

Spectroscopic characterization of diatomic molecules in the Martian Atmosphere

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Introduction:

Over the last decades, Mar's climate has changed significantly from a warmer, water-containing planet into a cold, dry global desert. The escape of atmospheric gases to space likely played a role in this change. Jeans escape of hydrogen, photochemical escape of oxygen, and acceleration of ions above their escape velocities by the interplanetary magnetic fields and solar wind plasma constitute pathways for the Martian atmospheric loss.

Processes involving diatomic molecules also play an important role for this depletion process. For example, it was proposed that the collisions of hot oxygen atoms with other energetic neutral atoms (ENAs) could drive the escape of light atmospheric gases, such as He [1], H₂ [2], and OH [3]. Our goal is to have a better understanding of the phenomena involving diatomic molecules, found in the upper atmosphere of Mars, through a spectral monitoring of their emissions and direct comparisons with synthetic spectra. In this work, we present results related to the electronic structure of CO and OH molecules, as a preliminary step to the construction of their line list, and corresponding synthetic spectra.

Computational Details:

We theoretically investigated the electronic structure of both CO and OH molecules using the high-level ab-initio calculations. We used the highly accurate Complete Active Space Self Consistent Field (CASSCF) method followed by the Multi-Reference Configuration Interaction MRCI calculations including Davidson correction (+Q) [4]. All calculations were performed using MOLPRO computing package [5].

For the OH molecule, the Oxygen atom was treated in an all-electron scheme using the correlation consistent polarized valence triple zeta (cc-pVTZ) including sp functions [6], the hydrogen atom was treated via the augmented correlation consistent polarized valence triple zeta (aug-cc-pVTZ) basis set including sp functions [7].

All the calculations of the active space are done in the C_{2v} subgroup symmetry, and contains 6σ (O: 1s, 2s, 2p±1; H: 1s, 2s, 2p₀) and 2π (O: 2p±1; H: 2p₀) and 0δ molecular orbitals. The active orbitals

then are distributed into 6a₁, 2b₁, 2b₂, 0a₂ denoted by [6,2,2,0] where 7 electrons are correlated.

For CO molecule, the basis sets used for both C and O atoms are cc-pV5Z for s, p, and d functions. The geometry optimization option was implemented in the self-consistent field calculations. The active space includes (O: 1s, 2s, 2p,3s; C: 1s, 2s, 2p,3s). Nine molecular orbitals are considered in the active space for which the irreducible representation includes 3a₁, 2a₂, 2b₁ and 2b₂ symmetry molecular orbitals denoted as [8,2,2,0]. All the electrons in the active space are correlated.

The spectroscopic constants were obtained by fitting the obtained potential energy curves to a polynomial function.

Results and discussion:

The potential energy curves of nine (Singlet and Triplet) electronic states of CO molecule, and eight (Doublet and Quartet) electronic states of OH molecule were calculated in the Λ-S representation. The Doublet states of OH molecule are shown in Figure 1, while selected singlet and triplet states of CO molecule are depicted in Figure 2. For CO molecule, all the states are converging to the same dissociation limit, which corresponds to the atomic ground states of carbon (3P) and oxygen (3P). Similarly, for OH molecule, the ground and first excited state correspond to the dissociation limit of O(³P)+H(²S), while higher excited states dissociate to O(¹D)+H(²S) and O(¹S)+H(²S).

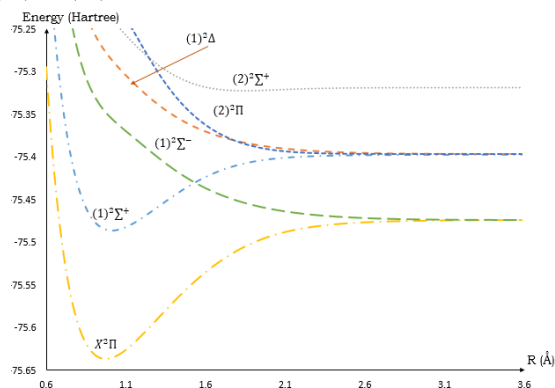


Figure 1: Calculated doublet electronic states of OH molecule

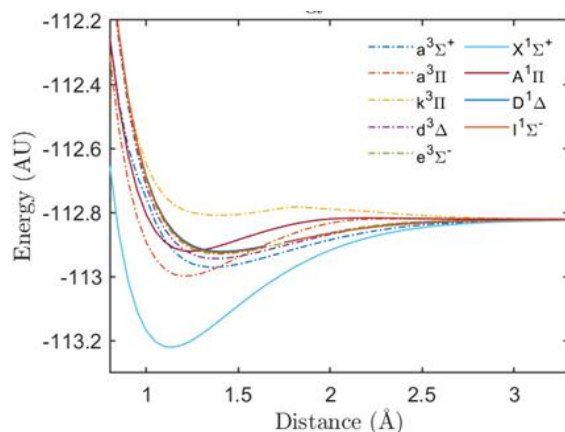


Figure 2: Calculated singlet and triplet states of CO molecule

Spectroscopic constants, such as the electronic energy relative with respect to the ground state energy T_e , the harmonic frequency ω_e , the internuclear distance R_e , the rotational constants B_e , and the dipole moment at equilibrium μ_e can be used to characterize the accuracy of potential energy curves.

We present some spectroscopic constant for the bound investigated molecular states of OH molecule, with a comparison of previously obtained results from the literature, in Table.1

State	Method	T_e (cm ⁻¹)	ΔT_e (%)	R_e (Å)	ΔR_e (%)	ω_e (cm ⁻¹)	$\Delta \omega_e$ (%)	B_e (cm ⁻²)	ΔB_e (%)
X ² Π	MRCI+Q	0		0.97 ^a		3731.83 ^a		18.82 ^a	
	MRCI+Q/V6Z			0.97 ^b	0	3734.02 ^b	0.06	18.87 ^b	0.28
	MRCI+Q/V6Z			0.97 ^c	0	3719.00 ^c	0.34	18.94 ^c	0.63
	MRCI			0.97 ^d	0	3737.70 ^d	0.16		
	Exp.			0.98 ^e	1.02	3713.00 ^e	0.51	18.87 ^e	0.37
(1) ² Σ ⁺	MRCI+Q	33046 ^f		1.01 ^f	4.12	3189.14 ^f	0.34	17.37 ^f	0.64
	MRCI+Q/V6Z			0.97 ^g	4.12	3178.25 ^g	0.34	17.26 ^g	0.64
	MRCI+Q/V6Z	32684 ^h	1.11	0.96 ^h	5.21	3230.00 ^h	1.26	17.40 ^h	0.17
	CI	32646 ⁱ	1.23	0.96 ⁱ	5.21	3198.50 ⁱ	0.29	17.50 ⁱ	0.74
(2) ² Σ ⁺	MRCI+Q	68868 ^j		1.84 ^j		980.91		5.51	
	MRCI+Q	70574 ^k	2.42	1.84 ^k	0				
(2) ² Σ ⁻	MRCI+Q	69774 ^l	1.30	1.86 ^l	1.08	2644.86		14.87	
	Exp.	80012		1.09					
(1) ² Π		81827		1.03		3197.27		16.91	
(3) ² Σ ⁻		86582		1.05		3419.26		15.98	
(1) ² Σ ⁻		110301		1.14		2116.00		13.77	
(1) ⁴ Δ		112322		1.13		2106.32		13.83	

a) Present work

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Table 1: Spectroscopic constant for the ground and excited electronic states of OH molecule

The obtained results show very good agreement with previously published work. More precisely, for OH molecule, the relative error of the internuclear distance at equilibrium (R_e) varies as: $0 < \Delta R_e/R_e <$

5.21 %. It is important to note here that our computed theoretical values agree closely to 100 % with the experimental ones for the ground X²Π and first excited state (1)²Σ⁺. Similarly, the values of B_e , T_e , ω_e and D_e vary as $0.17\% < \Delta B_e/B_e < 0.74\%$, $0.17\% < \Delta T_e/T_e < 0.74\%$, $1.11\% < \Delta \omega_e/\omega_e < 2.43\%$, $0.06\% < \Delta D_e/D_e < 1.26\%$.

We could not compare our values with previous work in the literature for the highest excited states (2)⁴Σ⁻, (1)⁴Π, (3)⁴Σ⁻, (1)⁴Σ⁺, and (1)⁴Δ, as up to our knowledge, they have been calculated here for the first time.

The spectroscopic constants of the ground and selected excited states of CO molecule are shown in Table 2.

States	$R_e/\text{Å}$	RE, R _e %	ω_e/cm^{-1}	RE, ω_e %	$\omega_e \chi_e/\text{cm}^{-1}$	RE, $\omega_e \chi_e$ %
[This work]	1.4037		1047.77		9.511	
[1]	1.4019	0.12	1058.71	-1.033	9.787	-2.82
[6]	1.3910		1094.75		10.705	
[7] [*]	1.3911	0.91	1092.22	-4.29	10.704	-11.15
		0.90		-4.07		-11.14
[8]	1.55		955		14.9	
[8] [*]	1.39	-9.43	(1092)	9.71	10.8	-36.16
		0.98		4.05		-11.93
[This work]	1.3606		1191.53		9.696	
[1]	1.3577	0.21	1214.10	-1.85	9.265	4.65
[2]	1.3450	1.15	1240	-3.90		
[7] [*]	1.3523	0.61	1228.6	-3.01	10.468	-7.37
[8]	1.48	-8.06	1147	3.88	10.6	-8.52
[8] [*]	1.35		1231		11.0	
[This work]	1.379		1140.17		8.953	
[1]	1.3740	0.36	1158.64	-1.59	9.092	-1.52
[6]	1.3694		1175.00		10.746	
		0.70		-2.96		-16.68
[7] [*]	1.3696		1171.94		10.635	
		0.68		-2.71		-15.81
[8]	1.5		1107		11.2	
[8] [*]	1.37	-8.06	1153	2.99	11.2	-20.06
		0.65		-1.11	7.2	24.34

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Table 2: Spectroscopic constant for the ground and excited electronic states of CO molecule

As is the case for OH molecule, the CO molecule results agree well with previously published work, especially those of experimental nature. For example, for the ground state, the relative error of R_e with experimental work is $\Delta R_e/R_e = 0.23\%$, while that for the A¹Π state is $\Delta R_e/R_e = 0.24\%$. In general, the relative errors vary as: $0.024\% < \Delta R_e/R_e < 9.43\%$, $0.21\% < \Delta \omega_e/\omega_e < 10\%$, $1.03\% < \Delta \omega_e \chi_e < 9.71\%$.

Conclusion

Ab-initio investigations of the lowest electronic states of CO and OH molecule were carried out via CASSCF/MRCI+Q method. The results show excellent agreement with the available theoretical and the experimental results for the majority of the calculated states. Our future work includes line lists calculations and the construction of synthetic emission spectra. We also plan to conduct a comparison with the recorded HOPE (EMUS) spectral data of atmospheric molecules, in an effort to maximize the scientific output of the Emirates Mars Mission.

Acknowledgement

N.El-Kork and M.Gacesa are partly supported by the internal grant (8474000336-KU-SPSC). Financial support for this work is provided by Khalifa University of Science and Technology under Award No. CIRA-2019-054, and the ASPIRE AARE award, under grant number 000329-00001. Support from the Scientific Computing Department at Khalifa University and computational resources at the Almesbar HPC cluster are gratefully acknowledged.

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