MOLECULAR MECHANICS PARAMETERS FOR ELECTRONICALLY EXCITED STATES: THE (n, π*) SINGLET STATE OF FORMALDEHYDE

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We have developed parameters for molecular mechanics and dynamics simulations of the excited (n, π*) singlet state in formaldehyde based on data from ab initio molecular orbital calculations. Structural parameters are derived from geometry optimizations, whereas the classical force constants are determined from fits to computed (scaled) vibrational frequencies. The partial atomic charges are obtained from a natural atomic orbital population analysis of the excited state wavefunction. The theoretical parameters are compared to those derived from experimental spectroscopic data. Some initial results with the excited state parameters on the structural relaxation of formaldehyde during a molecular dynamics simulation following optical excitation in the presence of a large number of water molecules are presented.

1. Introduction

The interaction between a molecular solute and a solvent may be examined in a variety of ways by computational techniques. We are engaged in a series of model calculations on formaldehyde (H_2CO) solvated by water molecules [1,2], using a combination of techniques including quantum mechanical electronic structure (ab initio molecular orbital) methods, purely classical molecular mechanics and dynamics simulations, and hybrid methods incorporating advantages of both approaches. Formaldehyde has substantial electronic and structural differences between its ground (S_0) and first excited (S_1) singlet states, hence there will be significant differences in the polar solvent–solute interactions between the two states. Our classical simulations on formaldehyde in water have, for example, indicated that a well defined solvent structure around the oxygen end of formaldehyde in its ground state is largely destroyed in the excited state [2]. The excitation of H_2CO in our previous work corresponded to a *vertical* electronic excitation, i.e. the H_2CO partial atomic charges where changed to those of the excited state, but the molecular geometry was not allowed to relax. The geometry changes following excitation are in fact substantial, including an increase of the car-

bonyl bond length by more than 0.1 Å and a change in molecular point group from C_{2v} (S_0) to C_s (S_1) due to pyramidalization around the carbon atom. Furthermore, the most intense line in the formaldehyde gas phase absorption spectrum occurs at 34035 cm^{-1} [3], whereas the adiabatic transition energy is 28188 cm^{-1} [4]. Thus, at the point of vertical excitation to the singlet (n, π*) state, the H_2CO molecule has 16.7 kcal/mol of excess vibrational energy which on a time scale of several picoseconds will be transferred to the surrounding water molecules. Short time simulations starting at the point of vertical excitation will show the dynamics of intramolecular and intermolecular relaxation. Simulations of the excited state formaldehyde equilibrated with the surrounding water molecules will reflect the intermolecular structure at long time. In this Letter, we describe our approach to a molecular mechanics parameterization of the (n, π*) state and present some initial results on the intramolecular relaxation following excitation.

In order to obtain physically meaningful results from such simulations, it is essential to use parameters that at least qualitatively describe the intermolecular and intramolecular energies and forces. Much work has been carried out to establish high quality parameter sets for use in classical simula-

tions of systems in their ground states [5–11], and numerous simulations of electronic ground state solutes surrounded by solvent (including H_2CO and water [12,13]) have been performed. However, only few simulations have been performed with an electronically excited solute molecule, [9,14,15] and there are no readily available parameter sets for excited states of, say, common organic molecules (although parameters for some very specific molecules have been presented [#1]). Electronically excited states possess widely different properties even within a limited class of molecules such as hydrocarbons, and it is difficult to create highly transferable parameter sets for this purpose. Similarly, schemes for parameterization of excited states by empirical adjustment of ground state parameters have not been developed yet. For most excited states of polyatomic molecules there are few experimental results to which simulation parameters can be fit; H_2CO is unusual in this regard, since both the molecular structure and vibrational frequencies are fully determined for the excited state. Electronic structure calculations provide a powerful approach to developing excited state parameters, although the well-known problems with excited state calculations complicate such advances. In this Letter, we compare excited state molecular mechanics parameters fit from experimental data with those calculated by a straightforward ab initio method that involves only a modest amount of computer time. We use excited formaldehyde as a suitable model system, but the method can be readily extended to most electronic states of other small to medium sized molecules.

2. Computational details

The requisite molecular mechanics parameters (reference geometry, force constants, atomic charges) for the S_1 state of formaldehyde have been obtained from ab initio calculations carried out with the GAMESS program [17] [#2]. Calculations were performed using the restricted open-shell Hartree–Fock (ROHF) approximation [18] and two basis sets: the standard split-valence 3-21G basis set [19]; and the 6-31G basis set [20] with polarization functions ($\alpha_d(C) = 0.75$ and $\alpha_d(O) = 0.85$) [21], here referred to as 6-31G+d. For each basis set, geometry optimization provided the equilibrium structure (C_s symmetry, $^1A''$) used as reference geometry. A normal mode analysis was carried out on each reference geometry and the vibrational frequencies were scaled by the standard factor of 0.89, as suggested by Pople and co-workers [22]. A modified version of Schachtschneider's vibrational analysis program [23] was then used to obtain the set of harmonic local mode force constants that best reproduced the normal mode frequencies. For simplicity, only diagonal force constants were used in the least squares fit. Specifically, we employed the C–O and C–H stretch coordinates and the O–C–H and H–C–H angle bends. The motion along the dihedral angle describing the out-of-plane CH_2 wag coordinate is of very low frequency, highly anharmonic, and the barrier to inversion through the planar geometry is small. Thus, a harmonic oscillator approximation is totally inadequate for this coordinate. Instead, the magnitude of the barrier was evaluated by optimization of H_2CO in the S_1 state with planarity imposed (C_{2v} symmetry, $^1A_2$), and the expansion coefficients (V_2, V_3) in a sum of two cosine terms were then determined from the computed ab initio barrier height and equilibrium wag angle,

$$V = 0.5V_2[1 - \cos(2\varphi)] + 0.5V_3[1 - \cos(3\varphi)].$$

φ is the improper H–H–C–O dihedral angle with $\varphi = 180°$ corresponding to the fully planar conformation. This functional form was chosen because it is easily incorporated in the molecular dynamics program (vide infra), and it is capable of representing the anharmonic, double well nature of the potential. The dihedral angle coordinate and the lowest frequency were subsequently removed from the fitting of harmonic force constants to normal mode frequencies. For comparison, the parameter fitting procedure was repeated using the experimentally determined excited state geometry [24], inversion barrier [24], and vibrational frequencies [25]. Formaldehyde partial atomic charges were obtained from the 6-31G+d wavefunction at the ROHF/

Table 1
Equilibrium geometries, classical force constants, and partial atomic charges for the $^1A''$ state of H_2CO

Coordinate [a]	Equilibrium geometries		
	experiment	ROHF/3-21G	ROHF/6-31G+d
C–O	1.325	1.410	1.355
C–H	1.095	1.074	1.078
O–C–H	115.4	113.9	113.1
H–C–H	118.0	119.6	118.2
φ [b]	142.2	139.6	135.4
α [c]	33.6	36.4	40.3

Coordinate [d]	Classical force constants		
	experiment	ROHF/3-21G	ROHF/6-31G+d
C–O	3.89	4.21	6.15
C–H	4.62	4.88	4.83
O–C–H	0.45	0.46	0.37
H–C–H	0.20	0.39	0.39
V_2	8.82	9.68	9.60
V_3	6.20	7.44	8.88

Atom	Partial atomic charges		
	6-31G+d [e,f]	ROHF/3-21G [f]	ROHF/6-31G+d [f]
O	−0.271(−0.168)	−0.250(−0.162)	−0.280(−0.175)
C	−0.062(−0.038)	−0.090(−0.058)	−0.040(−0.025)
H	0.167(0.104)	0.170(0.110)	0.160(0.099)

[a] Bond lengths in Å, angles in deg.

[b] φ is the H–H–C–O dihedral angle used in the potential energy function.

[c] α is the conventional wag angle, the angle between the C–O bond and the H–C–H plane.

[d] Stretch constants in mdyn/Å; bend constants in mdyn Å; inversion barrier constants in kcal/mol.

[e] ROHF/6-31G+d calculation at the experimental geometry.

[f] Values in parentheses have been scaled by the ratio of experimental to classical dipole moment, see text. This ratio is in the range 0.62–0.65 for all three parameter sets.

6-31G+d optimized geometry, the 6-31G+d wavefunction at the experimental geometry, and the 3-21G wavefunction at the ROHF/3-21G optimized geometry, respectively, using the natural atomic orbital [26] population analysis procedure. The resultant molecule mechanics parameters are shown in table 1.

3. Results and discussion

3.1. Parameters

The first excited singlet state in formaldehyde results from an $n_O \to \pi^*$ excitation, which shifts elec-
tron density from electronegative oxygen to carbon [27] [#3]. One result of this charge migration is a reduced molecular dipole as evidenced by the experimentally determined ground and excited state dipole moments of 2.33 D [28] and 1.57 D [29], respectively. Furthermore, the equilibrium geometry is changed from planar (C_{2v} symmetry, $^1A_1$) with $R_{CO} = 1.203$ Å ($\varphi = 180°$) [30], to a nonplanar, pyramidalized geometry (C_s symmetry, $^1A''$) with $R_{CO} = 1.325$ Å and $\varphi = 142.2°$ [24]. Examination of

[#3] Detailed analysis of the excited state charge distribution indicates that the excitation may also be considered as a localized oxygen p→p transition [27].

table 1 indicates that the fit to experimental or computed data produce parameter sets that possess many of the same features and reflect the same qualitative physical picture. In all three cases, the C–O bond stretching constant is much smaller than that for a typical C=O double bond (approximately 12–13 mdyn/Å [31]) in accordance with the increase in C–O bond length, the decrease in double bond character, and the significant decrease in the experimental "C–O stretch" frequency from 1746 cm^{-1} in the ground state to 1173 cm^{-1} in the excited state [32]. The C–H, O–C–H and H–C–H force constants for the excited state are similar to typical ground state values. The average error between the input frequencies and the fitted output frequencies was in all cases near 3%. Our force field assumptions are consistent with the standard choice of molecular dynamics parameter sets, but the absence of cross terms does limit the ability of the force constants to fully reproduce the input frequencies slightly. The energy curve for out-of-plane motion (fig. 1) are "ω-shaped" with nearly coalescing minima, since the computed and experimental values for the equilibrium wag angles are close. The curves also behave similarly for distortions beyond the minima. However, differences among the curves appear between the two
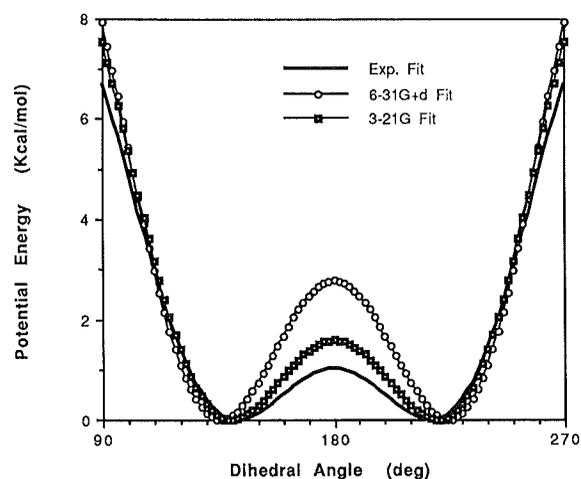

Fig. 1. H_2CO dihedral angle (φ) energy functions computed by fitting to the barrier height and equilibrium dihedral angle for experimental (solid line), ROHF/6-31G+d (line of small circles), and ROHF/3-21G (line of small squares) data. Angle $\varphi = 180°$ corresponds to a planar H_2CO. Potential curves are shifted so that all three have their minima at 0.0 kcal/mol.

equivalent minima due to the different inversion barriers produced by the various methods (2.77 at ROHF/6-31G+d; 1.59 at ROHF/3-21G; 1.02 kcal/mol from experiment [24]). The probability of inversion around the carbon atom depends on the barrier height. The barrier produced by the 6-31G+d calculations is significantly larger ($\approx 5k_BT$, $T=300$ K) than the experimental value ($\approx 2k_BT$) and would thus lead to the prediction of a smaller transition rate.

The partial charge on the carbon in the $^1A''$ state is slightly negative, in contrast to the ground state where the carbon charge is quite positive (≈ 0.33); the excited state oxygen charge becomes less negative by a similar amount [2]. However, the atomic charges and hence the classical molecular dipole moments (computed solely from the atomic point charges and the molecular geometry) produced by the natural atomic orbital population analysis method are substantial and larger than, for example, the equivalent charges and dipole moments produced by a fitting procedure such as the CHELP [33] program, which explicitly fits partial charges to reproduce the gas phase ab initio electrostatic potential. The natural population analysis of ground state formaldehyde at the RHF/6-31G+d level gives charges ($Q_O = -0.576$, $Q_C = +0.331$, $Q_H = +0.123$) and a classical dipole moment (3.96 D), which are different from the CHELP results with a similar basis set ($Q_O = -0.508$, $Q_C = +0.606$, $Q_H = -0.049$, dipole moment = 2.62 D) and larger than the experimental value (2.33 D); but, the quantum mechanical dipole moment at this computational level is 2.67 D in good agreement with the experimental value. Similarly, the ROHF/6-31G+d natural atomic charges for the structurally relaxed excited state ($Q_O = -0.280$, $Q_C = -0.040$, $Q_H = +0.160$) predict a classical dipole moment of 2.53 D, again considerably larger than the experimental value of 1.57 D or the quantum mechanical dipole of 1.64 D. However, the computed change in classical dipole moment (1.43 D) remains close to the experimental result (0.77 D) or quantum mechanical prediction (0.98 D). The magnitudes of the net atomic charges and (classical) dipole moments used in the simulations are of paramount importance for the description of the solute–solvent interactions. A fit of charges to the electrostatic potential may be preferable [33] or, when the dipole moment is experi-

mentally known, it may be advantageous to scale the charges so they actually reproduce the observed dipole by classical means (table 1). Charges based on the natural atomic orbital analysis scheme are appealing because of their insensitivity to basis set changes, but finding a proper, general procedure for generating atomic partial charges from isolated molecule calculations for use in condensed phase simulations remains a major concern.

3.2. Simulations

We are using the excited state parameters in molecular dynamics simulations of H_2CO in a cubic box with an edge of 18.6 Å containing 209 SPC [34] water molecules. The simulations are performed using the IMPACT program [#4], with conditions equivalent to those described previously ($T=298$ K) [2]. For an arbitrary equilibrated ground state configuration, the H_2CO parameters are changed to the excited state set, simulating instantaneous electronic excitation from S_0 to S_1. The molecular dynamics of this nonequilibrium system are followed for several thousand steps. A short timestep of 1.25×10^{-16} s is used so that the high frequency C–H vibrations can be accurately simulated.

Figs. 2a and 2b show the time evolution of the C–H stretch coordinates for excited state H_2CO during a sample trajectory using the molecular parameters obtained by fitting to the experimental frequencies, geometry, and inversion barrier. The zero of time is the point at which the parameters were changed from ground to excited state values. There is an obvious beat pattern between the two C–H stretch coordinates in which energy is shifted back and forth between the strongly coupled harmonic oscillators. Thus, at short times the C–H stretches are effectively decoupled from the other H_2CO internal coordinates and the surrounding water molecules. Fig. 3 shows the C–O stretch from the *same* excited state simulation. The motion in this coordinate does not have any well defined pattern, indicating that there are significant and irregular interactions between the C–
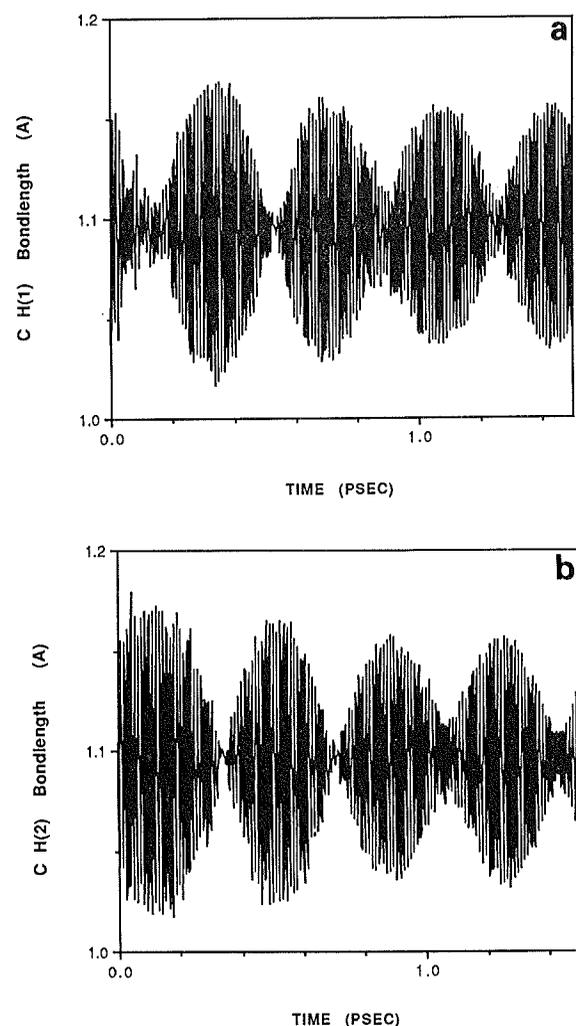
[#4] The "Integrated Modeling Program Using Applied Chemical Theory" (IMPACT) program is a package developed by R.M. Levy and co-workers at Rutgers University; for details see e.g. ref. [35].
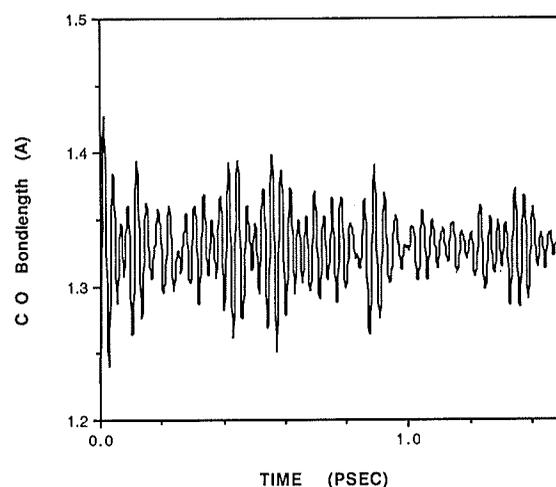

Fig. 2. C–H bond lengths as a function of time for excited formaldehyde in the presence of 209 SPC water molecules. (a) shows one C–H bond length and (b) shows the other C–H bond length.

O stretch and the surrounding waters. Initially, the C–O bond length expands rapidly, then the magnitudes of the C–O bond length oscillations diminish during the first picosecond, although the decreases cannot be represented by a smooth exponential decay. In this particular trajectory excess energy is quickly transferred from the excited C–O stretch to other coordinates. Fig. 4 shows the variation in the torsional angle, φ, for this particular sample trajectory. Each time the angle passes through 180°, the H_2CO has passed over the maximum in the excited

Fig. 3. C–O bond length as a function of time for excited form-aldehyde in the presence of 209 SPC water molecules.
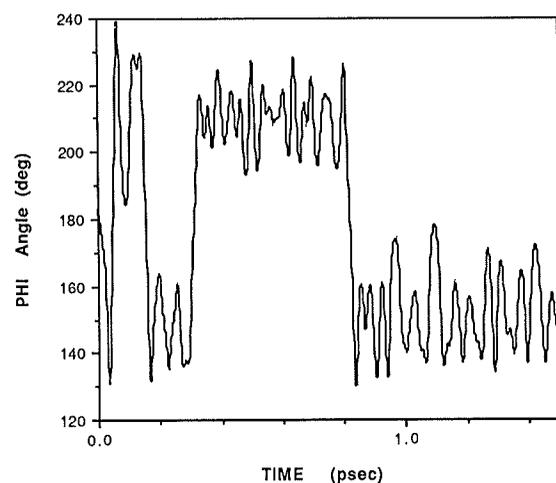
Fig. 4. Torsion angle as a function of time for excited formalde-hyde in the presence of 209 SPC water molecules. Angle $\varphi = 180°$ corresponds to a planar H_2CO, which is at a local maximum on the potential slice shown in fig. 1.

state torsional potential energy function. The molecule starts near the ground state minimum value of φ (at $180°$) but possesses excess energy, so it crosses the barrier several times during the first half picosecond. As with the C–O stretch, excess energy is quickly transferred to other degrees of freedom (such as motion of the surrounding water molecules), and the torsional angle settles down in the region of its

new equilibrium value. More detailed excited state simulations for the solvent dynamics are being carried out and will be described elsewhere.

4. Concluding remarks

We have experimented with an even simpler form for the excited state potential function in which the H–C–H bend (a redundant coordinate) was excluded. However, this simplified potential produced unphysical results during the molecular dynamics simulations. Without an explicit H–C–H force constant included, the H–C–H angle would occasionally open up to $180.0°$ and cause an unphysical discontinuity in the out-of-plane wag potential term (since the H–H–C–O dihedral angle is undefined when the H–C–H atoms are colinear). This subsequently caused unphysical changes in the other coordinates and the temperature of the system rose rapidly.

We also note that a purely harmonic energy function is unable to fully model the true, anharmonic molecular energy surface. For a typical ground state simulation, this represents a minor problem since the sampled molecular geometries will be near the geometry representing the energy surface minimum. However, a purely harmonic energy function could be severely inadequate for nonequilibrium excited state simulations. For example, an excited state H_2CO molecule that starts on a dynamics trajectory at or near the ground state equilibrium geometry has a C–O bond that is 0.12 Å shorter than the excited state equilibrium value. A harmonic force constant obtained by fitting to the excited state frequencies will be too small to fully reproduce the C–O bond energy in this region. This problem becomes most significant if one is interested in the details of energy transfer from the excited C–O bond to other internal coordinates, but it can be corrected by adding a cubic term to the harmonic energy function or by using a Morse potential. Changes in both lengths upon excitation for polyatomic molecules are, however, typically smaller than what is observed for H_2CO.

The intermolecular $H_2CO–H_2O$ potential function contains Lennard-Jones terms in addition to the Coulomb terms. We have not modified the Lennard-Jones constants in the H_2CO excited state, although we would expect them to be different from typical

atomic values used for ground state simulations. The increased diffuseness of the electron distribution will change, and presumably increase the polarizability in the excited state relative to the ground state. This implies changes in both the well-depth and minimum distance of, say, the $O(H2CO)-O(H2O)$ Lennard-Jones interaction. We intend to investigate these aspects in the near future.

The classical parameters for molecular mechanics and dynamics simulations produced here are in agreement with physical intuition about this excited state of formaldehyde, and the parameters produced using ab initio calculated frequencies, barriers, and geometries are similar to those produced using experimental data. The results obtained with the smaller 3-21G basis set are similar to those of the larger 6-31G+d basis set, in fact but perhaps fortuitously, they seem to more closely reproduce the formaldehyde force constants obtained by fitting to experimental data. If nonpolarized basis sets turn out to be generally adequate, molecules much larger than formaldehyde may be treated by our methods. Thus the general approach described here represents a promising way to calculate molecular parameters for electronically excited molecules where the previously published standard ground state parameters are inadequate.

Acknowledgement

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