THEORETICAL STUDY OF THE $X^2\Sigma^+$, $A^2\Pi$ AND $B^2\Sigma^+$ ELECTRONIC STATES OF CO$^+$ ION USING MRCI METHOD

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Abstract: The ab initio potential energy curves have been calculated for the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ states CO$^+$ using the multi-reference configuration interaction method (MRCI) with large active space and basis sets. The potential energy curves calculated for internuclear separations ranges from about 0.8 to 3.7 Angstrom. With the obtained potential energy curves, all of the electronic, vibrational and rotational constants are predicted by numerically solving the radial Schrodinger equation of nuclear motion. The electronic, vibrational, and rotational spectroscopic constants that are obtained after are compared with theoretical and experimental results currently available.

Keywords: potential energy curve; MRCI; vibrational levels; spectroscopic constants

1. Introduction:

The CO$^+$ ion holds a very special place in the history of molecular spectroscopy. Its presence has been revealed in a number of different objects such as molecular clouds, stars, comet tails and planet atmospheres. The study of the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ electronic states was carried out in order to explain the number of problems left in the interpretation of the experimental VUV absorption spectra of CO$^+$ ion. These visible and ultraviolet band spectra of the CO$^+$ ion can be explain with electronic transitions. So, we have seen from literatures a large number of experimental and theoretical studies have carried out for several low lying electronic states of the CO$^+$ ion. Mentioning few of them, in 1989 C.M. Marian et al. [1] calculated the potential energy curves, transition dipole moment and as well as radiative lifetime. In 1993, H. Lavendy et al [2] also reported the transition dipole moment and spectroscopic constants of different electronic states of CO$^+$ ion. P.A. Martin et al in 1995 [3], had done calculation on the multipole moments viz. dipole, quadrupole and octopole moments for $X^2\Sigma^+$, $A^2\Pi$ states. The same kind of work has been reported by K. Okada and S. Itawa, in 2000 [4], Vazquez et al in 2009 [5], and D. Shi et al. in 2011 [6] and others [7-11]. In this paper, we present our theoretical work to respond to the available experimental result and extend our work on previous theoretical work by using the multi reference single and double excitation configuration-interaction (MRCI) method. The potential energy curves (PECs) and spectroscopic constants of the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ electronic states have been the main focus of our studied in this paper.

2. Computational details:

The ab initio calculation has been performed using the MRCI method, which is one of the most reliable methods for studying electronic excited states. This is because of the electron correlation is fully considered in the calculation. The calculations in this paper are perform using ORCA 4.0.0.2 program package [12]. The calculations are perform in the following three steps. (i) A restricted open-shell Hartree-Fock (ROHF) calculation on CO$^+$ produced 92 molecular orbitals in the ORCA program; (ii) these molecular orbitals were used as initial guess for the state-average complete active space self-consistent field (SA-CASSCF) calculations; (iii) the final step was a multi-reference configuration interaction with single and double excitations (MRCISD), for which the MOs of SA-CASSCF was used [19,22].

The basis set used in the present work is the augmented correlation-consistent polarized valence triple-zeta (aug-cc-pVTZ) type of woon and Dunning for C the atomic orbitals 19s6p3d2f are contracted to 5s4p3d2f pattern {88111/3111/111/11} and the 19s6p3d2f atomic orbitals of O are contracted to 5s4p3d2f pattern {88111/3111/111/11}. The final basis set consists of 132 primitive Gaussian functions and 92 contracted basis

functions. In addition, there are 1016 configurations and 2352 CSFs in the CASSCF calculation. In the MRCI step, the calculation was performed by using the CAS (9, 8) reference wave functions and estimating higher-order excitations through the Davidson correction. The excitation type is selected as CISD (single, double excitation configuration interaction), the threshold for 0th order approximation to the target state is set to be T_{sel} = 10^{-6} and second threshold to the 0th order state is set to be T_{pre}= 10^{-4} which is dimensionless and refers to the weight of a given initial reference space. Finally, the ground state and the excited states single point energy of CO^+ are scanned in over the internuclear distance range from 0.8 to 3.7 angstrom. Based on the potential energy curves, the radial Schrodinger equation of nuclear motion is numerically solved using LEVEL 8.0 computer program of Le Roy [13]. All the vibrational energy levels and spectroscopic constants are obtained for each electronic bound state. The spectroscopic constants are also calculated from the potential energy curves for each electronic states.

3. Results and discussion:

3.1. Potential energy curves:

Figure 1 shows the three doublet electronic states of the CO^+ ion. The potential energy curves of the ground state $X^2\Sigma^+$ and the excited states $A^2\Pi$ and $B^2\Sigma^+$ has the minimum energy points which tells us that these are stable bound states. We find that the three potential energy curves smoothly converge to $C^+(^2P) + O(^3P)$ dissociation limits which is according to the diatomic molecular theory [21], the electronic states of CO^+ is related to a specific dissociation limit. These potential energy curves covered 58 single point energies for each curve that are calculated using MRCI method, this method involve solving the resulting Schrodinger equation for the electronic motion. The bond length and minimum energy of the ground state $X^2\Sigma^+$ of CO^+ ion are 1.107 Å and -112.646 hartree respectively. The minimum energy is set to be the reference zero energy level in the potential curve as shown in figure 1 and the potential energy curves (PECs) is express in wavenumber units. The results that we calculate includes Davidson [21] correction obtained from the MRCI+Q method. The values of excitation energy (T_e), equilibrium bond length (R_e) and Dissociation energy (D_e) shown in table I, II, III are obtained directly from the potential energy curve.
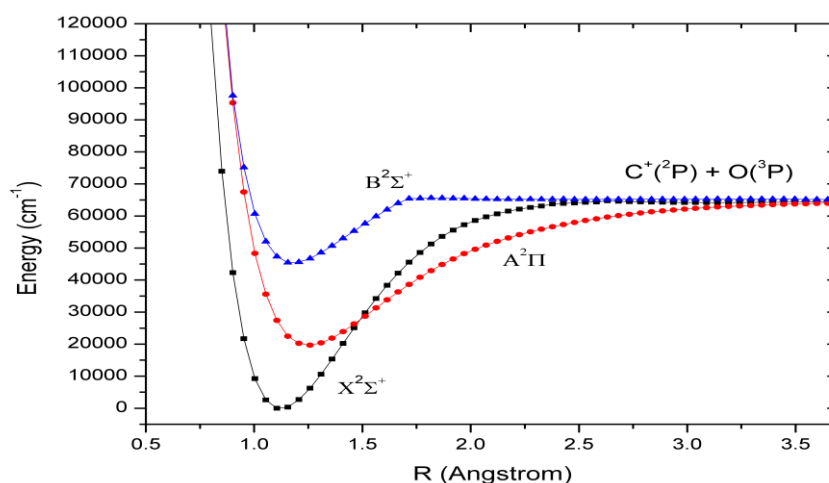

Figure 1: The potential energy curves of three low-lying states of CO^+ calculated with MRCI +Q.

3.2. Vibrational levels:

Using Level 8.0 program of Le Roy [13] the vibrational energy levels are determined by solving the Schrodinger equation of nuclear motion. In order to investigate all the vibrational levels accurately for each state, only the PECs can be used for studying the asymptotic energies. Based on this criterion, we use PECs to calculate the vibrational levels of $X^2\Sigma^+$, $A^2\Pi$, $B^2\Sigma^+$ states, respectively. We used 58 potential points with internucler distances ranging from 0.8 to 3.7 Angstrom for each state of CO^+ ion and take the radial integration mesh RH = 0.005 with integral area ranging from 0.50 to 20.0 Å. Finally, the predicted vibrational level and rotational constants of the three states are obtained. In total there are, 55 vibrational levels found for the ground
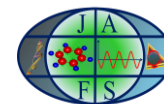
state $X^2\Sigma^+$, 66 for the $A^2\Pi$ state, 14 for the $B^2\Sigma^+$ state. The obtained vibration level and rotational constants are used for determine the spectroscopic parameters of the electronic state of the system.

TABLE I: Comparison of the spectroscopic constants of the (CO^+) $X^2\Sigma^+$ state of CO^+ ion

State	Method	Basis Set	R_e (A^0)	T_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	D_e (cm^{-1})	B_e (cm^{-1})	α(cm^{-1})	Ref
(CO^+) $X^2\Sigma^+$			1.1159	0	2215.1	15.27	67535[a]	1.977	0.0189	Expt[14]
			1.1151	0	2214.2	15.16		1.97694	0.018943	Expt[15]
	MRCI	AVQZ	1.119	0	2214.6	14.75	66731	1.981	0.0234	Theo[4]
	VCI	Minimal-STO	1.157	0	2069	13		1.837		Theo[11]
	MCSCF	GTO	1.106	0	2348	15		2.011	0.018	Theo[7]
	MRCI	aug-cc-pVTZ	1.107	0	2298.6	18.65	65525.6	1.957	0.0204	Present
					2256.8[c]	19.43[c]				
Deviation[14] (%)					(3.8)	(22.1)				
			0.8	0			3.0	1.0	7.9	
					1.9	27.2				

[a]Ref. 17, [b]Ref. 18, [c]values obtained by calculating using the parameters of Morse Potential by fitting to PECs, values in the bracket are deviation % of ω_e and $\omega_e x_e$ corresponding to the parameters having **c** superscript in it

TABLE II: Comparison of the spectroscopic constants of the (CO^+) $A^2\Pi$ state of CO^+ ion.

State	Method	Basis Set	R_e (A^0)	T_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	D_e (cm^{-1})	B_e(cm^{-1})	Ref
(CO^+) $A^2\Pi$			1.244	20733.3	1562	13.53	47128[b]	1.5894	Expt[14]
				20732.04	1561.8	13.48		1.589392	Expt[15]
	MRCI	AVQZ	1.246	20594	1570	12.86	46473		Theo[4]
	VCI	Minimal-STO	1.309	22825.76	1459	9			Theo[11]
	MCSCF	GTO	1.242	19760.58	1600	13		1.8	Theo[7]
	MRCI	aug-cc-pVTZ	1.261	19680.9	1574	14.08	44034.5	1.257	Present
					1521[c]	13.14[c]			
Deviation[14] (%)			1.4	5.1	0.8	4.1	6.6	20.9	
					(2.6)	(2.9)			

[a]Ref. 17, [b]Ref. 18, [c]values obtained by calculating using the parameters of Morse Potential by fitting to PECs, values in the bracket are deviation % of ω_e and $\omega_e x_e$ corresponding to the parameters having **c** superscript in it

TABLE III: Comparison of the spectroscopic constants of the (CO^+) $B^2\Sigma^+$ state of CO^+ ion.

State	Method	Basis Set	R_e (A^0)	T_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	D_e (cm^{-1})	B_e (cm^{-1})	Ref
(CO^+) $B^2\Sigma^+$			1.1694	45876.7	1734.1	27.92	37692[b]	1.7999	Expt[14]
			1.1689	45876.7	1734.6	28.27		1.79953	Expt[17]
	MRCI	AVQZ	1.17	45876.72	1742.7	25.99	37123		Theo[4]
	VCI	Minimal-STO	1.214	47828.6	1385	8		1.595	Theo[11]
	MCSCF	GTO	1.1684	46520	1778	23.5			Theo[7]
	MRCI	aug-cc-	1.168	47450.2	1689.5	20.87	18564.9	1.766	Present

	pVTZ					
Deviation[14] (%)	0.12	3.4	1548.2^c 2.6 (10.7)	32.27^c 25.3 (15.6)	50.7	1.9

^{a}Ref. 17, ^{b}Ref. 18, ^{c}values obtained by calculating using the parameters of Morse Potential by fitting to PECs, values in the bracket are deviation % of ω_e and $\omega_e x_e$ corresponding to the parameters having **c** superscript in it

3.3. Spectroscopic parameters:

The spectroscopic parameters can be obtain from the PECs as well as from a series of vibrational levels of ground and excited states of CO^+ ion obtained by solving the Schrodinger equation of nuclear motion. The Equilibrium bond length (**R_e**), excitation energy (**T_e**), and dissociation energy (**D_e**) are evaluated directly from the potential energy curves fitted to Morse function. Based on a series of vibrational levels of ground and excited states of CO^+ ion. The spectroscopic parameters **ω_e, $\omega_e x_e$** are obtained by uing least-square fit to $\Delta G_{v+1/2}$ = G(v+1) – G(v) where G_v is the vibrational energy relative to lowest vibrational level as shown in equation (1). The vibrational energy G_v can be express as follows

$$G_v = \omega_e \left(v + \frac{1}{2}\right) - \omega_e x_e \left(v + \frac{1}{2}\right)^2, \tag{1}$$

The rotational Constants B_e, α are obtained by least-squares fit to equation (2)

$$B_v = B_e - \alpha\left(v + \frac{1}{2}\right) + \gamma\left(v + \frac{1}{2}\right)^2, \tag{2}$$

The calculated results are given as shown in table I, II, III that we are comparing to the available experimental results and other theoretical values. The spectroscopic parameters, R_e and T_e, which are directly obtained from the PECs are in good agreement with the experimental values for all the three electronic states with the deviation ranges from 0.1% to 5.1% as seen in the above table. The other spectroscopic parameters such as ω_e, $\omega_e x_e$ Be, α and D_e are also quite in good agreement with the experimental values except for $\omega_e x_e$ in $X^2\Sigma^+$ and $B^2\Sigma^+$ state shows large deviation which is in the range of 15.6 to 27.2% and for the $A^2\Pi$ state the value of B_e deviate by value of 20.9%. The maximum deviation from the experimental values seen in value of D_e in $B^2\Sigma^+$ state of 50.7%, this is because in our case this state dissociate to lower dissociation limits. In summary in all the three states, our calculated spectroscopic parameters are comparable to the experimental values as well as the other theoretical values.

4. Conclusion:

In the present study, we are using MRCI method choosing an appropriate set of molecular orbitals with basis set augmented correlation-consistent polarized valence triple-zeta (aug-cc-pVTZ). The potential energy curves (PECs) that are obtained for three low-lying electronic states of CO^+ ion quite accurate and converge properly to correct dissociation limit. Based on the potentials obtained, all of the vibrational states and the spectroscopic constants are predicted when the rotational quantum number $J = 0$. It was found that the calculated potential energy curves, vibrational energy levels, and spectroscopic constants of the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ states of CO^+ are in good and comparable agreement with the experimental values as well as the other our theoretical values as shown in the above table.

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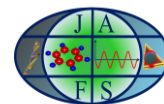
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