High Accuracy Spectral Lines For Radiation Transport In Stellar Atmosphere

Amit Raj Sharma

Department of Chemistry and Emerson Center for Scientific Computation
Emory University

Collaborators and Co-workers
Robert Warmbier, Ralf Schneider, Bastiaan J. Braams, Joel M. Bowman and
Peter H. Hauschildt

10th HITRAN Conference, 2008

- Introduction and general interest in hydrocarbons.
- High accuracy spectroscopic calculations.
- Development of Potential Energy and Dipole Moment surfaces.
- Results: Ethyl Cation and Methane.
- Conclusion.

- PHOENIX: Synthetic spectra for young brown dwarfs and substellar objects.

Selected molecules considered in the EOS

NH	C_2	CN	CO	MgH	CaH	SiH	TiO	H_2O	H_2
N_2	NO	CO_2	O_2	ZrO	VO	MgS	SiO	AlH	HCl
HF	HS	TiH	AlO	BO	CrO	LaO	MgO	ScO	YO
SiF	NaCl	CaOH	HCN	C_2H_2	CH_4	CH_2	C_2H	HCO	NH_2
LiOH	C_2O	AlOF	NaOH	MgOH	AlO_2	Al_2O	AlOH	SiH_2	SiO_2
H_2S	OCS	KOH	TiO_2	TiOCl	VO_2	FeF_2	YO_2	ZrO_2	BaOH
LaO_2	C_2H_4	C_3	SiC_2	CH_3	C_3H	NH_3	C_2N_2	C_2N	CaF_2
AlOCl	Si_2C	CS_2	$CaCl_2$	AlF	CaF	Si_2	SiS	CS	AlCl
KCl	CaCl	TiS	TiCl	SiN	AlS	AL_2	FeO	SiC	TiF_2
FeH	LiCl	NS	NaH	SO	S_2	$AlBO_2$	AlClF	$AlCl_2$	AlF_2
$AlOF_2$	AlO_2H	Al_2O_2	$BeBO_2$	OBF	HBO	HBO_2	HBS	BH_2	BO_2H_2
BH_3	H_3BO_3	KBO_2	$LiBO_2$	$NaBO_2$	BO_2	$BaCl_2$	BaF_2	BaO_2H_2	BaClF
$BeCl_2$	BeF_2	BeOH	BeH_2	BeH_2O_2	Be_2O	Be_3O_3	ClCN	CHCl	CHF
CHP	CH_3Cl	KCN	NaCN	BeC_2	C_2HCl	C_2HF	$(NaCN)_2$	C_4	C_5
CaO_2H_2	MgClF	SiH_3Cl	$FeCl_2$	K_2Cl_2	$MgCl_2$	Na_2Cl_2	$TiOCl_2$	$SrCl_2$	$TiCl_2$
$ZrCl_2$	$TiCl_3$	$ZrCl_3$	$ZrCl_4$	CrO_2	SiH_3F	OTiF	SiH_2F_2	MgF_2	SrF_2
ZrF_2	TiF_3	ZrF_4	FeO_2H_2	SrOH	$(KOH)_2$	$(LiOH)_2$	MgO_2H_2	$(NaOH)_2$	SrO_2H_2
PH_2	PH_3	SiH_4	Si_2N	PO_2	SO_2	P_4	Si_3	NO_2	NO_3
C_3N	C_2H_3	C_4H	HC_3N	C_4H_2	CH_3CN	HC_5N	C_6H	C_4H_2	C_6H_2
HC_7N	C_4H_4S	C_4H_4O	C_4H_6	C_6H_4	HC_9N	C_5H_5N	C_6H_5O	C_6H_6	C_6H_6O
$HC_{11}N$	OH^-	CH^-	C_2^-	OH	CH	CN^-	SiH^-	H_2^-	HS^-
CS^-	FeO^-	BO^-	$AlCl_2^-$	AlF_2^-	$AlOF_2^-$	$AlOH^-$	CO_2^-	NO^+	H_2^+
TiO^+	ZrO^+	$AlOH^+$	$BaOH^+$	HCO^+	$CaOH^+$	$SrOH^+$	H_3O^+	H_3^+	

Introduction

- Hydrocarbons; Ethyl cation ($C_2H_5^+$) and $C_2H_3^+$(1) are of interest in the field of Plasma chemistry, combustion and other fields.
- Recent observations on Titan measured ion density.
- Bridged global minimum and Y-Shape first order saddle point (local min for $C_2H_3^+$).
- Energy difference 7.14 kcal/mol ($C_2H_5^+$) and 3.414 kcal/mol ($C_2H_3^+$).
- Located accurately on PES (not explicitly added).
- We aim at performing high accuracy spectroscopic calculations using ab-initio based PES.

(1) A. R. Sharma, *et.al.* J. Chem. Phys., 2006; 125 (22) 224306

MULTIMODE

Watson Hamiltonian for a polyatomic molecule in normal coordinates:

$$\hat{H} = -\frac{\hbar^2}{2}\sum_{i=1}^{N}\frac{\partial^2}{\partial Q_i^2} + \frac{\hbar^2}{2}\sum_{\alpha=1}^{3}\sum_{\beta=1}^{3}(J_\alpha - \pi_\alpha)\mu_{\alpha\beta}(J_\beta - \pi_\beta)$$
$$-\frac{\hbar^2}{8}\sum_{\alpha=1}^{3}\mu_{\alpha\alpha} + V(Q_1, ..., Q_N)$$

J_α and π_α components of the total and vibrational angular momentum operator

μ effective reciprocal inertia tensor

Q_i mass-weighted normal coordinate for mode i

N number of vibrational degrees of freedom

S. Carter, J. M. Bowman and N. Handy, Theor. Chem. Acc. (1998)100,191-198

Non-rotating (J=0)

Watson hamiltonian(in atomic units):

$$\hat{H} = \frac{1}{2}\sum_{\alpha\beta}\hat{\pi}_\alpha \mu_{\alpha\beta}\hat{\pi}_\beta - \frac{1}{8}\sum_\alpha \mu_{\alpha\alpha} - \frac{1}{2}\sum_i \frac{\partial^2}{\partial Q_i^2} + V(Q_i,...,Q_N)$$

the VSCF method approximates the vibrational wave function as a Hartree product of single-mode wavefunctions called *modals*.

$$\Psi^n(Q_1,...,Q_N) = \prod_i^N \phi_i^{n_i}(Q_i)$$

VSCF method is a variational procedure for obtaining the modals, and the optimized wave function of the form is obtained by minimizing the total energy with respect to all the modals subject to the constraint $<\phi_i|\phi_j> = \delta_{ij}$;enforced by the Lagrange multipliers.

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

- VSCF eigenstates used for further accurate VCI calculations.

Adiabatic Rotation

Rotational energy calculated as function of nuclear coordinates and added to nonrotating system.

$$
\begin{aligned}
H^J_{K_a,K_c} &= H^{J=0} + E^J_{K_a,K_c}(\mathbf{Q}) \\
&= H^{J=0} + [A\hat{J}_z^2 + B\hat{J}_y^2 + C\hat{J}_x^2]
\end{aligned}
$$

Adiabatic Rotation Approximation (ARA): excellent agreement with exact calculations for HO_2 (near prolate symmetric top); good agreement H_2O (strongly asymmetric top)

S. Carter and J. M. Bowman, J. Chem. Phys. 108, 4397 (1998); S. Carter, J. M. Bowman and N. Handy, Theor. Chem. Acc. (1998)100,191-198

- Ro-vibrational calculations do require accurate PES description!!

Potential Energy Surface

- Electronic structure energy calculated at the highest level of theory.
- Nuclear configuration space sampled using MD and DMC.
- PES represented as many-body expansion.
- Translational and rotational invariance: PES is function of internuclear distances.
- Permutational invariance: polynomial basis invariant under group permutation operator.
- Invariant polynomial is unique product of primary and secondary generators.
- Computed using computational invariant theory (Magma)

- Fitting coefficients are solution of least square system of equations.
- Example:$(C_2H_5^+)$ 21 Primary inv. 1436 Secondary inv.(up to degree 7 of polynomial)
- Dimension : with symmetry 8717; without symmetry 1,184,040.
- Many successful application in Bowman Group.

Dipole Moment Surface

- Dipole moments computed using Molpro.
- DM is a vector quantity; cannot be expressed simply in terms of internuclear distances.
- Representation:

$$\mathbf{d} = \sum_i f_i(x)\mathbf{r}(i)$$

$\mathbf{d}$: fitted dipole moment vector, i: nuclear indices, x: function of internuclear distance and $\mathbf{r}(i)$: vector position of the i-th nucleus.

- The functions f_i are polynomials
- Constrained so that $\mathbf{d}$ satisfies the required permutational invariance and translation
- Coefficients of the f_i determined by least squares fitting.

Properties of the PES

- Fit has a root mean square(rms) fitting error $\approx$ milli-Hartree over all configurations ($\approx$ 1.4 kcal/mol).
- For points 0.0 to 0.1 Hartree (0 to 62.7 kcal/mol) above the global minimum, rms error $<$ milli-Hartree.
- Normal mode frequencies: Excellent agreement.
- Used of anharmonic ro-vibrational calculations.
- PES routinely generated for various molecules.

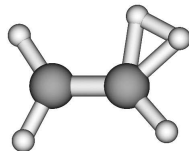# $C_2H_5^+$ Geometries

Global minimum and other stationary points on the PES .
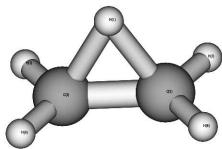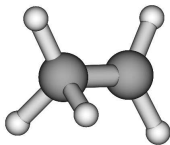
(a) 0.0   (b) 7.144   (c) 43.555
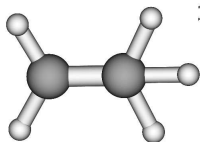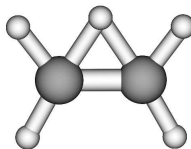
(d) 53.342   (e) 60.291

Energy relative to global minimum (kcal/mol).

$C_2H_5^+$ Global Min NMA

Harmonic frequencies (cm^{-1}) for the nonclassical bridged structure of $C_2H_5^+$

Mode Number	Symmetry	PES (1)	MP4(SDTQ) (2)	Quapp and Heidrich (3)	Trinquier (4)
1	B_2	753.4	733.72	763	425
2	B_1	817.5	827.60	865	902
3	A_2	1094.9	1081.36	1113	1136
4	B_1	1108.7	1104.49	1156	1223
5	A_1	1132.7	1138.32	1177	1233
6	A_2	1260.2	1251.80	1291	1336
7	B_2	1276.3	1283.77	1347	1384
8	A_1	1347.9	1351.07	1398	1428
9	B_2	1450.5	1476.49	1527	1568
10	A_1	1574.0	1569.44	1626	1696
11	A_1	2163.8	2175.33	2273	2316
12	B_2	3126.7	3136.51	3234	3283
13	A_1	3136.2	3139.82	3237	3290
14	A_2	3250.7	3243.94	3351	3397
15	B_1	3257.7	3261.09	3366	3413

1. Normal mode frequencies calculated from fitted PES.
2. Frequencies calculated at the MP4(SDTQ) level of theory with aug-cc-pVTZ basis.
3. Frequencies calculated using a 6-31G** basis set at the MP2 level of theory. (2002)
4. Frequencies calculated using a DZP basis set at the SCF level of theory. (1992)

$C_2H_3^+$ Global Min NMA

Harmonic frequencies (cm^{-1}) and zero point vibrational energy (kcal/mol) for nonclassical bridged structure.

Mode Number	Mode Description	Symmetry	PES(1)	RCCSD(T)(2)	Lee and Schaefer(3)	Lindh et al.(4)
1	HCCH asymm	a_2	534	572	587	617
2	HCCH asymm	b_2	594	580	513	696
3	HCCH symm opb	b_1	775	751	757	770
4	HCCH symm ipb	a_1	928	908	923	917
5	CHC ipb	b_2	1258	1255	1279	1315
6	CC stretch	a_1	1929	1932	2000	1939
7	CHC stretch	a_1	2358	2352	2471	2385
8	HCCH asymm stretch	b_2	3245	3265	3339	3304
9	HCCH symm stretch	a_1	3355	3370	3443	3403

(1)Normal mode frequencies calculated from fitted PES.
(2)Frequencies calculated at the RCCSD(T) level of theory with aug-cc-pVTZ basis.
(3)Frequencies calculated using a DZ+P basis set at the SCF/CISD level of theory.
(4)Frequencies calculated using a TZ2Pf basis set at the MP2 level of theory.

$C_2H_3^+$ Multimode Results

- Vibrational frequencies computed using Multimode (J=0).
  Diffusion Monte Carlo (DMC) ZPE is 7389.3 cm^{-1} ± 2.1 cm^{-1}.

State	5MR	5MR-4MR	5MR-3MR
(000000000) Zero-Point Energy	7367.0	-35.5	-4.8
(010000000) b_2	535.0	2.4	-11.1
(100000000) a_2	562.1	3.3	-11.3
(001000000) b_1	767.8	3.4	-10.3
(000100000) a_1	859.3	4.3	-20.3
(020000000) a_1	1067.1	2.3	-27.1
(000010000) b_2	1134.2	2.3	-4.9
(000200000) a_1	1874.7	4.7	-55.9
$\vdots$	$\vdots$	$\vdots$	$\vdots$
(010000100) b_2	2923.6	1.1	-9.0
(000011000) b_2	3042.4	1.4	9.0
(001000100) b_1	3104.6	3.4	-11.1
(000000010) b_2	3119.6 (3142.2)(1)	0.3	22.8
(000100100) a_1	3201.8	6.5	1.7
(000000001) a_1	3219.2	-4.2	6.7
(000010100) b_2	3442.9	4.2	-3.1
(010000010) a_1	3656.6	1.6	30.9

(1)Experimental data taken from Oka and co-workers

Methane: Multimode calculations

- Methane most widely studied molecule.
- Selected for first test calculations.
- Ro-vibrational states computed up to 6200 cm^{-1} (J=34).
- Calculations performed by Robert Warmbier.

$J, n_1 n_2 n_3 n_4$	exact	adiabatic	experiment(1)
1, 0000	10.40	9.92	10.48
1, 0001	1309.31, 1323.59	1318.45	1311.4, 1326.2
1, 0100	1531.96, 1532.09	1531.48	1544.0
1, 1000	2911.89	2911.27	-
1, 0010	3012.70, 3014.42	3012.87	3028.8, 3030.5
5, 0000	156.04	133.62	-
5, 0001	1433.79, 1484.90	1441.52	-
5, 0100	1678.69, 1679.91	1658.10	-
5, 1000	3057.82	3033.09	-
5, 0010	3155.29, 3161.13	3132.38	-
10, 0000	571.13	495.82	-
10, 0001	1820.51, 1912.41	1799.74	-
10, 0100	2096.97, 2100.87	2029.37	-
10, 1000	3473.43	3389.52	-
10, 0010	3565.92, 3576.88	3482.56	-

(1) References in: S. Carter and J.M. Bowman, J. Phys. Chem. A, 104 (11), 2355 -2361, 2000.
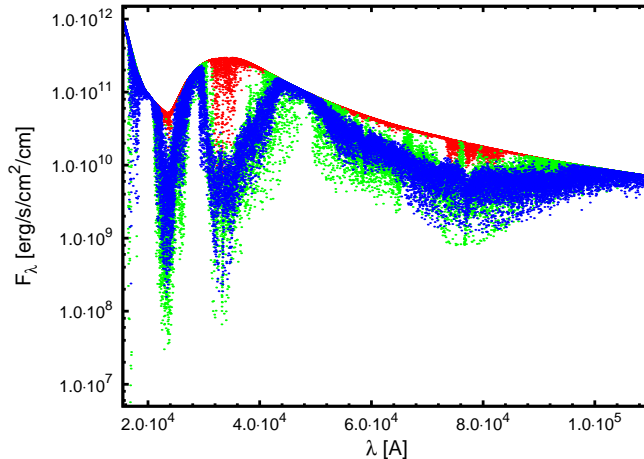
Spectroscopic data for CH4

Qualitative agreement with HITRAN database (green).
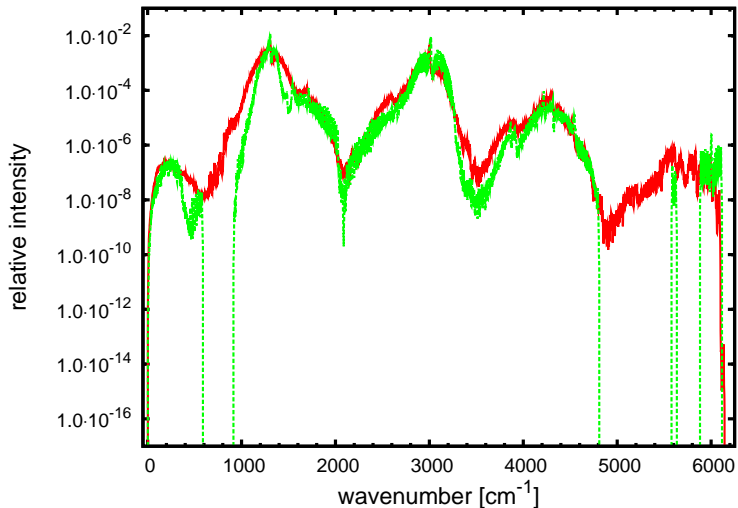
Radiation Transport

Radiation transport in model system using present dataset.
Comparison of radiative flux distribution with HITRAN(green) and
GEISA(red)

Conclusion

- Method of calculation of spectroscopic data from astrophysical applications.
- Einstein coefficients and line energies calculated for Methane.
- Good agreement with existing database HITRAN (spontaneous emission coeff.).
- Fill-in missing regions.
- More elaborate tests for radiation transport (work in progress).
- Spectroscopic data can be generated for other molecules!!
- Acknowledgement :US Department of Energy, Office of Science (#DE-FG02-07ER54914).

Thank You