
&+ \sum_{t=t'} k_{tttt} \left(\sum_\ell \langle v_t, \ell | q_{t_+}^2 q_{t_-}^2 | v_t, \ell \rangle \right) - \frac{1}{2} \sum_{t=t'} k_{tttt} \ell_t^2 + \Theta(q_\sigma^3) + \Theta(B_\alpha),
\end{aligned} \tag{5}$$

where $\Theta(B_\alpha)$ represents the Coriolis contribution. This procedure is easy to implement and has the main advantage of requiring independent matrix element calculations for each vibrational level $E_{v,\ell}$. Consequently, every processor in the cluster works independently. Given enough memory, near-perfect efficiency is obtained for this step, as shown in table 1. Thus, the execution speed depends only on the number of processors used.

While being very efficient, perturbation theory is sensitive to resonances like Fermi and Darling–Denisson resonances [48]. When these kinds of accidental degeneracy occur between two vibrational levels, which is quite common when one works with several million configurations, it is no longer valid to use this theory. To circumvent this problem, the energies of the two perturbed levels are to be obtained by direct diagonalization of the corresponding part of the

Table 1

Processing time for the solution of the vibrational Schrödinger equation by perturbational and variational methods as a function of the number of processors during the parallel execution. Main results obtained for average efficiency in the case of C_2H_4O ([2700–3200] cm^{-1} ($n = 1$) and [3080–3120] cm^{-1} ($n = 2$)).

M procs		1	2	5	10	
States coupled	$n = 1$	71	37	15	~ 7.5	t_M(min)
	$n = 2$	1785	923	375	197	
[S''$_{min}$–S''$_{maxi}$]		[1–1]	[1–0.5]	[1–0.2]	[1–0.1]	
$S''_M = \frac{t_1}{M \langle t_i \rangle}$	Pert	1	0.97	0.97	0.96	
	Var	1	0.96	0.95	0.92	

energy matrix corrected to first-order as mentioned in [32, 49]. This method of calculation is sufficient to determine (from a highly correlated wave function and a triple-ζ or higher basis set) the positions of the fundamental bands of small and medium [32, 49–51] organic compounds to within 2%, but generally is not sufficient for the study of a complete spectrum (combination and overtone bands).

3.3. Solution of the vibrational Schrödinger equation – variational approach

For a more comprehensive treatment of a complete vibrational spectrum, it is better to use a variational approach [52–55]. However there are several difficulties in this method:

- The amount of data extracted from the potential function (1) grows dramatically with the size of the molecule.

- It is important to choose all the N_n configurations $\{|(v, \ell), n > 0\rangle_{i_n}; 1 \leq i_n \leq N_n\}$ coupled directly ($n = 1$) or indirectly ($n > 1$), for both anharmonic and Coriolis contributions, with the subspace of the N_0 states we want to describe $\{|(v, \ell), n = 0\rangle_{i_0}; 1 \leq i_0 \leq N_0\}$. A single processor cannot reasonably handle the huge number of operations required.

- Gigantic matrices arise.

For these reasons, the strict application of the variational method to solve the vibrational problem is restricted to small systems or to a small number of simultaneously coupled variational degrees of freedom. Parallel computation in the development of variational algorithms enables us to solve some of these problems.

3.3.1. Parallel approach

The main advantage of our parallel approach is that the spectral window can be cut into (p) smaller windows, which are dealt with in independent processes. The aim of this step is to decrease the information needed to describe the modes $\left\{ |(v, \ell), n = 0\rangle_{j,i_0} ; 1 \leq j \leq p; 1 \leq i_0 \leq N_0^j \right\}$ in each window studied j, which is obviously less than for the entire spectral range ($N_0 = \sum_{j=1}^{p} N_0^j$). Another convenient advantage is that the user can compute a selected spectral area. However, two additional difficulties accompany these advantages. First, the narrower the division of the spectral range, the more the selection step of indirectly coupled states $\left\{ |(v, \ell), n \geq 1\rangle_{j,i_n} ; 1 \leq j \leq p; 1 \leq i_n \leq N_n^j \right\}$ will have to be iterated. In order to attenuate this additional excessive growth of the number of calculations per process, this part of our code has been totally parallelized. Second, the sum of the dimensions of all the sub matrices is always larger than that of the matrix obtained without subdivision ($\sum_{j=1}^{p>1} N_n^j \geq N_n^{p=1}$), because a configuration can interact with several states that do not belong to the same spectral window. In order to obtain totally independent sub matrices, this kind of configuration has to be added as often as needed. This difficulty leads to an increase in the number of calculations. Despite this, dimensions of each sub-matrix are, hopefully, much smaller than those without partition.

In conclusion, despite this redundancy of both calculation and information, the major advantage of this algorithm is to provide smaller matrices, containing all the information needed, which makes the execution of our code as easy as possible, faster and perfectly adapted to the parallel calculations.

3.3.2. Iterative construction of the variational matrix

Rather than building the matrix in a classical way (which means considering all the $|(v, \ell)\rangle$ configurations in a single calculation ($p = 1$), the technique used in the P_Anhar code is sequential inclusion in the variational space of states introduced by successively higher order anharmonic terms in the Hamiltonian in order to generate from each constant all N_n^j configurations $\left\{ |(v, \ell), n\rangle_{j,i_n} ; 1 \leq j \leq p; 1 \leq i_n \leq N_n^j \right\}$ (which belong to the $\left\{ |(v, \ell)\rangle_i ; 1 \leq i \leq N \right\}$) in interaction with the N_{n-1}^j states at the $n-1$th iteration in a particular window $\left\{ |(v, \ell), n - 1\rangle_{j,i_{n-1}} ; 1 \leq j \leq p; 1 \leq i_{n-1} \leq N_{n-1}^j \right\}$ (at least one harmonic configuration has to be in this pre-defined area). If $n = 1$, configurations selected by this criterion make up the first active space. The feasibility of the method depends of this choice. In order to illustrate the size of this kind of problem and illustrate the advantages of parallel execution, let us take again the example of a medium-sized compound, C_2H_4O. If an initial window ($p = 1$) composed of single $N_0^1 = 1$ reference state $|(v, \ell), 0\rangle_{1,1}$ (for which all the excitation levels are equal to zero)

and the potential functions obtained above at the B3LYP/6-31 + G(d, p) level are considered, only N_1^1 = 511 $\{|(v, \ell), n = 1\rangle_{1,i_1} ; 1 \leqslant i_1 \leqslant N_1^1\}$ and N_2^1 = 62002 $\{|(v, \ell), n = 2\rangle_{1,i_2} ; 1 \leqslant i_2 \leqslant N_2^1\}$ configurations need be taken into account for studying this reference. If a bigger but narrow spectral window is considered i.e. for example [3800–3120] cm^{-1} (see table 1), N_0^1 = 23 initial configurations, and the numbers of interactions increase to $N_1^1 = 45660$ and practically $N_2^1 \approx$ one million. If this technical difficulty linked to the problem size is taken into account, we arrive at a subdivision of the [200–4000] cm^{-1} window into 10 spectral subwindows with an "equivalent" density of states to achieve the highest possible efficiency. Technical details are reported in reference [21]. Results are reported in paragraph 3.5 of this work.

3.4. Performances

We observe in table 1 a satisfactory efficiency for the vibrational problem, which seems to indicate that these computational costs are not too disadvantageous. Efficiencies obtained for ethylene oxide are nearly 92%, which is very satisfying if we consider that this vibrational problem reaches the limit of what can be computed without parallel processing on a computer like one of the 2.2 GHz Intel Xeon used in our cluster. Increasing the number of PC's in our cluster (around 100 processors) should enable us to improve the wall time without degrading too much the efficiency (near 80%).

4. Results

Ethylene oxide, symmetry C_{2v}, has fifteen normal vibrations belonging to A_1 (5), A_2 (3), B_1 (4) and B_2 (3) symmetry classes. Both its structure (table 2) and IR spectrum (tables 3 and 4) have been studied by many authors. However, the attribution of several vibrational bands remains uncertain, in particular in the [800–1000] cm^{-1} area. Our B3LYP/6-31 + G(d, p) results for structural parameters and vibrations reported in figure 1 and in tables 2 and 4 are compared to experimental data (table 3) and previous theoretical calculations (table 4). Four points can be underlined for this study. First, our computed structural parameters are in good agreement with experimental data, which is a *sine qua non* condition for obtaining good harmonic results. Second, one can note that a harmonic study is not sufficient to dispel experimental ambiguities for this compound (table 4). Third, several resonances attributed in experiments found are confirmed by our anharmonic calculations, like the principal resonances $v_1/2v_2$ [61] and $v_9/v_2 + v_{10}$ [62,63] and many others of more or lesser importance (i.e. $v_1/2v_4 + v_{15}$; $v_1/v_7 + v_{12} + v_{15}$; $v_{15}/v_2 + v_{14}$). This justifies the use of a variational method. Fourth, considering the conditions chosen in

Table 2
Structural parameters (Å and °) of ethylene oxide.

	Experiment microwave [56, 57*]	RHF/ 6-311+ +G(2d,2p) [58]	MP2/ 6-311+ +G(2d,2p) [58]	B3LYP/ 6-31+G(d,p) this work	CCSD(T)/ cc-pVTZ this work
r(C-O)	1.436	1.401	1.442	1.435	1.432
r(C-C)	1.472	1.451	1.465	1.470	1.468
r(C-H)	1.082	1.074	1.080	1.089	1.084
θ(COC)	61.7	–		61.7	61.7
θ(HCH)	116.7	115.5	116.5	115.6	116.0
θ(HCO)	114.4*	115.2	114.8	115.1	115.1
θ(HCC)	119.6*	119.7	119.2	119.7	119.3

Table 3
Experimental wavenumbers (in cm^{-1}) for ethylene oxide.

		IR gaz phase			Raman liquid phase	IR solid phase		
		[59]	[60]	[61]	[62]	[63]	[64]	Assignment
A_1	ν_1	3,024	3,005	3,006	3,005	3,024	3,006–3,011	CH$_2$ s-str
	ν_2	1,498	1,490	1,498	1490	1,480–1,494	1,489	CH$_2$ scis
	ν_3	1,270	1,266	1,271	1,266	1,253–1,266	1,270–1,281	Ring str
	ν_4	1,120	1,120	1,120	1,120	1,119–1,147	1,120–1,124	CH$_2$wag
	ν_5	877	877	877	867	859–875	857–859	Ring deform
A_2	ν_6	3,065	3,063	3,063	3,063	3,051	–	CH$_2$ as-str
	ν_7	–	(1,345)	1,300	ia	1,043–1,046	–	CH$_2$twist
	ν_8	1,020	807	860	ia	837–857	–	CH$_2$rock
B_1	ν_9	2,978	3,019	3,006	3,005	2,996–3,005	2,997	CH$_2$ s-str
	ν_{10}	1,470	1,470	1,472	–	1,455–1,467	1,467-1,464	CH$_2$ scis
	ν_{11}	1,159	1,153	1,151	1,150	1,159–1,169	–	CH$_2$wag
	ν_{12}	822	892	892	–	816–825	–	Ring deform
B_2	ν_{13}	3,065	3,079	3,065	3,063	3,062–3,073	–	CH$_2$ as-str
	ν_{14}	1,147	1,143	1,142	1,150	1,146–1,160	1,147–1,152	CH$_2$twist
	ν_{15}	808	821	822	807	794-798	785–803	CH$_2$rock

ia : inactive.

this work [29,67], it is not surprising to see that torsion modes and ring deformation modes (COC) are not very well reproduced [59]. Nevertheless, our theoretical protocol yields an error under 2% for bands observed in the vibrational spectrum of C$_2$H$_4$O.
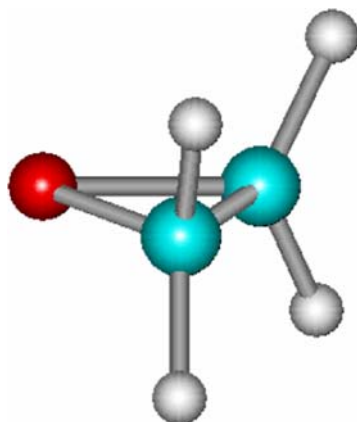
Figure 1. Structure of C_2H_4O.

Table 4
Our calculated harmonic (ω), anharmonic (ν) and previous theoretical wavenumbers (in cm^{-1}) for ethylene oxide. IR intensities are in brackets (km/mol).

		Scaled [65]	RHF MP2 6-311++G(2d,2p) [58]		B3LYP 6-31+G(d,p)this work			Assignment
			ω_i	ω_i	ω_i	ν_i^a	ν_i^b	
A_1	ν_1	2998	3267	3159	3105 (15)	3070	2957	CH_2s-str
	ν_2	1501	1681	1555	1545 (4)	1499	1500	CH_2scis
	ν_3	1281	1410	1297	1302 (14)	1273	1278	Ring str
	ν_4	1143	1277	1153	1152 (0)	1123	1123	CH_2wag
	ν_5	858	969	881	889 (78)	868	872	Ring deform
A_2	ν_6	3068	3338	3249	3183 (0)	3030	3020	CH_2as-str
	ν_7	1147	1294	1185	1176 (0)	1155	1116	CH_2twist
	ν_8	1024	1147	1055	1041 (0)	1015	975 986[c]	CH_2rock
B_1	ν_9	2984	3255	3152	3099 (37)	3008	2995	CH_2 s-str
	ν_{10}	1465	1632	1523	1509 (0)	1472	1463	CH_2 scis
	ν_{11}	1161	1282	1167	1155 (1)	1131	1122	CH_2wag
	ν_{12}	829	952	831	845 (11)	817	784 790[c]	Ring deform
B_2	ν_{13}	3086	3355	3264	3197 (48)	3044	3032	CH_2 as-str
	ν_{14}	1139	1287	1173	1166 (4)	1143	1125	CH_2twist
	ν_{15}	795	879	820	817 (0)	805	763 805[c]	CH_2rock

[a] Our perturbational results.
[b] Our variational results.
[c] B3LYP/cc-pVTZ anharmonic vibrational frequency results.

Acknowledgment

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