

THEORETICAL ASSIGNMENTS OF THE LOW-LYING ELECTRONIC STATES OF CARBON DIOXIDE*

Nicholas Wilhelm WINTER**

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109, USA

Charles F. BENDER*** ‡

Lawrence Livermore Laboratory, University of California, Livermore, California 94550, USA

and

William A. GODDARD III ‡ ‡

Arthur Amos Noyes Laboratory of Chemical Physics ‡ ‡ ‡, California Institute of Technology, Pasadena, California 91109, USA

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Extensive configuration interaction calculations (1000 to 1500 determinants) have been carried out for the six low-lying valence states of carbon dioxide in order to provide reliable assignments for the transitions to these states. In addition, Hartree-Fock calculations were performed on the lowest five (singlet and triplet) Rydberg states and the $^2\Pi_g$ state of the positive ion. These results yield an accurate description of the excited states of carbon dioxide and provide for definitive assignments of the transitions observed by optical and electron impact studies (for the five states known experimentally, the calculations agree to within 0.2 eV of the experimental transition energies).

1. Introduction

Carbon dioxide does not show strong absorption below 11 eV; however, several investigators have observed two weak absorption features in both optical [1-4] and electron impact spectroscopy [5-8]. The first transition begins slightly above 6 eV and the peak absorption occurs at 8.4 eV. The intensities and spac-

ings of the bands are irregular and no definite assignment has been made from the experimental spectra (it has generally been assigned as $^1\Pi_g$ or $^1\Delta_u$ on the basis of simple molecular orbital arguments). The second transition is composed of sharper and more regular bands with its peak intensity near 9.3 eV. There is no unambiguous assignment for this transition either although it has generally been assigned as $^1\Pi_g$. The next observed state of CO_2 is the optically allowed transition at 11.1 eV, and it has been assigned as either the $^1\Sigma_u^+$ or the $^1\Pi_u$ state. Above 11 eV there are several Rydberg series of CO_2 converging to the various states of CO_2^+ . The electron impact spectra of CO_2 [5-7] are in general agreement with the optical spectra except for the work of Hubin-Franskin and Collin [8]. Using the SF_6 scavenger technique they were able to observe structure in the 4 to 8 eV region that they attributed to low-lying triplet states of CO_2 .

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Further information on the excited states of CO_2 has been provided by Dixon [9] who studied the CO_2 chemiluminescence responsible for the carbon monoxide flame bands. He was able to establish the emitting state to be a ${}^1\text{B}_2$ state of bent (122°) CO_2 . Following the earlier predictions of Walsh [10] and Mulliken [11], he correlated the bent state with the ${}^1\Delta_u$ state of the linear molecule.

There has not been a good theoretical description of the excited states of CO_2 . Mulligan [12] carried out a minimum basis set, self-consistent field calculation on the ground state of CO_2 . He approximated the multi-center integrals and did not optimize the excited orbitals. As a result, this work provided little useful information on the excited states. McLean [13] and Peyerimhoff [14] obtained accurate Hartree-Fock (HF) wavefunctions for the ground state of CO_2 but did not consider excited states. More recently Krauss et al. [15] carried out HF calculations on the ${}^1\Delta_u$ and ${}^1\Sigma_u^+$ states but did not fully optimize the orbitals for each state. Julianne et al. [16] carried out HF calculations on the lowest three excited singlet states. However, they used small basis sets that led to errors of 1 to 2 eV.

2. Method of calculation

The calculations reported here are with the (9s5p) gaussian basis set of Huzinaga [17] contracted to a [4s2p] basis by Dunning [18]. For the Rydberg states this set was augmented with a single diffuse gaussian of s, x, y, and z symmetry on each of the three centers*.

Using the experimental geometry for the ground state** ($R_{\text{CO}} = 2.196 a_0 = 1.162 \text{ \AA}$), a separate open-shell HF calculation was carried out for each of the states in table 1. We have explicitly written the wavefunction for each state to emphasize the need for two configurations even at the HF level. In each case the coupling terms were chosen so that the wavefunction possesses the proper symmetry. These somewhat com-

* The exponents for the diffuse gaussians were $\zeta(3s) = 0.015$ and $\zeta(3p) = 0.025$ for the carbon atom and $\zeta(3s) = 0.028$ and $\zeta(3p) = 0.045$ for the oxygen atom.

** The optimum HF bond length for the ground state in this basis set is $2.204 a_0$, in good agreement with the experimental value.

Table 1
Forms of the wavefunctions for the SCF calculations

State	Form of the wavefunctions a)
${}^1\Sigma_g^+$	$\pi_{ux}^2 \pi_{uy}^2 \pi_{gx}^2 \pi_{gy}^2$
${}^3\Sigma_u^+$	$\pi_{ux}^2 \pi_{uy}^2 (\pi_{gx}^2 \pi_{gy}^2 2\pi_{uy} + \pi_{gy}^2 \pi_{gx}^2 2\pi_{ux})$
${}^{1,3}\Delta_u$	$\pi_{ux}^2 \pi_{uy}^2 (\pi_{gx}^2 \pi_{gy}^2 2\pi_{uy} - \pi_{gy}^2 \pi_{gx}^2 2\pi_{ux})$
${}^{1,3}\Delta_u$	$\pi_{ux}^2 \pi_{uy}^2 (\pi_{gx}^2 \pi_{gy}^2 2\pi_{ux} + \pi_{gy}^2 \pi_{gx}^2 2\pi_{uy})$
${}^{1,3}\Sigma_u^-$	$\pi_{ux}^2 \pi_{uy}^2 (\pi_{gx}^2 \pi_{gy}^2 2\pi_{ux} - \pi_{gy}^2 \pi_{gx}^2 2\pi_{uy})$
${}^{1,3}\Pi_g$	$\pi_{ux}^2 \pi_{uy}^2 (\pi_{gx}^2 \pi_{gy}^2 + \pi_{gy}^2 \pi_{gx}^2) 3s\sigma_g$
${}^{1,3}\Pi_u$	$\pi_{ux}^2 \pi_{uy}^2 (\pi_{gx}^2 \pi_{gy}^2 + \pi_{gy}^2 \pi_{gx}^2) 3p\sigma_u$
${}^1\Sigma_u^+$	$\pi_{ux}^2 \pi_{uy}^2 (\pi_{gx}^2 \pi_{gy}^2 3p\pi_{uy} + \pi_{gy}^2 \pi_{gx}^2 3p\pi_{ux})$

a) In each case the configuration

$$(1\sigma_g)^2 (2\sigma_g)^2 (3\sigma_g)^2 (4\sigma_g)^2 (1\sigma_u)^2 (2\sigma_u)^2 (3\sigma_u)^2$$

is understood to be present. The wavefunction is multiplied by an appropriate spin function and antisymmetrized. All orbitals are solved for self-consistently for each state. The notation $3s\sigma_g$, $3p\sigma_u$, and $3p\pi_u$ is meant only to show the basic form of the self-consistent orbitals found for these states.

plicated open-shell calculations were carried out with the Hunt-Hay-Goddard [19] open-shell program that uses the general open-shell formalism developed by Hunt et al. [20]. The last five states of table 1 are Rydberg states and required the presence of diffuse basis functions.

For the valence states (the first eight states of table 1) a pi-electron, configuration interaction (CI) calculation was carried out using the optimum HF σ -orbitals for each state. The CI wavefunctions were constructed by including all single and double excitations from the dominant HF configurations given in table 1. The resulting CI wavefunctions involved 1000 to 1500 determinants for each state. The calculated excitation energies for the various states are given in table 2. The valence state excitation energies come directly from the CI calculations and are relative to the X ${}^1\Sigma_g^+$ CI energy of -187.6868 au .

For the Rydberg states of CO_2 , HF calculations were carried out using the extended basis. The excitation energies given in table 2 for these states are calculated relative to the HF ground state energy (in the extended basis set) of -187.5561 au . The result for the ${}^2\Pi_g$ state of CO_2^+ is included since the difference

Table 2
Comparison of calculated vertical excitation energies with experimentally observed transitions

Present work		Experiment a)					
state	energy	Tanaka [1]	Inn [2]	Hubin-Franskin [8]	Meyer [6]	Rabalais [4]	Price [3]
$^3\Sigma_u^+$	7.35			7.5 ($^1\Sigma_u^-$)			
$^3\Delta_u$	7.83			8.0			
$^3\Sigma_u^-$	8.24						
$^1\Sigma_u^-$	8.27						
$^1\Delta_u$	8.38		8.41 ($^1\Pi_g$)	8.55 ($^1\Delta_u$)	8.52 ($^1\Pi_g$)	8.41 ($^1\Delta_u$)	8.49
$^3\Pi_g$	8.95						
$^1\Pi_g$	9.23		9.31	9.3 ($^1\Pi_g$)	9.30 ($^1\Pi_g$)	9.31 ($^1\Pi_g$)	9.29
$^1\Sigma_u^+$	11.07	11.05	11.08 ($^1\Pi_u$)	11.2 ($^1\Sigma_u^+$)	11.07 ($^1\Pi_u$)	11.08 ($^1\Sigma_u^+$)	11.07
$^3\Pi_u$	11.49						
$^1\Pi_u$	11.53	11.38		11.6	11.40 ($^1\Sigma_u^+$)		
CO_2^+							
$^2\Pi_g$	13.61	13.78					

a) The assignments given by the experimentalists are indicated in parentheses.

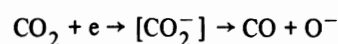
between the theoretical and experimental ionization potentials provides an estimate of the correlation energy error in the Rydberg states. We expect this difference (0.17 eV) to be larger than the actual correlation error in the $^1,^3\Pi_g$, $^1,^3\Pi_u$, and $^1\Sigma_u^+$ Rydberg states.

3. Comparison with experiment

The CI excitation energies for the valence states and the HF excitation energies for the Rydberg states are compared with various experimental observations in table 2. The assignments given by the different authors are included in parentheses in each column. There is little experimental information to provide a basis for these assignments.

Hubin-Franskin and Collin [8] are the only investigators to have observed the lower triplet states of CO_2 . If their energies are recalibrated on the basis of the $^1\Delta_u$ state at 8.4 eV, the agreement with the calculated energies of the $^3\Sigma_u^+$ state (7.35 eV) and the $^3\Delta_u$ state (7.83 eV) is excellent. However, the 8.0 eV feature probably contains unresolved contributions from the $^1,^3\Sigma_u^-$ states as well. As we have noted they observed several excitations at energies lower than 7.5 eV. Based on our results, these peaks *cannot* be

attributed to vertical excitations of linear CO_2 . The broad peak at 3.9 eV has been observed by Spence et al. [21] * at 3.8 eV using the trapped-electron method, and attributed to vibrational excitation of CO_2 through the formation of a compound state of CO_2^- . Schulz [23] has also observed that the dissociative attachment



proceeds through this state with onset at room temperature for 3.85 eV electrons. Configuration interaction calculations on the $^2\Pi_u$ state of CO_2^- with the [4s2p] basis indicate it lies 4.5 eV above the ground state of CO_2 in the Franck-Condon region. This is in agreement with the 4.4 eV peak in the cross section for the dissociative attachment. The remaining features reported by Hubin-Franskin and Collin between 4 eV and 7 eV cannot be resolved in the raw data and appear only in the deconvoluted spectra.

We have carried out less extensive CI calculations for the lower singlet and triplet states of CO_2 with $\angle\text{OCO} = 120^\circ$ and $R_{\text{CO}} = 2.596 a_0 = 1.374 \text{ \AA}$. In these calculations we used a minimum basis set of contracted gaussians and included single and double

* Metastable CO_2^- has been observed by Cooper and Compton [22].

excitations from each state. Combining these excitation energies with the energy required to bend the ground state found from generalized valence bond [24] calculations with the [4s2p] basis, we obtain the following adiabatic excitation energies:

$${}^3\Sigma_u^+({}^3B_2) 3.7 \text{ eV}, \quad {}^3\Delta_u({}^3A_2) 4.1,$$

$${}^1\Sigma_u^-({}^1A_2) 4.5, \quad {}^1\Delta_u({}^1B_2) 5.8.$$

Dixon has determined the adiabatic transition energy of the 1B_2 state to be 5.7 eV, which was later corrected by Benedict [25] to 5.6 eV. This is in good agreement with our calculated energy of 5.8 eV. Thus we conclude that the CO flame bands are associated with the same state (${}^1\Delta_u$) as is responsible for the 8.4 eV absorption in CO_2 . This disagrees with the suggestion by Rabalais et al. [4] that the Dixon state at 5.6 eV is due to the ${}^3\Sigma_u^+$ state and with the interpretation of Lassetre et al. [5-7] that the 8.4 eV feature arises from the ${}^1\Pi_g$ state.

4. Concluding remarks

The results presented in table 2 provide definitive assignments for the low-lying states of CO_2 . In addition, the theoretical adiabatic excitation energies are consistent with the CO_2 chemiluminescence observed by Dixon being due to the ${}^1\Delta_u$ state. It is also important to note that we have shown for the first time that there are *four* states (1A_1 , 3B_2 , 3A_2 , 1A_2) of CO_2 that are bound relative to $\text{CO}({}^1\Sigma^+) + \text{O}({}^3P)$. Previous analyses have followed Clyne and Thrush [26] in assuming one singlet and one triplet state (1A_1 , 3B_2) of CO_2 to be bound with respect to $\text{CO} + \text{O}$. In both cases the 1B_2 state is nearly bound. These states should play an important role in the recombination of CO and O and could conceivably provide alternative explanations of the problem of the apparent photostability of the Martian upper atmosphere. Calculations are in progress on the potential energy surfaces for these states.

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