

Theoretical study of the molecular properties of doubly ionized carbon monoxide

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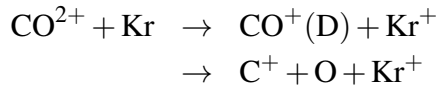
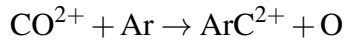
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Abstract

Doubly charged diatomic molecules are species which has been subject to experimental and theoretical investigation. Among the various species we concentrated here in to study the molecular properties of the CO^{2+} . In this analysis, we consider the following singlet and triplet electronic states $X^3\Pi$, $b^1\Pi$, $A^3\Sigma^+$, and $a^1\Sigma^+$. The spectroscopic constants calculated have been compared with the experimental measures and the state-of-the-art theoretical methods.

1 Introduction

The investigation of doubly charged carbon monoxide increasingly attracting the interest of experimentalists and theoreticians. A good description of the molecular properties these ions are very important to improve understand of reactions such as [1, 2, 3]



where M represents different rare gases, while ΔE is the energy for the electron-capture reaction.

Experimentally, techniques such as Auger spectroscopy [4, 5] and electron

impact [6] have been employed to look into the CO^{2+} dication. From the theoretical point view, Eland *et al.* performed electronic structure calculations using a state-averaged full valence complete active space self-consistent field (CASSCF) and internally contracted multireference configuration interaction (MRCI) approaches associate to cc-pV5Z (V5Z) basis set to compute the potential energy curves of CO^{2+} as well as for CO in its ground state [7]. Ref. [8] present a refined study relative to the vibronic (vibration-electronic) transition parameters as Franck-Condon factors for the bands $a^1\Sigma^+ \rightarrow X^3\Pi$, $b^1\Pi \rightarrow X^3\Pi$, $A^3\Sigma^+ \rightarrow X^3\Pi$, and $b^1\Pi \rightarrow a^1\Sigma^+$ systems of CO^{2+} dication.

However, in none of these works an analytical form to describe the interaction energy is shown. In this scenario, we

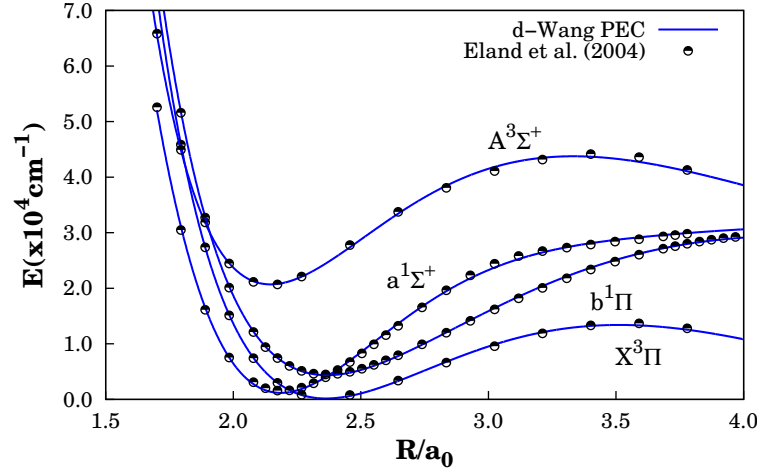


Figure 1: Potential energy curves for ground and three excited states of CO^{2+} dication. *Ab initio* points from [7] are also represented.

have utilized the modified version of the Wang's function to calculate the molecular properties of the CO^{2+} specie. In particular, the singlet and triplet electronic states $X^3\Pi$, $a^1\Sigma^+$, $b^1\Pi$, and $A^3\Sigma^+$ were considered.

So, we organized the article as follows: Section 2 describes the analytic representation to potential energy curves (PECs) used in this work. Our results are discussed in Section 3 and the concluding remarks are given in the last section.

2 Analytical PEC

The analytical PECs for ground and three electronically excited states were constructed based on the modified version of the Wang's representation reported by Machado *et al.*, so-called "d-Wang", defined as [9]:

$$V_d(R) = \left(\sum_{n=0}^{N-1} a_n R^n \right) e_d^{-a_n R} + \frac{C}{R} \quad (1)$$

where

$$e_d^{-aR} = (1 - daR)^{\frac{1}{d}} \quad (2)$$

in Eq. (1), the first term is the Varandas potential term and the last one is a repulsive ionic Coulombic term. C , d , and a_n are adjustable parameters and R stands for the internuclear distance.

To study the diatomic fragment CO^{2+} we extracted *ab initio* electronic energies from Ref. [7]. Once obtained these data, the parameters of the Eq. (1) have been fitted using the least-squares method. This is the procedure followed by Machado *et al.* to obtain the spectroscopic constants and the rovibrational spectra for homo- and heteronuclear molecules Be^{2+} , He^{2+} , BH^{2+} , and NH^{2+} .

3 Results

We start this discussion comparing in Fig. 1 the *ab initio* PECs from Ref. [7] with our interaction energies as a function of internuclear distances. As can be seen, the modeled potential accurately mimics the *ab initio* energies. It is interesting to analyze the values of d -parameter. Here we obtain the following values: -0.014

Table 1: Spectroscopic parameters for the ground and excited electronic states of CO^{2+} calculated using Eq. (1). Theoretical and experimental data are also included.

State designation	Method	R_e (a_0)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	D_e (cm^{-1})
$X^3\Pi$	d-Wang	2.3633	1443.5	38.51	13525.8
	Theo. [10]	2.3621	1396.3	36.49	13308.1
	Exp. [7]	2.3581	1435.2	24.60	-
	Exp. [5]	2.3640	1451.8	28.22	-
$a^1\Sigma^+$	d-Wang	2.1862	2038.2	34.68	29944.4
	Theo. [10]	2.1920	1946.6	30.14	32262.1
	Exp. [7]	2.1906	1920.5	16.70	-
	Exp. [5]	2.2034	1904.2	20.16	-
$b^1\Pi$	d-Wang	2.3673	1495.5	21.93	25020
	Exp. [7]	2.3621	1487.7	17.20	-
	Exp. [5]	2.3772	1455.0	15.32	-
	Exp. [5]	2.3432	1521.0	17.74	-
$A^3\Sigma^+$	d-Wang	2.1535	2026.9	43.32	23044
	Exp. [7]	2.1444	2043.8	16.30	-
	Exp. [5]	2.1467	2108.3	39.52	-
	Exp. [5]	2.1486	2070.0	37.00	-

to $X^3\Pi$, -0.009 to $a^1\Sigma^+$, -0.094 to $b^1\Pi$, and -0.058 to $A^3\Sigma^+$. Looking into results, it is possible to note that larger values of d lead us to smaller depth of the potential well. Based on the APECs obtained we calculate the spectroscopic parameters for CO^{2+} dication.

Table 1 summarize the spectroscopic parameters determined from Eqs. (1) and (2). Column one of this table indicates the electronic state of CO^{2+} dication, whereas the different methods are given in column two. The bond distances (R_e) are present in the third column and the harmonic vibrational frequencies calculated (ω_e) are listed in fourth column. The fifth and sixth columns of Table 1 show the first anharmonicity constant ($\omega_e x_e$) and the well depth (D_e), respectively. We highlight that spectroscopic constants taken from Ref. [10] correspond to coupled-cluster singles and doubles augmented by a perturbative treatment of triple excitations (CCSD(T)) using correlated consistent cc-pVTZ (VTZ) basis set.

The calculated equilibrium bond length for the ground electronic state is $2.3633 a_0$ which is only $0.0052 a_0$ smaller than experimental data [7]. For the other excited states we found deviations of $-0.0044 a_0$ for $a^1\Sigma^+$, $0.0052 a_0$ for $b^1\Pi$, and $0.0091 a_0$ for $A^3\Sigma^+$. In relation to theoretical data, there is a good overall agreement between the CCSD(T)/VTZ bond lengths for states $X^3\Pi$ and $a^1\Sigma^+$ and our calculated values.

In the case of the ground-state $X^3\Pi$ the vibrational frequency, ω_e , our result is better than that those reported with CCSD(T)/VTZ level of theory when compared with experimental ones. On the contrary, we can also observe for $\omega_e x_e$ relative differences of 2.02 cm^{-1} from Ref. [10], 13.91 cm^{-1} from [7], and 10.29 cm^{-1} from [5]. The difficulty in provid-

ing a proper description of D_e is evident at the various levels of theoretical and experimental investigations. A more detailed analysis is being prepared aiming this issue.

The calculated molecular spectroscopic parameters for $a^1\Sigma^+$ states agree reasonably well with experimental ones except the values for the vibrational anharmonicity. The agreements of our results for singlet state $b^1\Pi$ with those from Ref. [7] is noticeable. Yet, relatives deviations of $\Delta R_e = 0.0052 a_0$, $\Delta\omega_e = 7.8 \text{ cm}^{-1}$, and $\Delta\omega_e x_e = 4.73 \text{ cm}^{-1}$ it can be visualized.

To finish this section, Taking the fundamental frequency for triplet state $A^3\Sigma^+$, our calculation was 16.9 , 81.4 and 43.1 cm^{-1} smaller than Refs. [7] and [5], respectively. In our present work, the vibrational anharmonicity determined overestimate the experimental measures from [5] in 3.8 and 6.32 cm^{-1} . We also notice that the deviation associated to Ref. [7] is 27.02 cm^{-1} , i.e., it represents an unsatisfactory value of deviation.

4 Conclusion

This paper reports the results from a theoretical study in which the potential energy curves for four states of CO^{2+} dication were constructed using the modified analytical representation of Wang. The spectroscopic parameters obtained from these APECs agree well with available literature. For this reason, we believe that this work should be a good reference for the future research involving carbon monoxide doubly-charged ions.

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