A COMPUTATIONAL STUDY OF STABILITY AND TRANSITION DIPOLE MOMENT OF SEVERAL LOW LYING ELECTRONIC STATES OF THE CO MOLECULE

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Abstract: The potential energy surface for the X $^1\sum+$, A^1 π, $D'^1\sum+$, $B^1\sum+$,$E^1\pi$,$C^1\sum+$ and $C'^1\sum+$ of CO molecule have been calculated using the multiconfiguration self- consistent field and configuration interaction methods. The calculations have been carried out at 84 internuclear distances from 1.4 to 7 a_0 by the aug-cc-pVQZ basis set, the spectroscopic constants also are found to be in good agreement with the experimental data. Some states also have double potential i.e. the second and third state which correlates to the B $^1\sum^+$ and C $^1\sum^+$ Rydberg states at small internuclear distance (Re). The inner well corresponds to B $^1\sum^+$ and C $^1\sum^+$ while the outer one corresponds to $D'^1\sum^+$ and $C'^1\sum^+$.

1. Introduction:

After Hydrogen (H_2), carbon monoxide (CO) is the second most abundant molecule in the universe, it gives details information about the astrophysical environments due to its absorption and emission of photons .The presence and distribution of dark matter in galaxies may be inferred from CO emissions. Carbon monoxide is observed in comets, in planetary atmospheres, in the interstellar medium, and in the photospheres of the sun and stars [1]. Fox [2] has suggested CO molecule is the most important molecule with the largest uncertainties in its photo-dissociation cross sections and mechanisms. A number of ab initio calculation has been performed on CO but surprisingly enough, a complete study treating together valence and Rydberg states is still lacking [3]. A detailed study of $A^1\Pi$ to account for the small barrier in the potential energy curve was carried out by Varandas [4]. The energy region of interaction is relatively clear for 1Π states, the $(X^2\sum+)$ $3d\pi$ G $^1\pi$ state is neglected and its interaction seem to be perturbed [5] for the $v = 0$ level of G, but for $v = 1$ level of G is subject to significant perturbation [6]. The far-UV spectrum of CO presents numerous $^1\Pi$ rovibronic levels in the region 92000-105000 cm-1 which have been observed by several experimentalists [7]. In this paper we present our research work based on the potential energy curve of the CO molecule.

2. Results and discussion:

The ab- initio calculations have been performed using the multi-reference single and double excitation (MRDCI) method [8-11]. The atomic orbitals set employed in this work consists of contracted Cartesian Gaussian functions. For carbon the aug-cc-pVQZ [12] basis set [6s,5p,4d,3f,2g] is contracted to [6s,5p,4d,3f] augmented with two diffuse s (α_s =0.0230000 and 0.0055000 a_0^{-2}),two diffuse p (α_p=0.021000 and 0.0049000 a_0^{-2}),and two diffuse d (α_d=0.0150000 and 0.0032000 a_0^{-2}). For oxygen the augmented-cc-pVQZ [12] basis set [6s,5p,4d,3f,2g] is contracted to [6s,5p,4d,3f] augmented with two diffuse s (α_s =0.0320000 and 0.0022000 a_0^{-2}), two diffuse p (α_p =0.0310000 and 0.0011000 a_0^{-2}),and two diffuse d (α_d =0.0150000 and 0.0032000 a_0^{-2}) are added into this contracted basis set.

A self consistent field (SCF) calculation has been carried out for the $^1A_1$ state at each inter-nuclear considered in the present work. The resulting self consistent field molecular orbitals (SCF-MOs) form the orthonormal one electron basis for the subsequent CI treatment. The adiabatic MRDCI energies have been calculated at 84 internuclear separations in the range $1.4 \leq R \leq 7$ a_0. The MRDCI method is employed with configurations selection and perturbative energy correction [8-11]. A set of reference configurations is chosen based on the preliminary scan of the wave function of the lowest root of a given symmetry at representative inter-nuclear

distances. The Configuration interaction (CI) treatment itself is carried out by employing the table CI method [9-11] for efficient treatment of various open shell cases which arise because of single and double substitutions relative to the reference configurations.

2.1. Potential energy curve:

Potential energy curve for the X $^1\sum^+$, B$^1\sum^+$, D´1$\sum$+, A$^1\Pi$, and E $^1\Pi$ states of CO were computed for 84 nuclear separation from 1.4 to 7.0 a_0 .The potential energy curve are shown in fig.1.The second and third $^1\sum^+$ have two minima at small R, the B and C states, and at large R the D´1$\sum$+ and the new C´1$\sum$+ state. The two $^1\Pi$ potential are also shown together with that of X $^1\sum^+$ state.

2.1.1. X $^1\sum^+$:

The dissociation energy calculated for the the X $^1\sum^+$ state is 10.947 eV and the experimental value [13] is 11.23 ± 0.03 eV, and the theoretical result of Cooper and Langhoff is 10.86 eV and Cooper and Kirby is 10.98 eV. The agreement is unexpectedly good because no pair of excitation outside the valence band were included in the wave function, which was not specifically constructed to obtain accurate dissociation energies.

2.1.2. A $^1\Pi$:

The computed dissociation energy for the A$^1\Pi$ state is 3.04577 eV compared with the experimental value [14] of 3.17 eV. The error of 0.1242 eV in D_e as opposed to 0.283 eV for the X$^1\sum^+$ state, indicates that the valence space pair excitations are more effective in accounting for correlation energy in the X$^1\sum^+$ state than in the A $^1\Pi$ state. The dissociation energy was computed as the energy difference between the interpolated minimum of the potential and its value at 7.0 a_0. An interesting feature of the A$^1\Pi$ state is the potential maximum which we obtain as 838 cm-1 at 4.20 a_0. From examination of our CI wave function, we conclude that the dominant configuration is changing in the neighborhood of 4.0 a_0 from (..) $3\sigma^2 4\sigma^2 5\sigma 1\pi^4$ 2π ,which has a coefficient of 0.94 at R = 2.132 a_0 , to (..) $3\sigma^2 4\sigma 5\sigma 1\pi^3 2\pi^2$, which allows for the proper dissociation of the A$^1\Pi$ state to C(^{3}P)+ O(^{3}P). From a minimum basis set complete CI calculation, O'Neil and Schaefer predicted a maximum of 1135 cm^{-1} at 3.8 a_0. Cooper and Langhoff obtained a value of 3815 cm^{-1}, but they recognize that their orbitals do not allow for proper dissociation of the wave function.
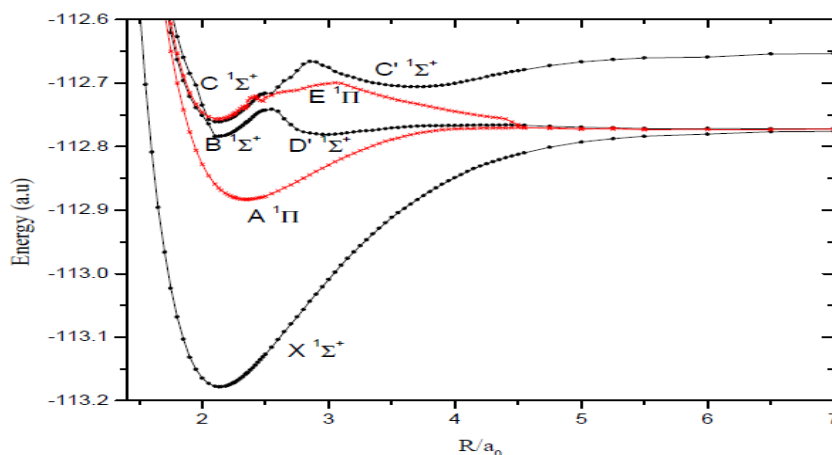

Figure 1: Potential energy curves for the lowest three adiabatic states of $^1\sum^+$ symmetry and the lowest two of $^1\Pi$ symmetry.

2.1.3. B $^1\sum^+$ and D$^{'}$ $^1\sum^+$:

As an adiabatic state, the second root of $^1\sum^+$ symmetry has two minima. At small R it is the well known B$^1\sum^+$ Rydberg state which has been extensively investigated, both in emission and in absorption, by Eidelsberg *et al.*[15] for all four isotopic species of CO based on ^{12}C, ^{13}C, ^{16}O, and ^{18}O. They also obtained data for ^{14}C-^{16}O.The primary electronic configuration for the B$^1\sum^+$ state is (..) $3\sigma^2 4\sigma^2 5\sigma 7\sigma 1\pi^4$, where 7σ is a 3s Rydberg orbital on carbon. At R≈ 2.2 a_0, there is a potential maximum in our calculated curve, which lies 0.65 eV above

the asymptotic energy limit. As R increases further, the energy drops and the calculated curve shows a second minimum at R≈ 3.0 a_0 which is characterized by the electron distribution $(..)5\sigma^2 1\pi^3 2\pi$. Thus, the second minimum in our calculations is not bound with respect to the separated atoms. The binding energy of this state $^1\sum^+$, sometimes denoted $^1\sum^+ (\pi-\pi^*)$, is 0.113 eV with respect to the outer maximum. This appears to be the D′1$\sum$+state observed by Wolk and Rich [16] who populated high-lying vibrational levels (v″=24-40) in the X $^1\sum^+$ state and then induced transitions to v′=0-3 of D′1$\sum$+.This state was also found in theoretical calculations of Coughran *et al.*[17] and appears as 4 $^1\sum^+$ the calculation of Cooper and Langhoff [18].

2.1.4. E$^1\Pi$:

The experimental dissociation energy for the ground state is 11.23 ± 0.03 eV, so that the observed minimum of E$^1\Pi$ state lies 0.3 eV above its separated atom limit. The minimum of the calculated 2$^1\Pi$ state lies 0.28 eV above the $C(^3P)$ + $O(^3P)$ limit, to which it dissociates adiabatically. The E$^1\Pi$ state is thus bound by a large potential maximum which a fit to our calculated points places at R =2.85 a_0. In the region of its minimum, the 2$^1\Pi$ state has Rydberg character with dominant configuration $(..) 5\sigma 1\pi^4 3\pi$ where 3π is a C 3p orbital. As R increases, the dominant configuration becomes $(..) 5\sigma 1\pi^3 2\pi^2$ for 2.65 ≤ R ≤ 3.0 a_0 and then $(..) 5\sigma^2 6\sigma 1\pi^3$ for 2.8 ≤ R ≤ 3.75 a_0.

2.2. Transition dipole moment (A$^1\Pi$-X$^1\sum^+$):

The best studied of the electronic transitions in CO is the fourth positive system A$^1\Pi$-X$^1\sum^+$ in the vacuum ultraviolet (VUV). Detailed information on the transition dipole moment function comes from measured fluorescence decay lifetimes under selective excitation by synchrotron radiation [19]. Perturbations by nearby a′ $^3\sum^+$, c $^3\sum^-$, d$^3\Delta$, I $\sum^-$ and D$^1\Delta$ states cause the measured, rotationally averaged decay rates to differ significantly from the unperturbed values. Under selective excitation of individual rovibronic levels, the lifetimes of perturbed levels are increased relative to those of unperturbed ones. Field *et al.*[19] have used deperturbed lifetimes for v′ =0-7 to fit an A$^1\Pi$-X$^1\sum^+$ transition dipole moment function for the A$^1\Pi$-X$^1\sum^+$ transitions. The dipole transition moment of Field *et al.*, [19] extended beyond the region of validity. The ab initio dipole transition moment remains positive throughout, but tends asymptotically to zero at large R (Fig. 2). This is the behavior one would expect for the dipole transition moment of two states, each the lowest of its symmetry, which dissociate to the same atomic limits and which do not undergo any rapid or profound changes of character with increasing R.
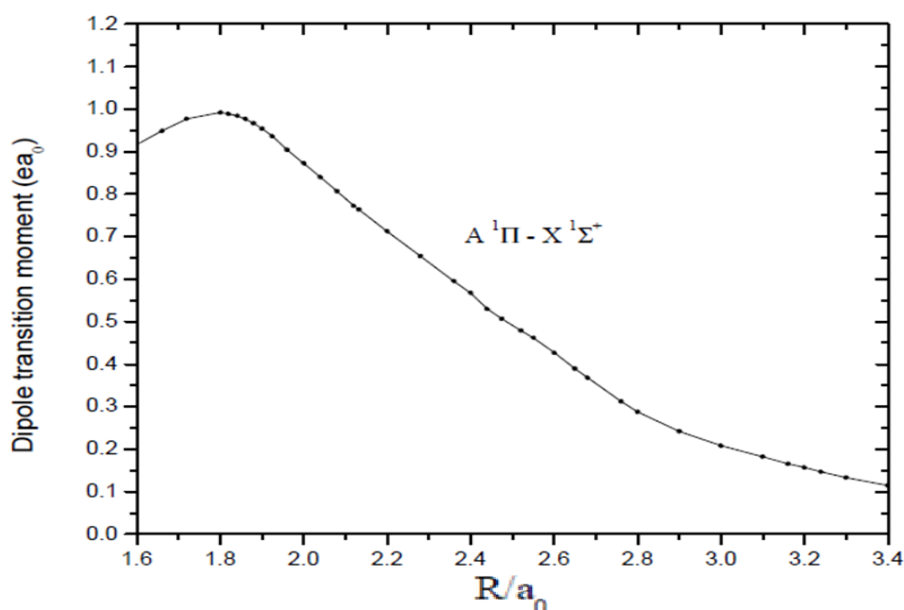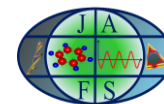

Figure 2: Dipole transition moment for the A$^1\Pi$-X$^1\sum^+$ system.

3. Conclusions:

Potential energy curve over a wide range of inter-nuclear separation has been calculated for five states of CO. We have shown that the $B^1\sum^+$ and $D'1\sum+$ state, which dissociates adiabatically to ground state atoms, has an unusual double-minimum, double-maximum potential. The inner well corresponds to the $B^1\sum^+$ Rydberg state and the shallow outer well to the $D'1\sum+$ state. The $C^{\ 1}\sum^+$ and $C'^{\ 1}\sum^+$ state was also found to possess a double-minimum potential. The inner well is the familiar $C^{\ 1}\sum^+$ Rydberg state but the outer well have been designated as $C'^{\ 1}\sum^+$. Our calculated potential energy surface provides explanation for the observed dissociation of CO molecule in the astrophysical plasma.

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