New Theoretical and Experimental Infrared Results on Formaldehyde in Solution

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An extension of our combined procedure to determine a complete quartic force field and to resolve a vibrational problem thanks to a variational treatment is proposed for quantitative calculations of vibrational spectra in solution. Energies and gradients are obtained through a polarizable continuum model (PCM), the so-called self-consistent isodensity (SCI)-PCM. We present in this paper new experimental results dealing with formaldehyde in solution in cyclohexane, chloroform, THF, acetonitrile, DMSO and water; the obtained vibrational spectra are then compared with CCSD(T)/cc-pVQZ calculations. In addition, density functional theory (DFT) calculations have been carried out with the aim of both anticipating and positioning these approaches for larger sized molecules.

1. Introduction

About 70 years after the first studies of Kirkwood[1] and Buckingham,[2] modeling a chemical system in solution is still challenging, more particularly in the spectroscopic characterization area. Although several improvements were achieved in quantum chemical calculations during the past decade,[3−6] taking solvent effects into account is far from being complete and really effective. The main theoretical difficulty is bound to the physical representation of the interactions between the solute and the solvent. In the case of a quantum modeling of vibrational frequencies some other problems may arise from, for example, the determination of the best-suited potential energy surface or the introduction of both anharmonicity and Coriolis effects.[7−24] In summary, the main issue of the present study lies in the simultaneous consideration of these two crucial points which, beyond three atoms, appears to be a very difficult task unless numerous estimates are introduced.

With regard to the solvent problem, the validity of molecular simulation results will be mostly limited by the accuracy of the mathematical models used to describe the solvents effects. Two theoretical approaches are nowadays mainly available. In the first approach, the model tries only to describe purely physical interactions between the solvent and the solute. In this case, the solvent is modeled by an appropriate chemical entity, perturbed by a set of charges able to modify both the electronic structure and the geometry of the solvent (cf. the Onsager self-consistent reaction field (SCRF),[25] COSMO,[26−27] IM,[28] Hybrid,[29] UHBD[30] and polarizable continuum model (PCM)[31]). In the second approach, the physical description of the solvent is achieved through the modeling of specific interactions with the solute. The studied solution looses its chemical characteristics and forms a solvent/solute complex, thus leading to a prohibitive dimension of the QM problem. Today, a lot of studies have been published using this approach, mainly because of the development of molecular dynamics and mixed methods such as QM/MM.[32−37] Computer resources have now become sufficiently powerful and abundant to enable simulations for systems with up to 10 000 atoms. As a result, many biochemically interesting molecules and molecular complexes can now be studied with detailed atomic information.[36]

Relative to the vibrational problem, all the simulation methods require both a potential energy surface and an appropriate mathematical treatment for the class of molecules to be studied. Ideally, a rigorous ab initio quantum mechanical method should be used.[38] In that case, both SCRF and self-consistent isodensity (SCI) PCM[39] class of models are perfectly well suited for the quantum vibrational treatment. However, for systems with more than a few dozen heavy atoms (which is often the case when the solvent is explicitly taken into account), a detailed quantum description is generally not feasible, even with the most powerful computers presently available. The use of molecular dynamics (MD) coupled with an harmonic vibrational treatment is nowadays one of the current way to overcome the previous quantum limitations.[40] We are fully aware that the choice of the vibrational treatment infers the choice of the solvent model (and conversely). Beyond these choices, a common shortcoming remains, which is concerned with the theoretical vibration field. All the previous mathematical studies (MM, MD or QM) show that although the shift associated with a vibrational band is fairly well reproduced,[41] it is not the case for the bands positions.

The purpose of this paper is then 2-fold. First, through the example of formaldehyde, we want to point out both advantages and limits of a QM approach, and in particular the strategies including both CCSD(T) and density functional theory (DFT) approaches. Surprisingly, there are very few experimental data on formaldehyde in solution. To our knowledge, only a complete study of a solution in acetonitrile[41] and an experimental value of ν(C=O) in the cyclohexane referenced in a theoretical work of Rivail[42] are available in the literature. Consequently, our second purpose is to complete the experimental data to test the

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TABLE 1: Various Solvents Used for the Experiments

solvents	formula	dielectric constant ε	dipole moment μ (D)
		Nonpolar	
cyclohexane	C_6H_{12}	2.02	0
chloroforme	$CHCl_3$	4.81	1.15
THF	C_4H_8O	7.58	1.75
		Polar	
acetonitrile	CH_3CN	37.5	3.45
DMSO	$(CH_3)_2SO$	46.7	3.90
		Protic	
water	H_2O	78.4	1.80

ability of current theoretical approaches, especially when the anharmonicity is taken into account.

This paper is organized as follows: In sections 2 and 3, we briefly summarize experimental conditions, methods and computational details; in section 4, we present experimental and theoretical anharmonic spectra for solutions of H_2CO in five different aprotic solvents (cyclohexane, $CHCl_3$, THF, CH_3CN and DMSO) and in water. An "economic" approach is proposed at the end of the paper. From these calculations, both band shifts and positions can be predicted.

2. Experimental Section

Formaldehyde was prepared by thermal decomposition (120–170 °C) of commercial paraformaldehyde (Aldrich) in the presence of N_2. Once cooled, the gas mixture was bubbled into the selected solvent for IR studies. In this study, we make the choice to work with a set of five solvents with very different physical properties (Table 1). Except H_2O, only aprotic solvents were used so as to avoid cationic polymerization of H_2CO.

The transmission spectra were collected on a non purged Avatar spectrometer of Thermo Nicolet with a resolution of 1 cm^{-1} after a signal averaging of 200 scans. A DTGS detector is used which allows us to investigate the absorption spectrum up to 400 cm^{-1}. The effective path length of the CaF_2 cell used for measurement was 0.1 mm. For all samples, the background spectrum is recorded with a pure solvent.

As stated above, the experimental studies of H_2CO in solution are somewhat sparse. Due to the presence of the solvent, the complete IR spectrum of H_2CO cannot be easily extracted from experimental data. So, only a few bands, namely the stretching $\nu(C=O)$ (ν_2) and his first overtone $2\nu_2$, the scissoring $\sigma(CH_2)$ (ν_3) and the symmetric stretching CH_2 ν_s (ν_1) have been generally identified. These data are compared to gas and solution data[41–45] in Table 2.

3. Computational Details

In the basis of curvilinear coordinates S_k and their conjugate moment P_{S_k} the quantum mechanical pure vibrational Hamil-

tonian is written as

$$H_v = \frac{1}{2}\sum_{i,j} g_{ij}(s)P_{S_i}P_{S_j} + V(s)$$

where g_{ij} is the element of the **G** matrix described by Wilson and $V(s)$ the potential function expressed from a complete set of quadratic, cubic and quartic force constants by

$$V(s) = \frac{1}{2}\sum_{i,j} f_{ij}S_iS_j + \frac{1}{6}\sum_{i,j,k} f_{ijk}S_iS_jS_k + \frac{1}{24}\sum_{i,j,k,l} f_{ijkl}S_iS_jS_kS_l$$

For systems in which anharmonicity is weak, it is possible to write the potential function $V(s)$ as a Taylor expansion series in terms of curvilinear displacement coordinates. Quadratic (f_{ij}), cubic (f_{ijk}), and quartic (f_{ijkl}) force constants are generally obtained either by fitting the electronic energy calculated by ab initio methods for various nuclear configurations close to the optimized geometry or by a finite difference procedure including first and second derivatives of the electronic energy with respect to the nuclear coordinates. In both cases, the required number of ab initio or DFT data points grows strongly with increasing size of the molecule, so that it becomes difficult to determine accurately a complete quartic force field for current organic and inorganic systems. To reduce the number of calculations, even for a system as small as H_2CO, we have used in this work the procedure implemented in our previously described code REGRESS EGH.[7] Briefly, this strategy includes in the same process of linear regression of values the energy and, if accessible, the corresponding first analytical derivatives obtained at each point of a well-suited grid. Thus, this approach allows the determination of the analytical form of the potential with a significantly reduced number of points to be calculated without affecting the accuracy of the results.

The kinetic part of the Hamiltonian also can be written as a Taylor expansion in terms of curvilinear coordinates:

$$T = \frac{1}{2}\sum_{i,j} g_{ij}(0) + \frac{1}{2}\sum_{i,j,k} g_{ijk}P_{S_i}S_kP_{S_j} + ...$$

in which $g_{ijk} = (\partial g_{ij}/\partial S_k)_0$ and where $g_{ij}(0)$ are the terms calculated in the harmonic approximation. This approach can be retained for the kinetic operator when large amplitude displacements are involved. In our calculations, both the kinetic and potential parts of the vibrational Hamiltonian are expressed in the basis of dimensionless normal coordinates q_i and conjugate momentum operators.

Due to the additional CPU time cost of the calculations when the solvent is taken into account, and because most general softwares are not able to compute the first analytical derivatives

TABLE 2: Experimental Results of the Formaldehyde in Solution

				solvent				
				nonpolar			polar	
	gas $\epsilon = 1.0$		C_6H_{12} $\epsilon = 2.0$	$CHCl_3$ $\epsilon = 4.8$	C_4H_8O $\epsilon = 7.6$	CH_3CN $\epsilon = 37.5$	$(CH_3)_2SO$ $\epsilon = 46.7$	H_2O
phase	our work			our work	our work	our work	our work	$\epsilon = 78.4$
ν_4 (τ) (CH_2)		1167^a						
ν_6 (ρ) (CH_2)		1249^a					1247^d	
ν_3 (σ) (CH_2)	1501	1500^a		1497			1503^d	
ν_2 (CO)	1745	1746^a	1735^c	1728	1728	1726	1723^d	1721	1723^e
$2\nu_2$ (CO)	3470	3472^b		3439	3437	3434		
ν_1 (ν_s) (CH_2)		2782^a		2792		2808	2797^d	
ν_5 (ν_{as}) (CH_2)		2843^a					2876^d	

^{a} Reference 43. ^{b} Reference 44. ^{c} Reference 42. ^{d} Reference 41. ^{e} Reference 45.

Infrared Results on Formaldehyde in Solution

J. Phys. Chem. A, Vol. 110, No. 25, 2006 **7795**

for reference methods such as the most appropriate CCSD(T), alternative theoretical strategies have to be developed.[46] For example, an interesting breakthrough is to couple the REGRESS EGH approach with parallel programming: indeed, every ab initio or DFT calculation is independent of the results for other points on the grid. So, the quartic force field calculation for H_2CO in solution at the CCSD(T)/cc-pVQZ level of theory can be done in less than 4 h with ten 1 GHz Intel Pentium III processors.

Ab initio and DFT calculations were carried out respectively either with the Dunning correlation consistent pVTZ and pVQZ basis sets[47] or with the well-suited 6-31+G** basis set as recommended elsewhere[48,49] for DFT approaches. CCSD(T) and DFT calculations were undertaken to determine structural parameters and harmonic wavenumbers. All the harmonic calculations were carried out with the GAUSSIAN 98 program;[50] the REGRESS EGH and the FORCE packages previously developed in our group[7] are used for all the force constants determination.

Once the potential energy function is obtained, the second step in the vibrational energy-level calculations consists of solving the vibrational Schrödinger equation. It is well-known that a perturbational process is not suitable in the case of formaldehyde because of strong Fermi and Darling–Dennison resonances. To bypass this kind of problem, we used our new parallel variational scheme adapted to the treatment of medium-sized systems (P_ANHAR_v1.1[51]). This approach consists of taking an inventory of the vibrational configurations potentially needed for the description of the problem on the grounds of the potential terms values, taking into account the symmetry of each state and cutting the process into several spectral windows which are dealt in independent processes. The major advantage of this algorithm lies in the ability to provide, in several spectral ranges, smaller matrixes that contain all the information needed, which makes the execution faster and perfectly adapted to parallel calculations. For each symmetry, submatrixes including from 20 000 to 30 000 configurations are diagonalized to obtain about 50 converged eigenvalues with an accuracy of 1 cm^{-1}. For details on the method, see ref 46.

4. Results

4.1. Anharmonic Approach. In the gas phase, H_2CO is one of the most studied non linear small molecules.[52] Its vibrational spectrum is perfectly known today. Nevertheless, it is only recently that the theoretical chemists were able to exactly model its mid-infrared (MIR) characteristics. Several reasons may be given to explain such a situation. First, this system shows numerous Fermi and Coriolis resonances including for instance those occurring either between the fundamental mode ν_5 [ν_{as}-(CH)] and the combination ν_3 [$\sigma(CH_2)$] + ν_6 [$\rho(CH_2)$] or between the lowest fundamental modes. As stated above, handling all these interactions is practically impossible with the only feasible method, i.e., the perturbational approach, as used 10 years ago. Second, the required development of data processing for the description of these interactions by variational methods was only achieved in the middle of the 90s. Nowadays, owing to efficient methods based on both perturbational and variational optimized concepts (namely PT2,[14] CVPT,[53] CC VSCF,[54−55] VSCF/VCI,[12,54−59] VCC,[60] PS VSCF[61] and PDV (Parallel Direct Variation)[46,51]), the average accuracy of current calculations on these small organic systems is close to 1−5 cm^{-1} for stretching and bending bands and about 10−20 cm^{-1} for motions of larger amplitude involving light atoms.[62] Finally, the main difficulty lies in the choice of the potential function

model and in the accuracy of the calculated force constants.[63] Today, these aspects are crucial for the study of the smallest systems because they condition the quality of the interpretation of experimental data.[64,65]

Modeling the MIR spectrum of organic molecules in solution meets the same requirements. However, an additional question arises through the connected problem of the solvent. To both disregard explicitly the molecules of solvent and develop our own theoretical "anharmonic" approach on an "isolated" system, we decided to choose a PCM model, namely SCI-PCM. The reasons for this choice are double. First of all, owing to the relatively low cost of the calculations in comparison to an explicit solvent model, such dielectric continuum theories are now widely used for the description of solvent effects in conjunction with quantum mechanical calculations. The second reason lies in the fact that the cavity surface is not defined by sensitive enlarged van der Waals radii like in the regular PCM model. In that case, the cavity is more easily described by the iso-electron density surfaces that only change with solvent-induced polarization of the solute. Moreover, these modifications are directly taken into account in the self-consistent SCF procedure, thus eliminating the well-known convergence problems for the globally spherical molecules such as H_2CO. As a result, the corresponding perturbed wave function is then used to resolve successfully the vibrational Schrödinger equation.[38]

A particular effort was done on the research of all the potential functions: one for H_2CO in the gas phase and six others for the different solvents used in experiments $\epsilon = 2.02−78.4$ (Table 3). Due to the C_{2v} symmetry of H_2CO, only a set of six displacement coordinates (Figure 1) has to be chosen for the determination of the 66 independent and nonnull force constants of the potential function. In this case, 66 (E+G) calculations (double redundancy) in the well-suited simplex sum grid (simplex-sum[7]) or 168 (E) calculations are required to obtain the complete quartic force field. For all the distorted structures generated by displacements of 0.02 Å for bond coordinates and 2° for angular coordinates, the corresponding energies were calculated at both CCSD(T) and B3LYP levels of theory using respectively the cc-pVXZ (X = T, Q) and 6-31+G** basis sets. The seven corresponding CCSD(T)/cc-pVQZ and B3LYP/6-31+G** quartic force field in a vacuum and in the different solvents are reported in Table 3 to illustrate how the modes' coupling may be affected by the taken into account of the solvent. Cubic and quartic terms which involve coupling between the dimensionless normal rocking mode (q_6) and the asymmetric stretching (q_5) on one hand, and between the scissoring (q_3) and the symmetric stretching (q_1) on the other hand, are the most affected by the presence of the solvent. Moreover, couplings in solution such as those occurring between the q_6, q_5 and q_1 modes remain weak but show a very varying value according to ϵ. In that case, the cubic terms are significantly affected. On the contrary, the strongest constants of other modes are weakly coupled. Considering these remarks, we can conclude that the vibrational representation of this molecule will be mainly influenced by the modification of the geometrical structure and by these higher coupling.

Structural, harmonic and anharmonic results (ν_4 [$\tau(CH_2)$] torsion, ν_6 [$\rho(CH_2)$] rocking, ν_3 [$\sigma(CH_2)$] scissoring, ν_2 [$\nu(CO)$] stretching, ν_1 [$\nu_s(CH_2)$] stretching, ν_5 [$\nu_{as}(CH_2)$] stretching) are reported in Tables 4−6.

Our gas phase data are compared with a nonexhaustive but representative set of experimental and theoretical data from the literature (Table 4). With regard to both fundamental and first

TABLE 3: Quadratic, Cubic and Quartic Force Constants (cm^{-1}) of H$_2$CO in Vacuo and in Solution, Calculated at Both B3LYP/6-31+G** and CCSD(T)/cc-pVQZ Levels of Theory, with Respect to Dimensionless Normal Coordinates^a

parameter	B3LYP 6-31+G** gas	CH$_3$CN $\epsilon = 37.5$	CCSD(T) cc-pVQZ gas	C$_6$H$_{12}$ $\epsilon = 2.02$	CHCl$_3$ $\epsilon = 4.81$	C$_4$H$_8$O $\epsilon = 7.58$	CH$_3$CN $\epsilon = 37.5$	DMSO $\epsilon = 46.7$	H$_2$O $\epsilon = 78.4$
$\omega_4\,[\tau(CH_2)]$	1194	1207	1190	1197	1202	1204	1205	1206	1206
$\omega_6\,[\rho(CH_2)]$	1262	1257	1271	1272	1271	1271	1271	1271	1270
$\omega_3\,[\sigma(CH_2)]$	1537	1533	1537	1537	1536	1536	1536	1535	1535
$\omega_2\,[\nu(CO)]$	1819	1791	1781	1775	1770	1768	1766	1766	1766
$\omega_1\,[\nu_s(CH)]$	2914	2948	2933	2946	2957	2959	2965	2965	2966
$\omega_5\,[\nu_{as}(CH)]$	2979	3020	3004	3019	3032	3036	3042	3042	3042
ϕ_{111}	−1357.7	−1373.1	−1350.2	−1355.9	−1358.8	−1360.6	−1364.4	−1362.2	−1363.3
ϕ_{211}	−21.8	−20.8	−20.8	−19.7	−19.1	−18.8	−18.8	−17.6	−18.6
ϕ_{221}	67.4	66.9	69.4	69.8	69.5	69.6	70.1	69.8	69.6
ϕ_{222}	569.8	555.3	556.9	550.6	543.4	541.1	538.4	537.4	537.2
ϕ_{311}	−2.9	−10.3	−1.2	−3.1	−5.2	−5.1	−6.1	−6.5	−6.7
ϕ_{321}	58.0	62.2	57.2	58.1	58.8	59.5	59.9	59.0	60.3
ϕ_{322}	120.4	127.9	131.8	132.8	133.9	134.4	134.7	134.2	134.6
ϕ_{331}	84.7	89.8	73.6	76.3	76.8	76.8	77.7	76.6	77.6
ϕ_{332}	108.1	112.7	124.6	125.5	126.0	125.9	125.7	126.3	125.7
ϕ_{333}	−45.1	−31.1	−27.7	−23.1	−17.9	−18.1	−16.0	−14.9	−14.9
ϕ_{441}	322.7	326.6	336.3	334.7	334.2	334.0	333.4	333.4	333.3
ϕ_{442}	30.6	27.5	49.1	46.7	45.1	44.2	43.1	43.0	42.8
ϕ_{443}	−63.1	−57.8	−58.8	−56.4	−55.0	−54.8	−54.1	−54.2	−54.1
ϕ_{551}	−1445.3	−1466.5	−1424.8	−1436.2	−1439.4	−1440.8	−1442.8	−1442.4	−1443.6
ϕ_{552}	−124.8	−127.8	−126.4	−126.3	−125.9	−126.1	−126.4	−125.9	−126.2
ϕ_{553}	126.7	114.1	127.2	123.8	120.3	119.9	118.7	118.6	118.4
ϕ_{651}	5.3	3.1	1.8	4.6	14.4	3.3	18.1	17.7	18.6
ϕ_{652}	−137.5	−149.1	−145.7	−149.1	−153.5	−153.8	−156.4	−156.3	−156.7
ϕ_{653}	190.1	193.5	184.4	183.6	185.8	185.0	186.5	186.7	186.7
ϕ_{661}	230.9	237.5	229.3	231.0	232.2	232.6	233.3	233.0	233.2
ϕ_{662}	15.4	12.2	20.8	19.8	18.8	18.4	17.9	18.0	17.6
ϕ_{663}	108.4	112.2	109.8	109.9	110.7	111.0	111.0	111.2	111.0
ϕ_{1111}	544.4	562.1	492.9	526.0	509.1	543.4	505.5	542.9	506.5
ϕ_{2111}	18.4	18.3	19.2	20.8	11.0	4.8	21.9	23.2	4.8
ϕ_{2211}	−29.8	−37.2	−33.3	−41.5	−41.5	−42.5	−40.2	−47.3	−38.9
ϕ_{2221}	8.0	7.9	1.0	4.3	6.2	7.2	10.6	9.5	9.0
ϕ_{2222}	166.5	159.1	141.2	150.0	140.1	141.9	156.3	143.4	166.7
ϕ_{3111}	−16.9	−18.2	−4.9	−12.3	−1.9	−1.5	−10.5	−16.0	−8.6
ϕ_{3211}	71.5	76.7	69.4	77.4	76.8	74.8	77.6	82.2	78.4
ϕ_{3221}	14.4	14.0	20.7	15.6	16.6	15.1	13.1	10.1	16.8
ϕ_{3222}	41.1	43.7	38.9	42.2	51.1	48.6	34.5	59.6	51.2
ϕ_{3311}	−146.6	−147.0	−137.6	−139.0	−140.5	−138.1	−136.9	−144.1	−134.9
ϕ_{3321}	−25.1	−24.0	−22.8	−23.0	−24.5	−21.1	−22.6	−22.7	−22.0
ϕ_{3331}	11.2	8.4	21.5	9.2	18.5	21.3	10.9	19.0	10.6
ϕ_{3332}	−9.0	−8.8	−5.4	−6.9	−6.4	−2.0	−9.4	−17.1	−4.4
ϕ_{3333}	9.8	16.1	12.5	4.5	7.3	19.9	7.4	30.7	7.5
ϕ_{4411}	−273.3	−275.3	−281.5	−277.9	−277.9	−279.1	−277.1	−278.1	−275.6
ϕ_{4421}	−24.1	−24.1	−31.5	−25.5	−25.8	−23.7	−25.3	−26.9	−25.8
ϕ_{4422}	−10.6	−10.5	−13.2	−11.8	−9.6	−10.8	−9.6	−10.4	−8.9
ϕ_{4431}	10.2	8.0	11.8	9.2	11.5	11.6	8.7	−12.2	−11.9
ϕ_{4432}	−13.0	−13.4	−9.6	−12.8	−15.0	−12.7	−13.5	−12.8	−13.9
ϕ_{4433}	10.9	10.2	8.8	9.1	9.5	9.1	9.3	10.6	11.3
ϕ_{4444}	139.5	133.7	156.7	141.8	140.0	139.3	146.4	140.1	143.5
ϕ_{5511}	591.0	591.6	572.1	569.5	563.7	564.3	558.2	555.1	560.1
ϕ_{5521}	43.6	40.3	43.7	37.5	41.2	32.8	32.6	38.7	39.1
ϕ_{5522}	−52.6	−62.3	−61.4	−67.8	−68.7	−72.4	−70.1	−72.0	−69.3
ϕ_{5531}	−25.4	−19.9	−37.4	−27.5	−33.4	−29.9	−29.9	−32.6	−30.6
ϕ_{5532}	96.5	102.6	101.2	103.7	104.5	105.6	106.2	104.3	105.8
ϕ_{5533}	−196.6	−191.1	−184.1	−185.6	−185.6	−186.2	−184.0	−183.9	−182.8
ϕ_{5544}	−324.7	−309.9	−328.3	−329.3	−334.0	−337.8	−341.6	−343.0	−341.3
ϕ_{5555}	637.8	621.4	600.7	591.3	600.4	586.7	587.8	589.6	602.8
ϕ_{6511}	7.9	3.5	2.6	2.7	6.2	2.1	4.1	−0.9	−6.8
ϕ_{6522}	8.4	9.3	11.6	12.0	10.0	12.5	8.2	9.5	10.2
ϕ_{6533}	15.7	16.7	17.0	16.5	11.3	15.8	9.1	8.7	10.4
ϕ_{6544}	0.8	5.3	1.1	2.4	1.8	4.2	0.5	−3.9	−1.9
ϕ_{6555}	−41.6	−88.5	−8.3	−67.0	−62.6	−43.2	−60.5	−80.5	−47.1
ϕ_{6611}	−213.2	−215.3	212.9	211.8	213.9	214.6	−214.6	218.6	212.5
ϕ_{6621}	−15.9	−14.1	−14.6	−13.3	−14.1	−11.2	−13.8	12.4	−12.0
ϕ_{6622}	0.3	3.1	2.6	2.0	3.4	2.7	4.8	5.1	6.4
ϕ_{6631}	−40.5	−44.1	−32.2	−34.2	−39.6	−35.8	−36.7	−40.6	−40.1
ϕ_{6632}	−21.0	−24.4	−21.1	−19.6	−22.7	−22.3	−22.7	−21.6	−23.3
ϕ_{6633}	37.8	41.1	34.4	33.5	35.0	35.1	36.1	35.4	36.4
ϕ_{6644}	28.9	29.4	29.0	29.1	30.6	30.6	32.6	34.0	33.3
ϕ_{6655}	−218.2	−198.4	−180.8	−209.9	−240.6	−240.8	−231.1	−254.0	−218.5
ϕ_{6665}	−17.3	−45.4	−0.8	−29.6	−37.3	−17.0	−34.7	−49.3	−22.4
ϕ_{6666}	92.4	102.3	82.5	84.1	92.1	91.5	92.7	88.3	92.0

^{a} The sign conventions for ϕ are consistent with a positive value for the eigenvectors L_{lk}.

overtones and combinations bands, our results are in very good agreement with the work of Martin et al.[68] and with the iterative refined theoretical approach developed by Ribeiro et al.[69] In comparison with the experimental data the average deviation of our non adjusted CCSD(T)/cc-pVQZ results is only of about 4.3 cm^{-1} (Table 4 and refs 41−43 and 66−72). As a

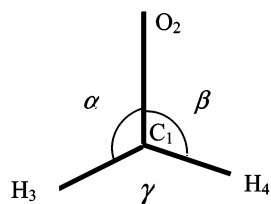Infrared Results on Formaldehyde in Solution

J. Phys. Chem. A, Vol. 110, No. 25, 2006 **7797**

symmetry group :
C_2v

$S_1(A_1) = 2^{-1/2} (r_{13} + r_{14})$

$S_2(A_1) = r_{12}$

$S_3(A_1) = 6^{-1/2} (\alpha + \beta - 2\gamma)$

$S_4(B_1) = \tau_{3124}$ *(torsion)*

$S_5(B_2) = 2^{-1/2} (r_{13} - r_{14})$

$S_6(B_2) = 2^{-1/2} (\alpha - \beta)$

Figure 1. Internal and symmetry coordinates for H_2CO.

consequence, these results will be used as our theoretical reference for the study of H_2CO shifts in solution.

B3LYP/6-31+G** and CCSD(T)/cc-pVQZ structural parameters of H_2CO in the six solvents are reported in Table 5. Our

results are compared with those previously obtained in the gaseous phase.[73] Few modifications are observed. Nevertheless, for all the theoretical conditions we can notice a systematic shortening of the C–H bond lengths concomitant with an average lengthening of the C=O bond length by about 0.03 Å. No significant variations in the bond angles are observed. Although they are weak, those geometrical modifications are important in the harmonic description of the problem (Table 3). In combination with an increase of ϵ, the harmonic wavenumbers variations ($\Delta\omega_i$) correlate closely to those observed for the bond lengths. As expected, the maximal deviation is observed for the two stretching ν(C–H) modes for which both mass and the increasing polarization of fields effects are dominant. All the displacements are correctly estimated at both harmonic and anharmonic levels of calculation:

TABLE 4: Experimental and Anharmonic Representative Results of H_2CO in the Gas Phase[a]

	ν_4 [$\tau(CH_2)$] (B_1)	ν_6 [$\rho(CH_2)$] (B_2)	ν_3 [$\sigma(CH_2)$] (A_1)	ν_2 [$\nu(CO)$] (A_1)	ν_1 [$\nu_s(CH_2)$] (A_1)	ν_5 [$\nu_{as}(CH_2)$] (B_2)
HF/6-311++G(2df,2p)[b]	(1337)	(1366)	(1648)	(1995)	(3092)	(3161)
CASSCF/DZP[c]	(1225)	(1311)	(1583)	(1780)	(3213)	(3306)
MP2/6-311G** [d]	(1212)	(1291)	(1568)	(1780)	(2971)	(3036)
MP2/aug-cc-pVTZ[e]	(1197) 1163	(1267) 1242	(1540) 1505	(1753) 1721	(2974) 2820	(3048) 2837
CCSD(T)/cc-pVQZ[f]	(1190) 1165	(1273) 1248	(1538) 1504	(1781) 1749	(2934) 2789	(3004) 2842
variation/dav[g]			1499.5	1746.1	2782.4	
B3LYP/6-31+G* [h]	(1191)	(1268)	(1545)	(1823)	(2931)	(2990)
B3LYP/6-311G** [i]				(1827)		
B97–1/TZ2P[j]	1181	1245	1499	1797	2743	2823
DFT/MM–FTTCF[k]	1141	1214	1471	1741	2769	2809
			Our Results			
B3LYP/6-31+G**	(1194) 1170	(1262) 1237	(1537) 1499	(1819) 1794	(2914) 2774	(2979) 2832
B3LYP/6-311+G**	(1198) 1174	(1259) 1236	(1531) 1495	(1815) 1779	(2884) 2743	(2941) 2805
B3LYP/cc-pVTZ	(1203) 1184	(1268) 1248	(1536) 1504	(1824) 1798	(2877) 2726	(2931) 2769
CCSD(T)/6-31+G**	(1188) 1148	(1278) 1248	(1562) 1522	(1771) 1737	(3002) 2847	(3079) 2887
CCSD(T)/cc-pVTZ	(1192) 1167	(1274) 1248	(1543) 1505	(1781) 1749	(2929) 2789	(2995) 2848
CCSD(T)/cc-pVQZ	(1190) 1165	(1271) 1246	(1537) 1499	(1781) 1750	(2933) 2791	(3004) 2850
exp[l]	1167	1249	1500	1746	2782	2843

[a] The values in parentheses relate to harmonic wavenumbers. [b] Reference 43. [c] Reference 66. [d] Reference 67. [e] Reference 62. [f] Reference 68. [g] Reference 69. [h] Reference 70. [i] Reference 42. [j] Reference 71. [k] Reference 72. [l] Reference 41.

TABLE 5: Structural Parameters of H_2CO in Vacuo and in Solution, Calculated at Both B3LYP/6-31+G and CCSD(T)/cc-pVQZ Levels of Theory**

	B3LYP 6-31+G**		CCSD(T) cc-pVQZ						
parameter	gas[a]	CH_3CN $\epsilon = 37.5$	gas[a]	C_6H_{12} $\epsilon = 2.02$	$CHCl_3$ $\epsilon = 4.81$	C_4H_8O $\epsilon = 7.58$	CH_3CN $\epsilon = 37.5$	$(CH_3)_2SO$ $\epsilon = 46.7$	H_2O $\epsilon = 78.4$
r_{CO} (Å)	1.210	1.215	1.208	1.208	1.210	1.210	1.211	1.211	1.211
r_{CH} (Å)	1.108	1.105	1.101	1.101	1.099	1.099	1.099	1.098	1.098
θ_{HCO} (deg)	116.2	116.6	116.4	116.6	116.6	116.8	116.8	116.8	116.8

[a] Experimental values (ref 73): r_{CO} (Å) = 1.203 ± 0.001, r_{CH} (Å) = 1.100 ± 0.002, θ_{HCO} (deg) = 116.3 ± 0.3.

TABLE 6: Wavenumbers (cm^{-1}) of H_2CO in Vacuo and in Solution, Calculated at Both B3LYP/6-31+G and CCSD(T)/cc-pVQZ Levels of Theory without Coriolis Coupling**

	B3LYP 6-31+G**		CCSD(T) cc-pVQZ						
parameter	gas	CH_3CN $\epsilon = 37.5$	gas	C_6H_{12} $\epsilon = 2.02$	$CHCl_3$ $\epsilon = 4.81$	C_4H_8O $\epsilon = 7.58$	CH_3CN $\epsilon = 37.5$	$(CH_3)_2SO$ $\epsilon = 46.7$	H_2O $\epsilon = 78.4$
ν_4 [$\tau(CH_2)$]	1170	1172	1165	1157	1162	1163	1166	1166	1166
ν_6 [$\rho(CH_2)$]	1237	1235	1246	1243	1239	1239	1243	1236	1239
ν_3 [$\sigma(CH_2)$]	1499	1494	1499	1496	1496	1497	1501	1498	1496
ν_2 [$\nu(CO)$]	1794	1763	1750	1741	1737	1735	1731	1733	1731
ν_1 [$\nu_s(CH)$]	2774	2804	2791	2800	2805	2813	2812	2813	2813
ν_5 [$\nu_{as}(CH)$]	2832	2848	2848	2846	2847	2848	2866	2860	2868
$2\nu_4$	2336	2341	2326	2310	2320	2321	2323	2325	2326
$\nu_4 + \nu_6$	2405	2405	2408	2402	2404	2404	2406	2407	2407
$2\nu_6$	2469	2461	2484	2481	2474	2475	2474	2474	2473
$\nu_4 + \nu_3$	2669	2664	2663	2653	2657	2659	2660	2660	2660
$\nu_6 + \nu_3$	2715	2708	2723	2714	2712	2711	2713	2714	2714
$\nu_4 + \nu_2$	2959	2930	2904	2891	2892	2891	2893	2893	2893
$2\nu_3$	2997	2986	2997	2990	2989	2994	2990	2991	2988
$\nu_6 + \nu_2$	3033	3001	2996	2991	2984	2983	2984	2986	2988
$\nu_3 + \nu_2$	3284	3251	3245	3231	3224	3225	3223	3223	3223
$3\nu_4$	3490	3498	3483	3450	3465	3463	3470	3474	3474
$2\nu_2$	3572	3506	3487[a]	3466	3455[a]	3455[a]	3454[a]	3456	3454

[a] 3470 (gas), 3439 cm^{-1} (CHCl$_3$), 3437 cm^{-1} (C$_4$H$_8$O), 3434 cm^{-1} (CH$_3$CN): our experimental values.

(2a)

(2b)
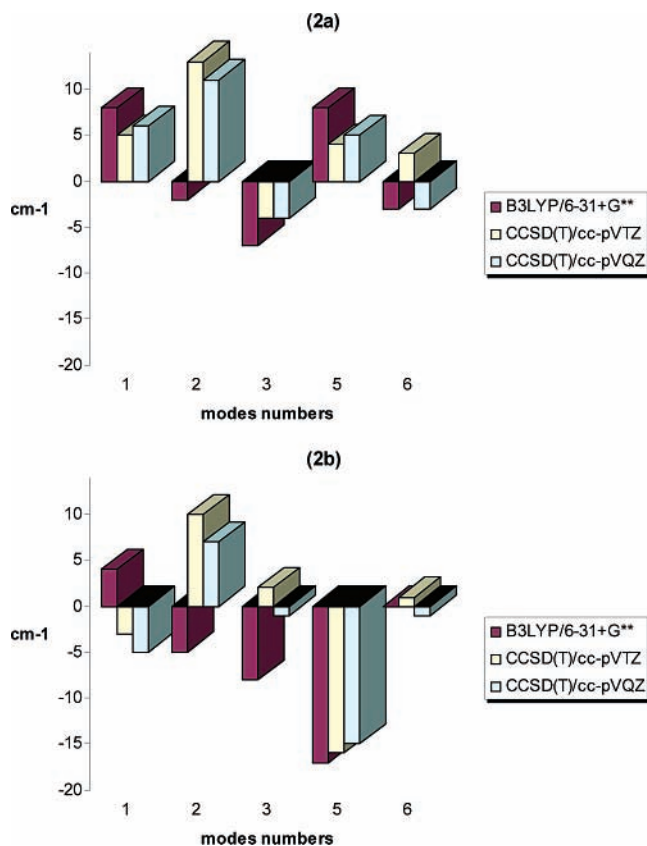
Figure 2. Harmonic $[(\omega^{solv} - \omega^{gas})_{theory} - (\nu^{solv} - \nu^{gas})_{exp}]$ (a) and anharmonic $[(\nu^{solv} - \nu^{gas})_{theory} - (\nu^{solv} - \nu^{gas})_{exp}]$ (b) deviations obtained at B3LYP/6-31+G**, CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ levels of theory for the $(H_2CO + CH_3CN)$ system. ν_{exp} = this work.

(i) In general, for all the solvents, the calculation of both ν_2 and ν_3 fundamental modes is only slightly improved (3−5 cm^{-1}) when the anharmonic hypothesis is taken into account.

(ii) The problem of the ν_5 mode (ν_{as} stretching C−H) is more critical because our experimental value in CH_3CN deviates by 11 cm^{-1} from that of Wong et al.[43]

(iii) Concerning both ν_1 and ν_6 modes, it is unfortunate that not enough experimental date are available.

For the experimentally well-known CH_3CN solvent, we have reported on Figure 2 the average deviations relative to experimental data:

$$\chi = [(y^{solv} - y^{gas})_{theory} - (\nu^{solv} - \nu^{gas})_{exp}] = [\Delta y_{theory} - \Delta \nu_{exp}]$$

calculated at both harmonic $y = \omega$ (2a) and anharmonic $y = \nu$ (2b) levels of approximation for the three B3LYP/6-31+G**, CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ levels of theory. These data add new elements, making one question itself about the ability of such approaches to well-describe the solvent effect.

(i) Whatever the degree of sophistication of the method may be, the harmonic value of χ is near zero, which means that the

harmonic description of the shift ($\Delta \omega_i$) is then in fairly good agreement with the corresponding experimental data.

(ii) Interestingly, these displacements never exceed 12 cm^{-1} ($\sim$1%) if we do not take into account our "nonmorsificate" ν-(C−H) stretches calculations.

(iii) The use of anharmonicity clearly affects our conclusions. The average CCSD(T)/cc-pVXZ value of $\Delta \nu_i$ corresponds to a change of 50% of significance whatever the basis set used (X = T or Q).

(iv) Finally and paradoxically, although the frequency of ν-(C=O) (ν_2) is the least successfully modeled at the B3LYP level of theory, due to an overestimation of the corresponding bond length, the corresponding shift of this mode is correctly reproduced at the same level. This peculiarity, which is well-known for the ν(C=O) calculation is not observed for the shift $\Delta \nu$(C=O). These considerations are worthy of remark for the study of larger molecules for which only the use of DFT is nowadays possible.

In conclusion, we can say that an accurate investigation of the geometrical modifications undergone by a molecule in solution is only needed to predict the shifts in the corresponding vibrational spectrum positions. Such an observation decreases the benefit of an improvement like anharmonicity to model correctly the interaction with the solvent of a molecule in vibration and explains the success of some much less sophisticated treatments (Tables 4 and 6). Nevertheless, the use of our original approach is justified in that it allows a fair reproduction (within 1%) of all the band positions of the spectrum. Through the present paper we have shown that these conditions are thoroughly fulfilled in the case of the formaldehyde molecule at the CCSD(T)/cc-pVXZ (X = T, Q) levels, thus validating the use of PCM models with an anharmonic treatment in MIR. Pure DFT approaches[74] represent in that case a very satisfactory compromise for the study of systems larger than H_2CO (up to 30 atoms): indeed, we have obtained average deviations relative to experimental data that are systematically of the order of 10 cm^{-1} (these values are comparable to the values obtained for the CCSD (T)/cc-pVQZ study of H_2CO in acetonitrile). Beyond this critical size, the "ab initio" treatment of the complete system seems nowadays unreachable.

4.2. Toward a More Economic Solution for the Study of "Uncoupled" Modes? The previous conclusions thus prompt the theoricians in chemistry to look for more adaptable solutions. We propose a very simple model for the study of chemical groups in solution. First of all, insofar as strongly correlated methods are useless for the determination of $\Delta \omega_i = \omega_i^{solv} - \omega_i^{gas}$, we propose an a priori use of either HF or DFT methods with double ζ basis set to effectively calculate these values. Moreover, we are convinced that the use of the B3LYP/6-31+G** quartic force fields represents an economic compromise with respect to approaches that are strongly correlated as far as

TABLE 7: Empirical Wavenumbers ΔΔ (cm^{-1}) of the ($H_2CO + CH_3CN$) Solution

	ν_4 (B$_1$)	ν_6 (B$_2$)	ν_3 (A$_1$)	ν_2 (A$_1$)	ν_1 (A$_1$)	ν_5 (B$_2$)
ω^{gas} CCSD(T)/cc-pVQZ	(1190)	(1271)	(1537)	(1781)	(2933)	(3004)
$\Delta Z\omega = \omega^{solv} - \omega^{gas}$ B3LYP/6-31+G**	+13	−5	−4	−28	+34	+41
$\Delta Z\nu$ B3LYP/6-31+G**	−35	−22	−39	−28	−144	−172
ΔΔ	1168	1244	1494	1725	2823	2873
CCSD(T)/cc-pVQZ[a]	1166	1243	1501	1731	2812	2866
exp[b]		1247	1503	1723	2797	2876
exp[c]				1726	2808	

[a] Our best estimation. [b] Reference 41. [c] This work.

Infrared Results on Formaldehyde in Solution

J. Phys. Chem. A, Vol. 110, No. 25, 2006 **7799**

anharmonicity ($\Delta\nu$) is concerned. Finally, a gas phase reference calculation (CCSD(T)/cc-pVTZ for example) is needed to compute adequately both the structural properties of the solutes and the optimized harmonic frequencies ω^{gas}. The results for the (H$_2$CO+CH$_3$CN) system are reported in Table 7. These estimated values are noted $\Delta\Delta = \omega^{gas}$(CCSD(T)/cc-pVQZ) + $\Delta\omega$ (B3LYP/6-31+G**) + $\Delta\nu$ (B3LYP/6-31+G**) and are compared to our best previous estimation (CCSD(T)/cc-pVQZ). When modes are weakly coupled (Table 3), the $\Delta\Delta$ approach seems very promising if we refer to the results obtained for the ν_3, ν_4, ν_6 modes, and for the almost pure CO stretching ν_2 mode and its first overtone $2\nu_2$ as evidenced experimentally by us. For the study of more coupled modes, the anharmonicity account is nowadays accessible for medium sized systems with the use of perturbational approaches as a replacement of the empirical addition of the ($\Delta\nu$) term previously cited. In that case, a supplementary difficulty must be considered because all the cubic and quartic force constants calculated at the B3LYP/6-31+G** level ($\Delta\nu$) must be expressed in the basis of the dimensionless normal modes calculated at the best ω^{gas} level of theory. No significant changes are observed in the present study.

To conclude, we remain very careful on this approach, which has, for the main purpose, to deal at best with every effect taken separately from the others. Actually, our proposal should not be considered as a "rigorous" procedure but rather as an approached model whose aim is to allow the modeling of "isolated" vibrators such as those used, for example, in the experimental characterization of the two A and I amide modes of proteins in solution. [36,75−77]

References and Notes

(1) Kirkwood, J. G. *J. Chem. Phys.* **1934**, *2*, 351.

(2) Buckingham, A. D. *Proc. R. Soc. A* **1958**, *248*, 169.

(3) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999.

(4) Barone, V.; Improta, R.; Rega, N. *Theor. Chem. Acc.* **2004**, *111*, 237.

(5) Cossi, M.; Rega. N.; Scalmani, G.; Barone, V. *J. Comput. Chem.* **2003**, *24*, 669.

(6) Leach. In *Molecular Modelling. Principles and Applications*; Longman, A. R., Ed.; World Scientific: Singapore, 1996.

(7) Carbonnière, P.; Bégué, D.; Dargelos, A.; Pouchan, C. *Chem. Phys.* **2004**, *300*, 41 and references therein.

(8) Light, J. C.; Carrington, T. *Adv. Chem. Phys.* **2000**, *114*, 263.

(9) Viel, A.; Leforestier, C. *J. Chem. Phys.* **2000**, *112*, 1212.

(10) Carney, G. D. *Adv. Chem. Phys.* **1978**, *37*, 305.

(11) Romanowski, H.; Bowman, J. M.; Harding, L. B. *J. Chem. Phys.* **1985**, *82*, 4155.

(12) Cassam-Chenaï, P.; Lievin, J. *Int. J. Quantum Chem.* **2003**, *93*, 245.

(13) Dhont, G.; Chambaud, G.; Groenenboom, G. C.; Van Der Avoird, A. *Mol. Phys.* **2004**, *102*, 2285.

(14) Barone, V. *J. Chem. Phys.* **2005**, *122*, 014108/1.

(15) Barchewitz, P. *Spectroscopie infrarouge − Vibrations moléculaires*; Gauthier-Villars & Cie: Paris, 1961.

(16) Pliva, J. *J. Mol. Spectrosc.* **1990**, *139*, 278

(17) Willetts, A.; Handy, N. C. *Chem. Phys. Lett.* **1995**, *235*, 286.

(18) Pouchan, C.; Zaki, K. *J. Chem. Phys.* **1997**, *107*, 342.

(19) Martin, J. M. L.; Lee, T. J.; Taylor, P. R.; François, J. P. *J. Chem. Phys.* **1995**, *102*, 2589.

(20) Breidung, J.; Thiel, W. *J. Mol. Struct.* **2001**, *599*, 239.

(21) Carter, S.; Culik, S. J.; Bowman J. M. *J. Chem. Phys.* **1997**, *107*, 10458.

(22) Koput, J.; Carter, S.; Handy, N. C. *J. Chem. Phys.* **2001**, *115*, 8345.

(23) Culot, F.; Lievin, J. *Theor. Chim. Acta* **1995**, *89*, 227.

(24) Gohaud, N.; Bégué, D.; Pouchan, C. *Lecture Series on Computer and Computanional Science* **2004**, *1*, 828.

(25) Wong, M. W.; Frisch, M. J.; Wiberg, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 4776.

(26) Klamt, A.; Schueuermann, G. *J. Chem. Soc., Perkins Tans.* **1993**, *5*, 799.

(27) Balridge, K.; Klamt, A. *J. Chem. Phys.* **1997**, *106*, 6622.

(28) Roux, B.; Simonson. T. *Biophys. Chem.* **1999**, *78*, 1.

(29) Papazyan, A.; Warshel. A. *J. Phys. Chem. B* **1997**, *101*, 11254.

(30) Gilson, M. K.; McCammon, J. A.; Madura. J. D. *J. Comput. Chem.* **1995**, *16*, 1081.

(31) Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117.

(32) Garcia-Viloca, M.; Nam, K.; Alhambra, C.; Gao, J. *J. Phys. Chem. B* **2004**, *108*, 13501.

(33) Schmitz, M.; Tavan, P. *J. Chem. Phys.* **2004**, *121*, 12233.

(34) Brinkmann, N. R.; Carmichael, I. *J. Phys. Chem. A* **2004**, *108*, 9390.

(35) Assfeld, X.; Rivail, J. L. *Chem. Phys. Lett.* **1996**, *263*, 100.

(36) Gaigeot, M. P.; Sprik, M. *J. Phys. Chem. B* **2003**, *107*, 10344.

(37) Jorgensen, W. L.; Chandrasekhar, J.; Madura, J. D.; Impey, R. W.; Klein, M. L. *J. Chem. Phys.* **1983**, *79*, 926.

(38) Bégué, D.; Carbonnière, P.; Barone, V.; Pouchan, C. *Chem. Phys. Lett.* **2005**, *416*, 206.

(39) Foresman, J. B.; Keith, T. A.; Wiberg, K. B.; Snoonian, J.; Frisch, M. J. *J. Phys. Chem.* **1996**, *100*, 16098.

(40) Besley, N. A. *Chem. Phys. Lett.* **2004**, *390*, 124.

(41) Nakawaga, T.; Kondo, S.; Saeki, S. *J. Chem. Phys.* **1982**, *76*, 3860.

(42) Rivail, J. L.; Rinaldi, D.; Dillet, V. *J. Chim. Phys.* **1998**, *95*, 1818.

(43) Wong, M. W.; Wiberg, K. B.; Frisch, M. *J. Chem. Phys.* **1991**, *95*, 8991.

(44) Bouwens; R. J.; Hammerschmidt, J. A.; Grzeskowiak, M. M.; Steginck, T. A., Yorba, P. M.; Polik, W. F. *J. Chem. Phys.* **1996**, *104* (2), 460.

(45) Dimitrova, Y. *J. Mol. Struct. (THEOCHEM)* **1997**, *391*, 251.

(46) Gohaud, N.; Bégué, D.; Darrigan, C.; Pouchan, C. *J. Comput. Chem.* **2005**, *26*, 743 and references therein.

(47) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(48) Carbonnière, P.; Lucca, T.; Pouchan, C.; Rega, N.; Barone, V. *J. Comput. Chem.* **2005**, *26*, 384.

(49) Boese, A. D.; Klopper, W.; Martin, J. M. L. *Int. J. Quantum Chem.* **2005**, *104*, 830.

(50) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian Inc.: Pittsburgh PA, 1998.

(51) Bégué, D.; Gohaud, N.; Pouchan, C. P_Anhar_v1.1. FR 2606, UMR 5624, Université de Pau et des Pays de l'Adour, 2006.

(52) Bruna, P. J.; Hachey, M. R. J.; Grein, F. *J. Mol. Struct. (THEOCHEM)* **1997**, *400*, 177 and references therein.

(53) Wang, X. G.; Sibert, E. L., III; Martin, J. M. L. *J. Chem. Phys.* **2000**, *112*, 1353.

(54) Norris, L. S.; Ratner, M. A.; Roitberg, A. E.; Gerber, R. B. *J. Chem. Phys.* **1996**, *105*, 11261.

(55) Taketsugu, T.; Yagi, K.; Gordon, M. S. *Int. J. Quantum Chem.* **2005**, *104*, 758.

(56) Bowman, J. M. *J. Chem. Phys.* **1978**, *68*, 608.

(57) Thompson, T. C.; Truhlar, D. G. *Chem. Phys. Lett.* **1980**, *75*, 87.

(58) Carter, S.; Handy, N. C. *J. Chem. Phys.* **2000**, *113*, 987.

(59) Roitberg, A.; Gerber, R. B.; Elber, R.; Ratner, M. A. *Science* **1995**, *268*, 1319.

(60) Christiansen, O. *J. Chem. Phys.* **2004**, *120*, 2149.

(61) Wright, N. J.; Gerber, R. B. *J. Chem. Phys.* **2001**, *114*, 8763.

(62) Yagi, K.; Hirao, K.; Taketsugu, T.; Schmidt, M. W.; Gordon, M. S. *J. Chem. Phys.* **2004**, *121*, 1383.

(63) Mardis, K. L.; Sibert, E. L., III. *J. Mol. Spectrosc.* **1998**, *187*, 167.

(64) Léonard, C.; Chambaud, G.; Carter, S. *Chem. Phys. Lett.* **2004**, *398*, 123.

(65) Ribeiro, F.; Iung, C.; Leforestier, C. *J. Chem. Phys.* **2005**, *123*, 054106. and refs. therein.

(66) Naka, K.; Morita, A.; Kato, S. *J. Chem. Phys.* **1999**, *110*(7), 3484.

(67) Luckhaus, D.; Coffey, M. J.; Fritz, M. D.; Crim, F. F. *J. Chem. Phys.* **1996**, *104*, 3472.

(68) Martin, J. M. L.; Lee, T. J.; Taylor, P. R. *J. Mol. Spectrosc.* **1993**, *160*, 105.

(69) Ribeiro, F. .Calcul d'états vibrationnels excites de molecules polyatomiques. Ph.D., Montpellier, France, 2003.

(70) Cappelli, C.; Corni, S.; Tomasi, J. *J. Chem. Phys.* **2001**, *115*, 5531.

(71) Burcl, R.; Carter, S.; Handy, N. C. *Chem. Phys. Lett.* **2003**, *380*, 237.

(72) Schmitz, M.; Tavan, P. *J. Chem. Phys.* **2004**, *121*, 12247.

(73) Duncan, J. L. *Mol. Phys.* **1974**, *28*, 1174.

(74) Bégué, D.; Benidar, A.; Guillemin, J. C.; Pouchan, C. To be published.

(75) Simonson. T. *Rep. Prog. Phys.* **2003**, *66*, 737.

(76) Borgis, D.; Lévy, N.; Marchi. M. *J. Chem. Phys.* **2003**, *119*, 3516.

(77) Watson, T. M.; Hirst, J. D. *J. Phys. Chem. A* **2002**, *106*, 7858.