



IWNest PUBLISHER

Journal of Industrial Engineering Research

(ISSN: 2077-4559)

Journal home page: <http://www.iwnest.com/AACE/>

Combinational and perturbing effects of l-type doubling on Carbon dioxide

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ARTICLE INFO

Article history:

Received 2 February 2015

Received in revised form 28 February 2015

Accepted 10 March 2015

ABSTRACT

The study of Combinational and perturbing effects of l-type doubling by using Gaussian 09 program of CO₂, as a linear molecule using semi empirical quantum programs. (pm6), HF and DFT methods this by using different bases sets so this methods gives approximant results with experimental result to produce effect of Renner – Teller.

Keywords:

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To Cite This Article: Zeyad Adnan Saleh and Dukra Kamal Taha., Combinational and perturbing effects of l-type doubling on Carbon dioxide. *J. Ind. Eng. Res.*, 1(1), 1-3, 2015

INTRODUCTION

Carbon dioxide, CO₂, is a linear molecule with a total of sixteen bonding electrons in its valence shell. Carbon is the central atom of the molecule and a principal axis, the z-axis, is visualized as a single axis that goes through the center of carbon and the two oxygens atoms. For convention, blue atomic orbital lobes are positive phases, red atomic orbitals are negative phases, with respect to the wave function from the solution of the Schrödinger equation.[1] In carbon dioxide the carbon 2s (−19.4 eV), carbon 2p (−10.7 eV), and oxygen 2p (−15.9 eV) energies associated with the atomic orbitals are in proximity whereas the oxygen 2s energy (−32.4 eV) is different.[2].

Where l-type doubling for linear molecules we do in general have degeneracy in l. Since there is no physical difference between when a linear molecule rotates right or left both +l and −l would have the same energy. There are, however, times when this is not true, in those cases we have l-type doubling. There are two reasons for l-type doubling. First, when the bending vibration is excited the molecule bends and becomes more and more an asymmetric top. For asymmetric tops we have no degeneracy for the same absolute values of l, since rotating left or right has a physical meaning for an asymmetric top. Second, we have the Coriolis force. When a rotating object is moving away from the center it seems to slow down. If it on the other hand encloses the center it seems to accelerate. In a molecule we have this case when we have anti-symmetric stretching, in this case the center nucleus moves closer to one of the outer nuclei but away from the other. In perspective of the other nuclei it will therefore accelerate respectively retardate, causing the molecule to bend. The l-type doubling is given by:

$$\Delta v = qJ(J+1) \quad (1)$$

where Δv is the split in cm^{-1} , q the l-type doubling coefficient, J the rotational quantum number. The size of the l-doubling constant is for a linear molecule

$$q_v = -\frac{B_v^2}{\omega_2} \left(1 + \frac{4\omega_2^2}{\omega_s^2 - \omega_2^2} \right) (v_2+1)$$

Theoretical Part:

By using a Gaussian 09 program to study −l- doubling effect of CO₂, molecule using semi empirical quantum programs . (pm6) ,HF and DFT methods this by using different bases sets such as pm6 , AM3, 6-31G ,6-31G(d,p),.....etc.

So Renner-Teller effect In a zero-approximation levels with the same vibrancies state has the same energy, i.e. the electronic angular momentum do not interact with the vibration angular reality momentum. In this is not always the case, especially not for CO₂ The splitting between these levels is called the Renner-Teller effect. When the molecule is bent, i.e. when the bending vibration is excited, the potential function splits in two. In symmetric terms this has the effect that the symmetric group is changed from D ∞ h to D2h. The symmetric species $\angle g$ splits into A₂ and B₂, $\angle u$ to A₁ and B₁, $\otimes g$ to A₁ and B₁, and $\otimes u$ to A₂ and B₂ in this new symmetry.

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These components are sometimes^[4] referred to as $\angle(+)$ and $\angle(-)$ etc., where the sign indicates the level with the higher and lower energies. Which symmetry term that corresponds to each energy level is difficult to know since the both potential functions touch each other and the electron therefore can go from one to another. It has as effect that the bending vibration is split, for $v_2=1$ it results in $\Sigma^+g, \Delta g$ and Σ^-g sub states. The energy levels that the Renner-Teller effect gives rise to can be calculated from the formulas: When $K = 0$ (Σ vibrancies states):

$$G(v_2, K) = \omega_2 (v_2+1) \sqrt{(1 + \epsilon)}$$

When $K \neq 0$, $v_2 = K - 1$ (lowest single vibrancies level of Π, Δ, \dots):

$$G(v_2, K) = \omega_2 \left[(v_2+1) - \frac{1}{8} \epsilon^2 K(K+1) \right]$$

When $K \neq 0$, $v_2 > K - 1$ (remaining Π, Δ, \dots)

$$G(v_2, K) = \omega_2 (v_2+1) \left(1 - \frac{1}{8} \epsilon^2 \right) \omega_2 v_2 \sqrt{(1 + v_2)^2 + K^2} \frac{dy}{dx}$$

Results And Analysis:

From calculated l-type resonance The l-type resonance is a result of the sub states lying close together. According to Gausses the table (1) shows result of -l- doubling using different bases *set al.* there is l-type resonance in CO_2 , and as a result the 020-vibrational level consists of two close laying states This is agreed by Kawaguschi *et al.* [5] but not by Rohlging.

Rolfings states that the molecule could be well described without l-type resonance, and that the 020-vibrational [3]. Because the two sub-states should lie so close to each other they will perturb each other, this results in that at high J-values the second component

Table 1: shows -l- doubling of CO_2

Calculation Methods		(cm^{-1}) -l- doubling			
		Q ₀₁₀	Q ₀₂₀	Q ₀₃₀	Q ₀₄₀
Semi-empirical	PM6	-0.00076	-0.001144652	-0.00153	-0.001907753
Hartree Fock	6-311G*	-0.0006	-0.000905453	-0.00121	-0.001509089
Density functional theory / B3LYP	6-311G**	-0.00061	-0.000910542	-0.00121	-0.001517569
	aug-cc-pVDZ	-0.0006	-0.000901418	-0.0012	-0.001502363
	Paug-cc-pVTZ	-0.00061	-0.00091353	-0.00122	-0.00152255
	aug-cc-pVQZ	-0.00061	-0.000916151	-0.00122	-0.001526918
	SDD	-0.00058	-0.000877115	-0.00117	-0.001461859

Renner –Teller calculation:

The carbon dioxide based on a C atom and an O–O legend fragment. Carbon has 2S and $2P_{x,y,z}$ orbital's and the O–O fragment has 2S and $2P_{x,y,z}$ orbital's that are involved in the formation of molecular orbital geometrical of CO_2 ^[6] this results which showed b. Since CO_2 has $D_{\infty h}$ symmetry the central atom's orbital symmetry labels can be obtained from the corresponding point group table: $2S = \sigma_g$, $2P_z = \sigma_u$ and $2P_{x,y} = \pi_u$. The LGO symmetry lables can be calculated using the point group table as well: $\Gamma_{\sigma} = 2\sigma_g + 2\sigma_u$ and $\Gamma_{\pi} = 2\pi_g + 2\pi_u$. The MO diagram for CO_2 is more complicated than the diagram for B_2 . The following diagram fails to label orbital symmetries but the LGO $2P_{x,y}$ participate in the formation of π double bonds. The $2\pi_g$ orbital are nonbonding because the C $2P_{x,y}$ atomic orbitals are π_u . The LGO $2P_z$ orbital are involved in σ bonds as shown in fig.(1).

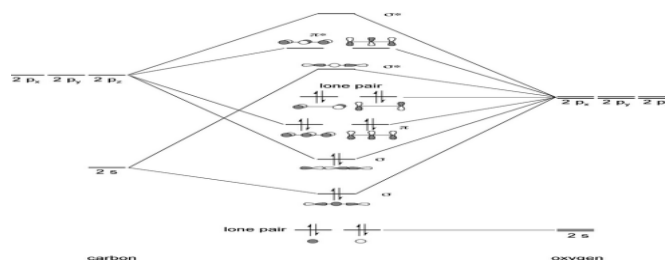


Fig. 1: shows spilt of state in CO_2 molecule.

So Tables 2 shows vibration energies are determined as the difference energies CO₂Table (2) shows the energy of vibrational state of in CO₂ molecule.

State	(eV) Energy state						
	Semi-empirical	Hartree Fock	Density functional theory / B3LYP				
	PM6	6-311G*	6-311G**	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	SDD
(0,10)	0.066696	0.095085	0.082688	0.082688	0.083556	0.083804	0.076118
(0,2,0)	0.133392	0.19017	0.165376	0.165376	0.167112	0.167607	0.152235
(1,0,0)	0.170707	0.188682	0.170459	0.167855	0.169715	0.169963	0.169963
(1,1,0)	0.237403	0.283767	0.253147	0.250543	0.253271	0.253767	0.24608
(0,0,1)	0.287734	0.32133	0.301991	0.296164	0.297528	0.298024	0.283271
(1,2,0)	0.304098	0.378852	0.335835	0.333231	0.336826	0.33757	0.322198
(2,0,0)	0.341413	0.377365	0.340918	0.335711	0.33943	0.339926	0.339926
(2,1,0)	0.408109	0.47245	0.423605	0.418399	0.422986	0.423729	0.416043
(1,0,1)	0.458441	0.510013	0.47245	0.46402	0.467243	0.467987	0.453234
(2,2,0)	0.458441	0.510013	0.47245	0.46402	0.467243	0.467987	0.453234
(3,0,0)	0.51212	0.566047	0.511376	0.503566	0.509145	0.509889	0.509889
(3,1,0)	0.578816	0.661132	0.594064	0.586254	0.592701	0.593692	0.586006
(2,0,1)	0.629148	0.698695	0.642908	0.631875	0.636958	0.63795	0.623197
(3,2,0)	0.645512	0.756217	0.676752	0.668942	0.676256	0.677496	0.662124
(4,0,0)	0.682827	0.754729	0.681835	0.671422	0.67886	0.679851	0.679851
(2,1,1)	0.695844	0.79378	0.725596	0.714563	0.720514	0.721257	0.699315
(4,1,0)	0.749523	0.849814	0.764523	0.75411	0.762416	0.763655	0.755969
(3,0,1)	0.799854	0.887377	0.813367	0.79973	0.806673	0.807417	0.79316
(3,1,1)	0.86655	0.982462	0.896055	0.882418	0.890229	0.89122	0.869278

From table (2) the split of (2,0,0) vibrational state caused by Renner-Teller effect in CO₂ molecules to four approximate state (1,2,0), (2,1,0), (2,0,0) and (0,0,1) as studied in experimental.

Conclusion:

A double resonance four-wave mixing approach was used to unambiguously identify the vibrancies R-T manifold in the state (1,2,0), (2,1,0), (2,0,0) and (0,0,1) as studied in experimental electronic transition. An assignment of the levels was carried out by a R-T analysis, leading to a relatively large ϵ_6 in the ground state for the second lowest bending mode as previously

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