Computational Studies on Topics of Environmental Interest: From Kinetics to Excited States

by

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To you, my dear sister,
because your path was always there
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To my parents,
for all their love, support,
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through these years.

To my dearest professors,
because in me there is a little
of every one of you.

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Abstract

There are a number of critical environmental issues associated with a changing atmosphere and a great deal of research and development activity is aimed at understanding and solving some of the problems that arise from industrial development. This thesis concentrates on computational studies on systems of environmental interest, covering aspects related to the calculation of kinetic parameters and excited states.

Aldehydes, known to play an important role in the pollution of the troposphere, are emitted as primary pollutants from partial oxidation of hydrocarbon fuels and arise as secondary pollutants from the oxidation of volatile organic compounds. Once in the atmosphere, aldehydes either photolyse or react further with OH radicals during the day, or with NO_3 radicals during the night. High-level *ab initio* calculations have been performed to examine the OH and NO_3 hydrogen-abstraction reactions from a series of aldehydes (XCHO, X = F, Cl, H, CH_3). In addition, classical transition state theory has been applied for the calculation of the rate constants. The importance of considering the reactant complex formation in the kinetics of some of these reactions is discussed, and new theoretical predictions for kinetic data are reported.

Polycyclic aromatic compounds (PACs) are of great interest to the petroleum industry since they interfere with refining operations, and federal environmental regulations have been created to reduce their emission to the atmosphere. The characterization of PACs in petroleum-related samples is extremely difficult. Theoretical semi-empirical methods have been used to study the effects of methyl and reduced-ring substitution on the excited states of naphthalene, the smallest polycyclic aromatic hydrocarbon. Regularities are found and an explanation is given for an “anomalous” behaviour.

List of Acronyms

AM1	Austin model 1
AO	Atomic orbital
au	Atomic units
BH&H	Becke half and half
BSSE	Basis set superposition error
B3LYP	Hybrid DFT functional B3 + LYP
B3P86	Hybrid DFT functional B3 + P86
B3PW91	Hybrid DFT functional B3 + PW91
BLYP	GGA functional B + LYP
BH&HLYP	Hybrid DFT functional BH&H + LYP
CASSCF	Complete active-space self-consistent field
CC	Coupled cluster
CCSD(T)	Coupled cluster including single, doubles and triplets (perturbative way)
CF	Configuration function
CI	Configuration interaction
CIS	Configuration interaction including singly excited determinants
CNDO	Complete neglect of differential overlap
CNDO/S	Spectroscopic CNDO
CP	Counterpoise
CPU	Central processor unit
DFP	Davidson-Fletcher-Powell
DFT	Density functional theory
EF	Eigenvector following
GDIIS	Geometric direct inversion of the iterative subspace
GGA	Generalized gradient approximation
GTO	Gaussian-type orbital
HA	Hydrogen affinity
HF	Hartree-Fock
HMO	Hückel molecular orbital theory
HOMO	Highest occupied MO

HPLC	High performance liquid chromatography
H, H1, H2	HOMO, HOMO-1, HOMO-2 orbitals
INDO	Intermediate neglect of differential overlap
INDO/S	Spectroscopic INDO
IRC	Intrinsic reaction coordinate
JT	Jahn-Teller
LSDA	Local spin density approximation
LDA	Local density approximation
LUMO	Lowest unoccupied MO
L, L1, L2	LUMO, LUMO+1, LUMO+2 orbitals
MEE	Maximum excitation energy
MNDO	Modified neglect of differential overlap
MO	Molecular orbital
MP	Møller-Plesset
MR-CI	Multi-reference CI
MRD-CI	Multi-reference double excitation CI
NDDO	Neglect of diatomic differential overlap
PACs	Polycyclic aromatic compounds
PAHs	Polycyclic aromatic hydrocarbons
PAN	Peroxyacetyl nitrate
PCA	Principal component analysis
PEH	Potential energy hypersurface
PMP2	Projected Spin-unrestricted Møller-Plesset (second order)
PPP	Pariser-Parr-Pople method
PT	Perturbation theory
Prod	Products
PUHF	Projected spin-unrestricted Hartree-Fock
RC	Reactant complex
React	Reactants
RH	Roothaan-Hall
ROHF	Spin-restricted open-shell calculation

RPA	Random phase approximation
RRKM/QET	Rice-Ramsperger-Kassel-Marcus/quasi-equilibrium theory
SAM1	Semi-*ab initio* method 1
SCF	Self-consistent-field
SCRF	Self-consistent reaction field
SINDO1	Symmetrically orthogonalized INDO
STO	Slater-type orbital
TCE	Thermal correction to the energy
TD-HF	Time-dependent HF
TD-DFT	Time-dependent DFT
TNDO	Typed neglect of differential overlap
TS	Transition state
TST	Transition state theory
UHF	Spin-unrestricted Hartree-Fock
UMP	Spin-unrestricted Møller-Plesset
UV-vis	Ultraviolet-visible
VTST	Variational TST
ZDO	Zero differential overlap
ZINDO	see INDO/S
ZINDO/S	see INDO/S
ZPE	Zero-point energy correction
(FC)	Using the frozen-core approximation

List of Symbols

$\hat{H}$	Hamiltonian operator
Ψ	Total wavefunction
ε	Energy of the stationary states
ε_0	Exact ground state energy
ϕ	Molecular orbital
α, β	Spin functions
χ	Spin-orbital
N	Number of electrons
$\hat{F}$	HF operator
ε_i	Orbital energies
$\hat{J}$	Coulomb operator
$\hat{K}$	Exchange operator
M	Number of basis functions
Φ_0	HF ground state wavefunction
$(\mu\nu\|\lambda\sigma)$	Two-electron integrals: (ij|kl), (aa|bb), (ab|ba)
Φ_S	Configuration functions
ρ	Electron probability density
E_{xc}	Exchange-correlation energy
δ_{ij}	Kronecker delta symbol, $\delta_{ij} = \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases}$
Q	Molecular partition function
g	Degeneracy factor
i	Index that numbers the states or energy levels
Q_{trans}	Translational partition function
Q_{rot}	Rotational partition function
$Q_{int\text{-}rot}$	Internal-rotational partition function
Q_{vib}	Vibrational partition function
Q_{elect}	Electronic partition function
k_B	Boltzmann's constant
T	Temperature

V	Molar volume of an ideal gas
p^0	Standard pressure
R	Ideal gas constant
h	Planck's constant
m	Mass of a molecule
I, I_X	Moments of inertia (X = A, B, C)
k	Force constant
x	Displacement
c	speed of light
$\bar{\nu}$	Wavenumber
V_0	Barrier to internal rotation
G	Gibbs free energy
N	Number of indistinguishable independent particles
n	number of moles
N_A	Avogadro's number
K_{eq}	Equilibrium constant
Q^X	Standard molar partition function of X (divided by N_A)
$\Delta_r E_0$	Molar reaction internal energy at T = 0 K
ΔE_0	Hypothetical energy of activation at 0 K
$\nu^{\neq}$	Imaginary frequency of the TS
$\bar{\nu}^{\neq}$	Imaginary wavenumber of the TS
k	Rate constant
κ	Tunneling factor
$k(E)$	Microcanonical rate constant
k_{uni}	Rate constant for a unimolecular reaction
V^*	Potential at the maximum of the Eckart barrier
$\Delta s_{½}$	Full width of the barrier at half its height
T^*	Characteristic tunneling temperature
E_a	Arrhenius activation energy
A	Arrhenius pre-exponential factor

E_a^{eff}	Effective activation energy (for a complex mechanism)
ΔH	Reaction enthalpy
k_{eff}	Effective rate constant (for a complex mechanism)
k_D	Direct rate constant (for an elementary or direct mechanism)
E^X	Total energy of X at 0 K
Q_{IR}^{TS}	Internal-rotational partition function of the TS
Q_{corr}^{TS}	Corrected total partition function of the TS
Å	Angström
DH_{298}	Bond enthalpy at 298 K
λ	Wavelength
J_{ab}	Molecular Coulomb integrals
K_{ab}	Molecular exchange integrals
Ψ_{CIS}	CIS wavefunction
c_i	CIS coefficients
f	Oscillator strength
μ_{fi}	Electric dipole transition moment
ε	Molar absorption or extinction coefficient
ΔE	Excitation or transition energy
f_σ, f_π	Overlap weighting factors
c_h	CIS coefficients calculated by HyperChem

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