

Two-photon excitation for C_{2v} molecules based on the full relativistic theory

—Characteristic symmetry for C_{2v} group

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Received 10 December 2011; revised 11 January 2012; accepted 22 January 2012

ABSTRACT

The present work explores a new phenomenon that not all the transition probability of two photon processes is negligible at low irradiance. The irreducible representation $2B_2$ of C_{2v} is unexpected, for there is no much deviation in oscillator strength for two-photon and single-photon process A_1 to $2B_2$. This new phenomenon is only possible to be explored by the symmetrical consideration: the necessary and sufficient condition is molecular plane coincident with yz plane or the operation $\sigma'_v(yz)$ for group C_{2v} . It is only possible to be evaluated out by use of the full relativistic quantum mechanical theory.

Keywords: Two-Photon Excitation; C_{2v} Group; The Full Relativistic Quantum Mechanical Theory

1. INTRODUCTION

Since two-photon absorption had been theoretically described by Maria Göppert-Mayer as early as in 1931, the multiphoton process has been one of the most interested focuses after laser sources and synchrotron radiation. Two-photon absorption has been widely exploited in different fields due to its quadratic dependence on the irradiance, which makes it possible to confine the laser excitation to the focal volume. Such feature has led to a large number of technological applications, such as multiphoton fluorescence microscopy and two-photon photopolymerization.

The water molecule with only 10 electrons is an ideal system for comparing theory and experiment [1]. The process $\bar{X} \rightarrow \bar{B}$ of H_2O system has been excited by use of 266 nm two-photon excitation energy of 7.5186 eV.

However, some of theoretical methods of two-photon absorption spectra were determined based on the density functional theory (DFT) with B3LYP functional as implemented at the Gaussian 03 package [2]. This is a non-

relativistic theory. It is better to use the full relativistic theory which is involved in both space and time symmetry [3]. The inclusion of inversion with the spatial rotation as a symmetry operation suggests through the relativistic equivalence of space and time that we also include a time-reversal operation, which is related with 4-dimensional Minkowski space. Time-reversal symmetry is introduced in Atomic and Molecular reaction Statics in 1996 [4].

Both furan (C_4H_4O) and molecule CHe^{2++} are the C_{2v} symmetry. All the carbon, hydrogen and oxygen atoms of furan form a planar ring with $2p\pi$ delocalization. It is necessary to explore its two photon processes and related with fluorescence. Molecule CHe^{2++} is one of possible species to solidify the α -particle emitted from plutonium atom, which is the most significant. It is to prove that there are no much deviation in the oscillator strength for single-photon and two-photon process A_1 to $1B_2$ of group C_{2v} .

2. THE FULL RELATIVISTIC THEORY

Symmetry plays an important role for quantum mechanical theory. There are three levels for quantum mechanical method: Non-relativistic based on the single point group, relativistic based on the double group and relativistic based on the full symmetry group or quaternion symmetry.

In consideration of the equivalence of space and time, for the relativistic theory based on the full symmetry group or quaternion symmetry, the time reversal symmetry operation is included in the symmetry group. It is well known that the product of two symmetry operators is represented by the product of the corresponding unitary matrices in the theory of group representation, however, time reversal symmetry operation is an antiunitary operator. The inclusion both of space and time operations, the group is called the full symmetry group, and their group representation is called a co-representation, this nomenclature is introduced by Wigner. The co-repre-

sensation is not unitary representation; however, it is still possible to be broken down to irreducible form. The third level, *i.e.*, relativistic quantum mechanical theory based on the full symmetry group or quaternion symmetry is firstly applied by the work of T. Saue and the others [5].

Time reversal operator or called Kramer operator [4] is defined as follows

$$\hat{K}\psi(r,t) = \psi^*(r,-t) \tag{1}$$

If Hamiltonian \hat{H} is a real function of r , then

$$\begin{aligned} \hat{K}\hat{H}(r)\psi(r,t) &= \hat{H}^*(r)\psi^*(r,-t) \\ &= \hat{H}(r)\psi^*(r,-t) = \hat{H}\hat{K}\psi(r,t) \end{aligned} \tag{2}$$

i.e.

$$[\hat{H}, \hat{K}] = 0 \tag{3}$$

The commutator (3) is the necessary and sufficient condition for two operators \hat{K} and \hat{H} having the same set of eigenfunctions, that is, the state is invariant to time reversal(motion reversal).

It is proved that time reversal operator is antiunitary [4], *i.e.*

$$\langle \hat{K}\psi | \hat{K}\phi \rangle = \langle \psi | \phi \rangle^* = \langle \phi | \psi \rangle \tag{4}$$

It is also anti-linear operator.

Kramer theorem [4,6]: It can be proved that $\hat{K}^2 = -1$ corresponding to J value of half odd integer, *i.e.* fermions, there will be the new double degeneracy by time reversal; and $\hat{K}^2 = +1$ corresponding to J value of integer, *i.e.* bosons, with no double degeneracy.

For the time-independent Dirac equation

$$\hat{h}_D\psi = E\psi \text{ and } \hat{h}_D = \beta^m mc^2 + c(\alpha \cdot \hat{p}) + \hat{V} \tag{5}$$

$$\text{where, } \alpha = \begin{bmatrix} 0 & \sigma \\ \sigma & 0 \end{bmatrix}; \beta' = \begin{bmatrix} 0 & 0 \\ 0 & 2I_2 \end{bmatrix}; \tag{6}$$

$I_2 - 2 \times 2$, unit matrix.

And Pauli spins matrices

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}; \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}; \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \tag{7}$$

If $\hat{V} = 0$, It is the Dirac equation of free electrons.

Now, time reversal operator is defined using another equivalent method, *i.e.* Kramer theorem [4,7], in which $\hat{K}^2 = -1$, that is $\hat{K}^2\phi = -\phi = \bar{\phi}$, in which the state are recovered by twice of time reversal, however, the wave function is changed to the negative; If $\hat{K}^2 = +1$, that is $\hat{K}^2\phi = \phi$, in which the state are recovered by twice of time reversal, the wave function is unchanged. Then ϕ and $\bar{\phi}$ are said to form a Kramers pair. Therefore, the operator can be expanded in terms of Kramer's partners $\{\phi\}$ and $\{\bar{\phi}\}$. For example, Hermitian of one-electron

operator [5,7] is defined as follows

$$\begin{aligned} \hat{h}_D &= \begin{pmatrix} A & B \\ -B^* & A^* \end{pmatrix} \\ &= \begin{pmatrix} \hat{V} & -ic\hat{d}_z & 0 & -ic\hat{d}_- \\ -ic\hat{d}_z & -2mc^2 + \hat{V} & -ic\hat{d}_- & 0 \\ 0 & -ic\hat{d}_+ & \hat{V} & ic\hat{d}_z \\ -ic\hat{d}_+ & 0 & ic\hat{d}_z & -2mc^2 + \hat{V} \end{pmatrix} \end{aligned} \tag{8}$$

where

$$\hat{d}_z = \frac{\partial}{\partial z}, \hat{d}_\pm = \frac{\partial}{\partial x} \pm i \frac{\partial}{\partial y}. \tag{9}$$

It is easy to know

$$A = \begin{pmatrix} \hat{V} & -ic\hat{d}_z \\ -ic\hat{d}_z & -2mc^2 + \hat{V} \end{pmatrix} = A^+ \tag{10}$$

$$B = \begin{pmatrix} 0 & -ic\hat{d}_- \\ -ic\hat{d}_- & 0 \end{pmatrix} = -B^+ = \begin{pmatrix} 0 & -ic\hat{d}_+ \\ -ic\hat{d}_+ & 0 \end{pmatrix} \tag{11}$$

That is, A is a Hermitian and B is antihermitian. For Kramer's partners, Dirac operator \hat{h}_D can be expressed as

$$\begin{aligned} \hat{h}_D &= I_2 \otimes \begin{pmatrix} \hat{V} & 0 \\ 0 & -2mc^2 + \hat{V} \end{pmatrix} - c i \otimes \begin{pmatrix} 0 & \hat{d}_z \\ \hat{d}_z & 0 \end{pmatrix} \\ &\quad - c j \otimes \begin{pmatrix} 0 & \hat{d}_y \\ \hat{d}_y & 0 \end{pmatrix} - c k \otimes \begin{pmatrix} 0 & \hat{d}_x \\ \hat{d}_x & 0 \end{pmatrix} \end{aligned} \tag{12}$$

where, \hat{h}_D is expressed as the quaternion, which exhibits the time reversal symmetry.

Quaternion algebra [8] was developed by Hamilton and Fresenius, however, limited applications of quaternion in quantum mechanics have been made in recent years.

Quaternion is expressed as

$$q = \sum_{\lambda=0}^3 V_\lambda e_\lambda = V_0 + V_1 \check{i} + V_2 \check{j} + V_3 \check{k} \tag{13}$$

where

$$e_1 = \check{i} \leftrightarrow i\sigma_z; e_2 = \check{j} \leftrightarrow i\sigma_y; e_3 = \check{k} \leftrightarrow i\sigma_x. \tag{14}$$

where $\check{i}, \check{j}, \check{k}$ are quaternion units, i -imaginary, V_0, V_1, V_2 and V_3 are real part, σ_z, σ_y and σ_x are Pauli spins matrices in (7). Quaternion includes 3-dimension complex space and one dimension real space. It is known from (7) to (11) that quaternion algebra includes both time and space reversal symmetry, then, it is called the full symmetry group, its matrix representation

is called co-representation. The \hat{h}_D in (12) is the Dirac operator of full symmetry group. The Dirac equation can therefore be rewritten into quaternion algebra form

$${}^q\hat{h}_D {}^q\psi = E {}^q\psi \quad (15)$$

In this paper, the study of furan (C₄H₄O) and CHE²⁺⁺ molecule are based on the full relativistic quantum mechanical theory for two-photon excitation, and the SAC-CI (The Symmetry Adapted Cluster/Configuration Interaction Method (SAC-CI)) method [11] for single-photon excitation, which would be preferable by comparison.

3. TWO PHOTON PROCESSES

The transition probability of the two photon and three photon processes are obtained from the second-order and three-order approximation coefficients of time-dependent perturbation theory [9], separately. Let us now write the Hamiltonian operator as

$$H = H_0 + H' \quad (16)$$

where H' is the perturbation added on H_0 . Following the electromagnetic theory, the x component of the perturbation H' is expressed as

$$H' = \mu_x E_x = \mu_x E_x^0 (e^{i\omega t} + e^{-i\omega t}), \text{ etc.} \quad (17)$$

Substituting **Eq.16** into the time-dependent Schrödinger equation, then

$$\begin{aligned} \frac{dC_n^{(0)}}{dt} &= 0, \quad i\hbar \frac{dC_n^{(1)}}{dx} = \sum_m C_m^{(0)} \langle \Psi_n^0 | H' | \Psi_m^0 \rangle \\ i\hbar \frac{dC_n^{(2)}}{dt} &= \sum_m C_m^{(1)} \langle \Psi_n^0 | H' | \Psi_m^0 \rangle, \text{ etc.} \end{aligned} \quad (18)$$

Carrying out the integration, we have the transition probabilities for the single photon and two photon processes

$$W_{k \rightarrow n}^{(1)} = \frac{|C_n^{(1)}|^2}{t} = \frac{2\pi}{\hbar} |H'_{nk}|^2 \delta(E_n - E_k) \quad (19)$$

And

$$W_{k \rightarrow n}^{(2)} = \frac{2\pi}{\hbar} \left| \sum_m \frac{H'_{nm} H'_{mk}}{\hbar \omega_{mk}} \right|^2 \delta(E_n - E_k) \quad (20)$$

where $\delta(E_n - E_k)$ satisfies the resonance relation.

In **Eq.18**, the zeroth-order coefficient, *i.e.* the zeroth-order approximation representation is a constant, and the first and secondary approximations are also given. The transition probabilities are given in **Eq.19** for single-photon and in **Eq.20** for two-photon absorptions. The use of two identical photon absorption is just a particular case of **Eq.20**.

The n th-order time-dependent perturbation theory is not only a mathematical method, but also with more physical significance. In fact, Göppert-Mayer noticed that the second-order perturbation theory is able to describe two-photon absorption. In the two-photon absorption, the two photons simultaneously transfer their energy to the atom. Furthermore, it became clear after Göppert-Mayer's work that higher-order perturbation theory reveals multiphoton absorption processes.

The parity selection rules can be described as follows [10]. The Racah's normalized electronic multipole moment is expressed as

$$C_q^k(\theta, \phi) = \left[\frac{4\pi}{(2k+1)} \right]^{1/2} Y_q^k(\theta, \phi) \quad (21)$$

where, for $k = 0, 1, 2, 3, \dots$, are called monopole, dipole, quadrupole, octapole moments... The electronic dipole transitions of single photon processes connect two states with different parity, for operator $C_q^1(\theta, \phi)$ has an odd parity. However, for electronic dipole transitions of two photon processes, the connected states are with common parity due to the second-order approximation coefficients of **Eq.18**.

Symmetry selection rules based on the irreducible representation of group are the same for both single-photon and two-photon absorptions.

The transition probability is a key to apprehend the two photon processes [9]. The transition probability of single photon processes is proportional to the square of transition moment from **Eq.19**, *i.e.* to the square of electric vector which is proportional to irradiance, however, the transition probability of two photon processes is proportional to the product of two transition moment, therefore, proportional to its quadratic dependence on the irradiance. This is why the transition probability of two photon processes could be negligible at low irradiance; however, it will be increased rapidly with the irradiance.

4. TWO PHOTON EXCITATION OF C₄H₄O AND CHE²⁺⁺

In order to review two photon excitation of furan and CHE²⁺⁺, the energy, excitation energy and oscillator strength at light speed 137.036 au are listed in **Table 1** and **Table 2**, which is compared with the results of single-photon excitation by SAC-CI method (The Symmetry Adapted Cluster/Configuration Interaction Method (SAC-CI)) [11].

For a given initial irreducible representation, the final irreducible representation is determined from the **Table 3**. For example, from the initial state A_1 and its y components of transition moment, then, and the final state is B_2 .

Table 1. The calculations of two photon excitation at light speed 137.036 au for furan (C₄H₄O), (Two photon and Single-photon both at the same geometry/Å, deg: CO = 1.3553; CH1 = 1.07693; CH = 1.07832; CC1 = 1.35563; CC = 1.4295; HCO = 115.81476; COC = 106.90016; CCO = 110.53531; HCC = 126.50286; Ground state \tilde{X}^1A_1 ; DIPLEN: the component of dipole length integrals).

Process	Two photon (DIRAC10/6-311G ^{**}) E/au = -228.7900456			Single-photon (SAC-CI/6-311G ^{**}) E/au = -228.6796844		
	Excitation energy/eV	Oscillator strength	DIPLEN/au	Excitation energy/eV	Oscillator strength	DIPLEN/au
A ₁	Excitations are from this state			Excitations are from this state		
1A ₁	7.5737	0.85D-08	-0.21D-03 (Z)	7.0065	0.0012	-0.0835 (Z)
2A ₁	8.1797	0.41D-06	-0.14D-02 (Z)	9.2248	0.6202	1.6566 (Z)
1B ₁	4.2142	0.14D-08	-0.11D-03 (X)	8.4775	0.0293	-0.3756 (X)
2B ₁	6.9253	0.80D-09	-0.69D-04 (X)	9.1635	0.0032	0.1189 (X)
1B ₂	4.2142	0.11D-09	-0.14D-04 (Y)	7.0326	0.1838	-1.0328 (Y)
2B ₂	6.4534	0.1384	0.94 (Y)	9.7175	0.1899	0.8930 (Y)
1A ₂	4.2143	0.0000	0.0000	7.7168	0.0000	0.0000
2A ₂	6.9253	0.0000	0.0000	8.7891	0.0000	0.0000

Table 2. The calculations of two photon excitation at light speed 137.036 au for CHE²⁺⁺ (Two photon and Single-photon both at the same geometry/Å, deg: CHE = 1.1135; HeCHE = 102.0; Ground state \tilde{X}^1A_1).

Process	Two photon (DIRAC10/6-311G ^{**}) E/au = -42.070062877425833		Single-photon (SAC-CI/6-311G ^{**}) E/au = -42.0534355	
	Excitation energy/eV	Oscillator strength	Excitation energy/eV	Oscillator strength
A ₁	Excitations from this state		Excitations from this state	
1A ₁	4.6730	0.11D-07	9.9793	0.0213
2A ₁	9.1500	0.95D-01	20.9675	0.0413
3A ₁	20.9650	0.56D-07	22.0924	0.0007
4A ₁	21.5643	0.12D-01	25.5951	0.2256
1B ₁	3.26160	0.24D-01	4.0982	0.0283
2B ₁	4.6730	0.35D-06	23.0959	0.1111
3B ₁	6.4494	0.74D-09	24.9701	0.0978
4B ₁	20.9650	0.0000	27.7899	0.0086
1B ₂	6.4494	0.66D-07	11.6169	0.0000
2B ₂	10.9457	0.2381	23.0489	0.2309
3B ₂	20.9650	0.31D-06	27.1677	0.2770
4B ₂	21.1171	0.84D-09	30.1624	0.0522
1A ₂	4.6731	0.0000	19.7793	0.0000
2A ₂	6.4494	0.0000	28.9774	0.0000
3A ₂	21.1171	0.0000	34.0372	0.0000
4A ₂	21.8390	0.0000	35.2053	0.0000

Table 3. The dipole transition moment E1 and components of transition moment for C_{2v}.

A ₁ ↔ A ₁ : E1[z]	A ₁ ↔ B ₁ : E1[x]	A ₁ ↔ B ₂ : E1[y]	A ₂ ↔ A ₂ : E1[z]	A ₁ ↔ A ₂
A ₂ ↔ B ₁ : E1[y]	A ₂ ↔ B ₂ : E1[x]	B ₁ ↔ B ₁ : E1[z]	B ₂ ↔ B ₂ : E1[z]	B ₁ ↔ B ₂

5. CHARACTERISTIC SYMMETRY OF TWO PHOTON EXCITATION FOR C_{2v}

In the general, people used to consider the transition probability negligible for two photon processes. From **Tables 1** and **2**, it is obvious that the oscillator strength of two-photon excitation is about 10^{-6} to 10^{-9} less than that of single-photon excitation. There is no much deviation in the oscillator strength of process A_1 to $2B_2$ for both two-photon and single-photon. Therefore, we would come to the conclusion that not all the transition probability of two photon processes is negligible, it depends on the symmetry of group.

The (19) multiplied by delta function $\delta(E_n - E_k)$, then, it is the transition probability of single-photon absorption process with dipole integral element H'_{nk} for k state to n state, which is determined by the resonance relation of single-photon process.

The (20) multiplied by delta function $\delta(E_n - E_k)$, then, it is the transition probability of two-photon absorption process with the product of dipole integral elements H'_{mk} and H'_{nm} for k state to m state and m state to n state. The k state to n state is determined by the resonance relation of two-photon process, *i.e.*

$\hbar\omega_1 + \hbar\omega_2 = E_n - E_k$ or $2\hbar\omega = E_n - E_k$ for two identical photons.

However, consider the characteristic symmetry of group C_{2v} , both C_4H_4O and CHe^{2++} molecule are on the yz plane with the operation $\sigma'_v(yz)$, not so as the operation $\sigma_v(xz)$ perpendicular to molecular plane, therefore, the contribution of y components of transition moment are rather significant. Therefore, the summation for all possible intermediate states m would lead to remarkable transition probability.

In this case, there will be no much deviation for two photon and single-photon processes in the oscillator strength, such as, process A_1 to $2B_2$. For the higher or lower excited states, at least one of intermediate transition moment elements will be quite small and its oscillator strengths negligible. The necessary and sufficient conditions are determined by the operation $\sigma'_v(yz)$ for group C_{2v} .

6. CONCLUSION

The relativistic quantum mechanical theory based on the full symmetry group or quaternion symmetry, *i.e.* inclusion both of space and time operations, is most suitable method for the calculation of two photon processes. Neither non-relativistic, such as DFT implemented [2] at the Gaussian 03 package, nor relativistic without time

reversal would be suggested for the two photon processes.

It is found that not all the transition probability of two photon processes is negligible at low irradiance, which depends on the symmetry of group. The irreducible representation $2B_2$ of C_{2v} is unexpected. There is no much deviation in the oscillator strength of process A_1 to $2B_2$. This new phenomenon is only possible to be explored by the symmetrical consideration: the necessary and sufficient condition is molecular plane coincident with yz plane or the operation $\sigma'_v(yz)$ for group C_{2v} .

If two photon process of A_1 to $2B_2$ of furan is successfully used, it will produce much higher-contrast images for two-photon fluorescence microscopy.

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