

臭氧分子在激光场中的多光子激发*

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摘要: 采用二次量子化方法和酉变换讨论了 O_3 分子在激光场中的多光子激发. 推导出了 O_3 分子的振动 Hamiltonian 算子、从基态到各激发态的跃迁几率公式, 以及 O_3 分子从激光场中吸收的光子数公式, 并分析了计算结果. 这包括对 O_3 分子伸缩振动能谱的计算及与实验结果的比较, 跃迁几率随外场频率的变化、随时间的变化, 以及 O_3 分子在辐射场中的能量吸收情况(取光场强度为 $5 \times 10^{-2} \text{ W/cm}^2$). 建立讨论所有具有 C_{2v} 对称分子从基态到第四激发态以下各态多光子激发问题的模型.

关键词: 多光子; 激发; 臭氧分子; 激光

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Multiphoton Excitation of an Ozone Molecule in Laser Fields*

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Abstract The multiphoton excitation of O_3 molecules in laser fields is discussed using the second quantization and unitary transformations. It is successful to derive the total Hamiltonian (including the stretch-vibration Hamiltonian of an ozone molecule, the laser fields Hamiltonian and the interaction Hamiltonian between O_3 and laser fields), the transition probabilities from the ground state to excited states and the expressions for the average number of photons absorbed by molecules from laser fields. The calculated stretch-vibration energy spectrum of O_3 molecules is in good agreement with that of experiments. There are two peaks of single-photon transition at 1042.5 and 1103.0 cm^{-1} , respectively. The three peaks of the two-photon transition are at 1027.5 , 1055.5 and 1101.0 cm^{-1} respectively. The peaks at 1014.5 , 1028.0 , 1043.0 and 1100.5 cm^{-1} are four peaks of the three-photon transition. The amplitudes of the three-photon transition probability are about 6 orders of magnitude less than those of the two-photon transition which are about 14 orders of magnitude less than those of the single-photon transition. The laser field intensity is taken as $5 \times 10^{-2} \text{ W/cm}^2$, which is different from 10^9 W/cm^2 in the former researches. This theoretical model can be used to discuss the multiphoton excitation for all of the molecules with a C_{2v} symmetry, but inadequate to calculate the n -photon ($n \geq 4$) transition. In the computational process, it is found that the transition probability changes with the intensity of the laser field, which needs further research in the future.

Key words Multiphoton, Excitation, Ozone, Laser

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1 Introduction

Multiphoton phenomena have long been found in experiments. The theoretical investigation of this active subject is developing in depth^[1,2]. A molecule (or atom) may absorb n photons from radiative fields if the total energy of the n photons is equal to the spacing between its energy levels , and thus the transition of the molecule from the lower energy level into the higher one happens.

Over the past 20 years , both theoretical and experimental investigations of the molecular excitation in intense laser fields have advanced considerably^[1-5]. Generally speaking , there are two kinds of theories to describe the multiphoton excitation of molecules : one is the semiclassical theory in which the molecule is treated as a quantum system and the external fields are treated as a classical one , and the other is the pure quantum theory in which both molecules and the fields are quantized.

This work , using the pure quantum theory , is organized as follows : first of all , we derived the stretch vibration Hamiltonian of an ozone molecule , the transition probabilities from the ground state to excited states and the expressions for the average number of photons absorbed by molecules from laser fields. Then we calculated the stretch vibration spectrum of O_3 and the changing in transition probabilities with the frequencies of laser fields. Finally , we present time-dependent transition probabilities and the average number of photons absorbed by the molecule at frequency 1103 , 1101 and 1028 cm^{-1} , respectively.

2 Theory

2.1 The Hamiltonian of O_3 under the Born-Oppenheimer approximation

From the adiabatic Born-Oppenheimer separation of nuclear and electronic motions , the vibrational Hamiltonian for a polyatomic molecule can be written as

$$H = V(\{S_k\}) - \frac{\hbar^2}{2} g^{1/4} \times \sum_{ij} \frac{\partial}{\partial S_i} g^{-1/2} G_{ij} \frac{\partial}{\partial S_j} g^{1/4} \quad (1)$$

$V(\{S_k\})$ is the potential energy^[6] , the second term in Eq.(1) represents the kinetic energy of the nuclei , $g^{1/2}$ is the Jacobian for the transformation from the Cartesian coordinates to the $\{S_k\}$, and the G_{ij} is the elements of the G matrix^[7] in the $\{S_k\}$ system. For O_3 , we have

$$\begin{cases} G_{11} = \frac{2}{m_0} , & G_{12} = \frac{\cos\varphi_e}{m_0} , & G_{13} = -\frac{\sin\varphi_e}{m_0 r_e} , \\ G_{22} = \frac{2}{m_0} , & G_{23} = -\frac{\sin\varphi_e}{m_0 r_e} , \\ G_{33} = \frac{2}{m_0 r_e^2} (2 - \cos\varphi_e) , \\ G_{ij} = G_{ji} \quad (i > j ; \quad i, j = 1, 2, 3, \dots, 21) \end{cases} \quad (2)$$

where m_0 is the oxygen atom's mass , r_e is the equilibrium bond length and φ_e is the equilibrium bond angle.

Using the second quantization and unitary transformations , we can get a generalized Hamiltonian for O_3 as follows^[1,2]

$$H_{\text{Mol}} = \sum_{i=1}^2 [\tilde{\omega} (N_i) N_i - \varepsilon N_i^2 + \tilde{\alpha} N_i^3] + Z_1 \sum_{i<j} N_i N_j + \sum_{i \neq j} a_i^+ a_j \tilde{\gamma} (N_i , N_j) + Z_2 \sum_{i \neq j} a_i^+ a_i^+ a_j a_j + \tilde{\beta} \sum_{i \neq j} a_i^+ a_i^+ a_i^+ a_j a_j a_j + \sum_{i=1}^2 \tilde{\Omega} (N_i) B^+ B \quad (3)$$

Where

$$\begin{aligned} \tilde{\gamma} (N_i , N_j) &= \gamma + 8 \left(\frac{\beta}{\omega} \right)^2 \left(2\eta - \gamma - \frac{7\gamma^2}{3\omega} \right) \times \\ &\quad (N_i + N_j + 1) + \frac{1}{6} [h^2 (H_i^{N+1} + H_j^N) - \\ &\quad g^2 (G_i^{N+1} + G_j^N)] , \\ \tilde{\omega} (N_i) &= \omega - \varepsilon - \left(\frac{\eta^2}{2\omega} + \frac{194\beta^2\gamma^2}{3\omega^3} \right) + \\ &\quad 36 \left(\frac{\beta}{\omega} \right)^2 (\eta + \gamma) + g^2 G_i^N - h^2 H_i^N , \\ Z_1 &= 24 \left(\frac{\beta}{\omega} \right)^2 \left(3\eta + 3\gamma - \frac{28}{9} \frac{\gamma^2}{\omega} \right) , \\ Z_2 &= 2 \left(\frac{\beta}{\omega} \right)^2 \left(5\gamma - 3\eta + 36 \frac{\gamma^2}{\omega} \right) , \\ \tilde{\Omega} (N_i) &= \Omega - g^2 G_i^N - h^2 H_i^N , \\ \tilde{\varepsilon} &= \varepsilon + \frac{82\beta^2\gamma^2}{3\omega^3} , \\ G_i^N &= \left(\omega - \frac{4}{3}\Omega - 2\varepsilon N_i \right)^{-1} , \\ H_i^N &= \left(\omega + \frac{4}{3}\Omega - 2\varepsilon N_i \right)^{-1} \end{aligned} \quad (4)$$

In Eq. (3), the first five terms describe the stretch vibration of the molecule, and the last term describes the bend vibration. In Eq. (4), we have

$$\begin{aligned} \mu &= \frac{1}{G_{11}}, \quad \mu_3 = \frac{1}{G_{33}}, \quad \varepsilon = 30 \frac{\beta^2}{\omega} - 6\delta, \\ \omega &= \sqrt{\frac{k_{11}}{\mu}}, \quad \eta = \frac{k_{12}}{2\mu\omega} - \frac{\mu\omega G_{12}}{2}, \quad \Omega_3 = \sqrt{\frac{k_{33}}{\mu_3}}, \\ g &= \frac{k_{13}}{2M^{1/2}} + \frac{G_{13}M^{1/2}}{2}, \quad h = \frac{k_{13}}{2M^{1/2}} - \frac{G_{13}M^{1/2}}{2}, \\ \gamma &= \frac{k_{12}}{2\mu\omega} + \frac{\mu\omega G_{12}}{2}, \quad \beta = \frac{k_{111}}{6} \left(\frac{1}{2\mu\omega} \right)^{3/2}, \\ M &= \mu\omega\mu_3\Omega_3 \end{aligned} \quad (5)$$

All the needed parameters are listed in Table 1^[8]. The energy levels calculated by Eq. (3) do not agree well with those of experiments. Therefore we must optimize it.

Neglecting the bending vibration

$$\begin{aligned} H_{\text{Mol}} &= \sum_{i=1}^2 [\tilde{\omega}(N_i)N_i - \tilde{\varepsilon}N_i^2 + \tilde{\alpha}N_i^3] + \\ &Z_1 \sum_{i<j} N_i N_j + \sum_{i \neq j} a_i^+ a_j \tilde{\eta}(N_i, N_j) + \\ &Z_2 \sum_{i \neq j} a_i^+ a_i^+ a_j a_j + \tilde{\beta} \sum_{i \neq j} a_i^+ a_i^+ a_i^+ a_j a_j a_j \end{aligned} \quad (6)$$

Table 1 The needed parameters

r_e/pm	$\varphi_e/(\circ)$	$m_0/10^{-26}\text{kg}$	k_{11}/Nm^{-1}	k_{12}/Nm^{-1}	$(k_{13}/r_e)/\text{Nm}^{-1}$	$(k_{33}/r_e^2)/\text{Nm}^{-1}$	$r_e k_{111}/\text{Nm}^{-1}$	$r_e^2 k_{1111}/\text{Nm}^{-1}$
127.8	116.8	2.6568	684	107.5	-59.34	231.44	-7027.98	37686.40
β/cm^{-1}	ω/cm^{-1}	Ω/cm^{-1}	δ/cm^{-1}	γ/cm^{-1}	η/cm^{-1}	g/cm^{-1}	h/cm^{-1}	$\varepsilon/\text{cm}^{-1}$
-33.75	1204.6	1097.0	1.48	-41.13	230.45	-249.53	78.17	19.49

Table 2 Stretch vibration spectrum of $\text{O}_3(\text{cm}^{-1})$

v	v_1	v_2	Values calc.	Values obs. ^[9]	v	v_1	v_2	Values calc.	Values obs. ^[9]
1	0	1	1041.59	1042.10	4	0	4	4001.97	4001.40
	1	0	1105.28	1103.10		1	3	4024.62	4021.90
2	0	2	2058.79	2057.89	2	2	4127.25	4126.50	
	1	1	2110.50	2110.80	3	1	4236.25	4235.70	
	2	0	2202.89	2201.20	4	0	4369.94	4370.30	
3	0	3	3046.86	3046.10	5	4	4922.79	4923.60	
	3	0	3085.70	3083.70	5	0	4935.08	4936.00	
	1	2	3178.83	3186.40	0	5	5052.30	5052.60	
	2	1	3290.98	3290.00	3	2	5152.60	5151.90	
					2	3	5287.50	5285.70	
					1	4	5440.27	5441.00	

where $\tilde{\alpha}$ and $\tilde{\beta}$ are two coefficients. All of the coefficients in Hamiltonian (6) are optimized as

$$\begin{aligned} \tilde{\omega}(N_i) &= 1331.57 + \frac{62267.67}{-258.07 - 38.98N_i} - \\ &\frac{6134.27}{2667.27 - 38.98N_i} \\ \tilde{\eta}(N_i, N_j) &= -45.63 + 6.829(N_i + N_j) + \\ &\frac{1022.38}{2628.29 - 38.98N_i} + \frac{1022.38}{2667.27 - 38.98N_j} - \\ &\frac{10377.95}{-297.05 - 38.98N_i} - \frac{10377.95}{-258.07 - 38.98N_j} \\ Z_1 &= 3.826, \quad Z_2 = 0.116, \\ \tilde{\alpha} &= 1.928, \quad \tilde{\beta} = -0.054, \quad \tilde{\varepsilon} = 48.13 \end{aligned} \quad (7)$$

The stretch vibration spectrum of O_3 obtained by using this Hamiltonian agrees well with that of experiments (see Table 2).

2.2 Interaction Hamiltonian between O_3 and laser fields

Let the symmetric axis of O_3 be z axis (Fig. 1), and its dipole moment can be written as

$$p_z = q \cos \frac{\varphi}{2} (r_1 + r_2) \quad (8)$$

Expanding the dipole moment about the equilibrium position of O_3 and keeping the first-order approximation, we have

$$p_z = p_z(\varphi_e, r_e, r_e) + \sum_{i=1}^2 \left(\frac{\partial p_z}{\partial r_i} \right)_{r_e} (r_i - r_e) + \left(\frac{\partial p_z}{\partial \varphi} \right)_{\varphi_e} (\varphi - \varphi_e) + \dots \quad (9)$$

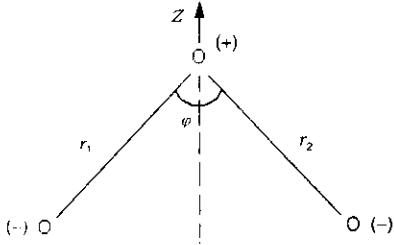


Fig. 1 The electrical dipole moment of O_3

Neglecting the influence of the variation of bond angles on the dipole moment, we get the total Hamiltonian as follows:

$$H_{MF} = H_{Mol} + H_F + \sum_{i=1}^2 V_{rad}(a_i^+ c + a_i c^+) \quad (10)$$

where H_{Mol} is equivalent to Eq.(6). $H_F = \omega_F c^+ c$, the Hamiltonian of a monochromatic quantum field. The third term in Eq.(10) is the interaction Hamiltonian. And

$$V_{rad} = -2.22 \times 10^{-12} \sqrt{\omega_F} \quad (11)$$

The eigenstate of H_{MF} is $|v_1, v_2, |N-v\rangle$, and $\{v_i\}$ is the quantum number of two vibrations. $v = v_1 + v_2$, the label of the v th vibration energy band. N is the photon number of the laser field at the beginning. The transition probability into band v from the ground state ($|0, 0\rangle$) is given by

$$P_{0v}(t) = \sum_{\alpha \in v} |\langle \alpha | e^{-iH_{MF}t/\hbar} | 0 \rangle|^2 \quad (12)$$

The average photon number absorbed by the molecule is

$$n(t) = \sum_v \sum_{\alpha \in v} \frac{E_\alpha}{\hbar \omega_F} |\langle \alpha | e^{-iH_{MF}t/\hbar} | 0 \rangle|^2 \quad (13)$$

The long-time average of the transition probability is written as

$$\overline{P_{0v}(\omega_F)} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T P_{0v}(t) dt \quad (14)$$

The long-time average number of photon absorbed by the molecule can be calculated by

$$\overline{n(\omega_F)} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T n(t) dt \quad (15)$$

3 Results

3.1 The stretch-vibration spectrum of an ozone molecule

The energy levels of bands 1 through 5 have been calculated using Eq.(6). Theoretical and experimental values are listed in Table 2.

3.2 Long-time-averaged transition probability

The long-time-averaged transition probability for exciting into a stretching band v from the ground state P_{0v} is given by Eq.(14). Fig. 2 ~ 4 show $\log \overline{P_{0v}}$ ($v = 1, 2, 3$) as a function of field frequency, with a laser intensity of $5 \times 10^{-2} \text{ W/cm}^2$. In Fig. 2 a peak at 1042.5 cm^{-1} designates the single-photon transition into the 1st energy level of band 1 from the ground state, and another peak at 1103.0 cm^{-1} designates the single-photon transition into the 2nd energy level of band 1 from the ground state. Transition into the second band is shown in Fig. 3. The peaks at 1027.5 , 1055.5 and 1101.0 cm^{-1} describe the transition into the 1st, 2nd and 3rd energy levels of band 2 from the ground state. Fig. 4 shows the three-photon transition probabilities, the peaks at 1014.5 , 1028.0 , 1043.0 and 1100.5 cm^{-1} describe the transition into the 1st, 2nd, 3rd and 4th energy levels of band 3 from the ground state.

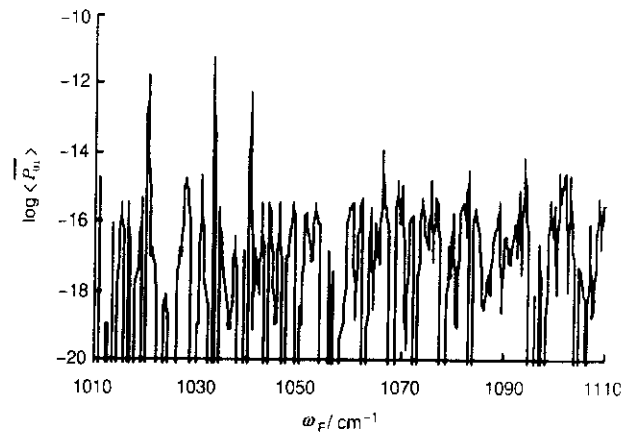


Fig. 2 Peaks of single-photon transitions

3.3 Time-dependent transition probabilities

Time-dependent transition probabilities (Eq. 12)

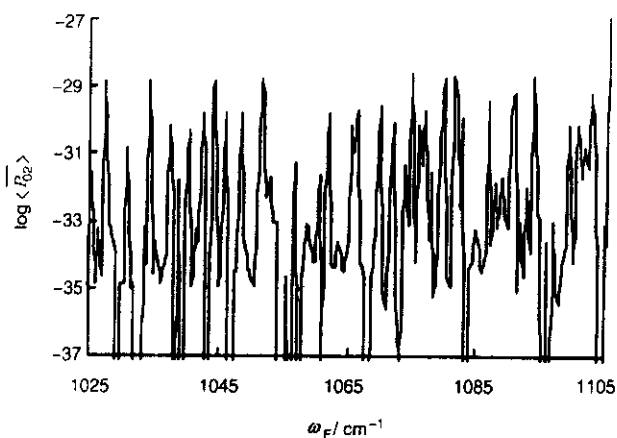


Fig. 3 Peaks of two-photon transitions

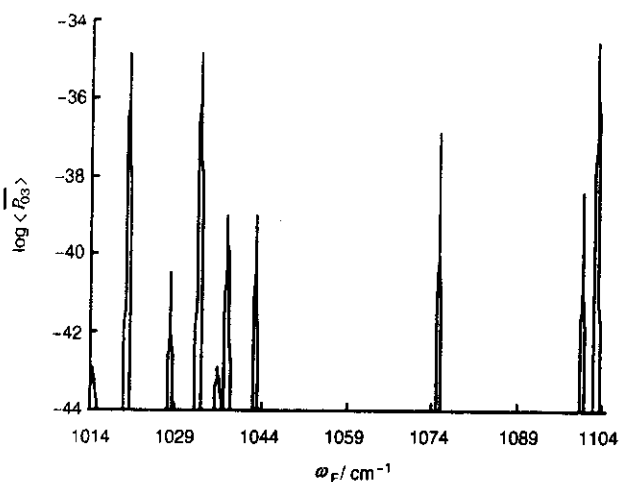
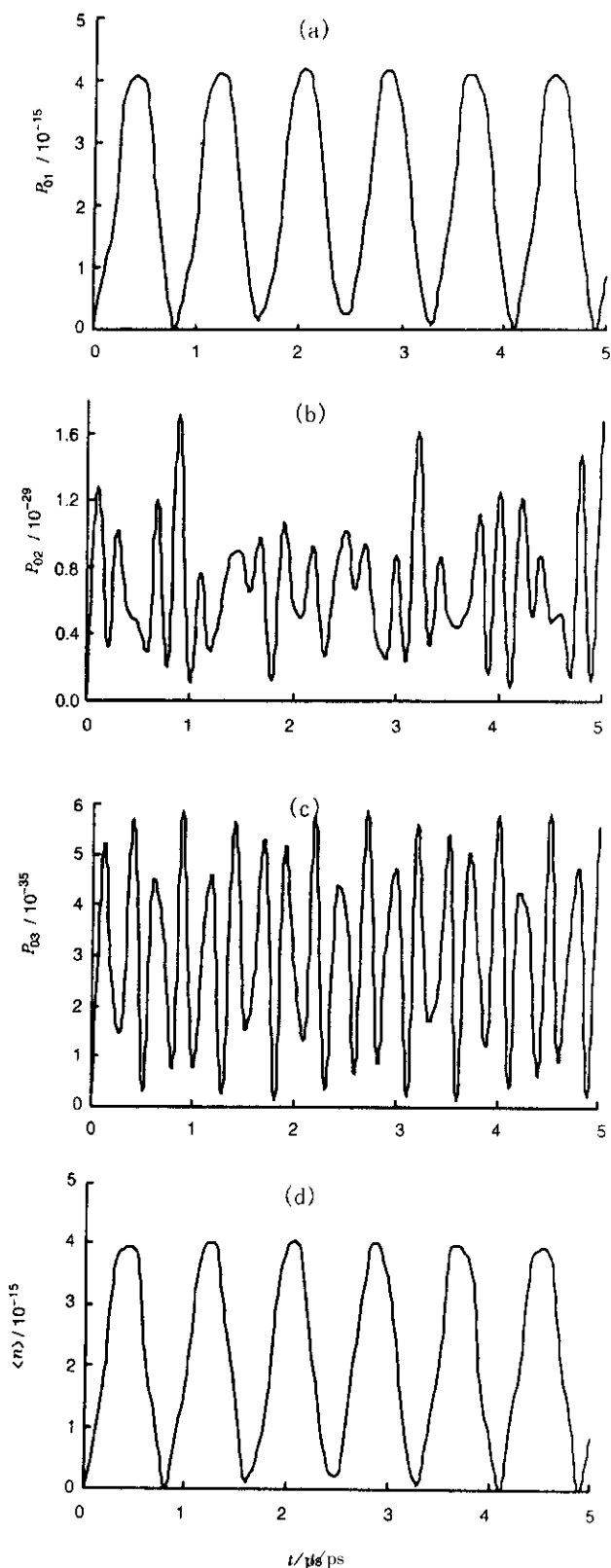


Fig. 4 Peaks of three-photon transitions

are shown in Fig. 5 ~ 7 at three laser frequencies. Fig. 5 shows the result of a calculation performed at $\omega_F = 1103.0 \text{ cm}^{-1}$. In Fig. 5(a), the single-photon transition probability $P_{01}(t)$ varies periodically with time increase. Its period is about 0.8 ps, and the amplitude is about 2.1×10^{-15} . In Fig. 5(b), $P_{02}(t)$ also varies periodically with time increase. Its period is about 0.3 ps, and the amplitude is about 0.7×10^{-29} , which is about 14 orders of magnitude less than that of $P_{01}(t)$. In Fig. 5(c), the period of $P_{03}(t)$ is about 0.3 ps, the same as $P_{02}(t)$, and the amplitude is about 2.5×10^{-35} , which is about 6 orders of magnitude less than that of $P_{02}(t)$. So the single-photon transition is easy to occur under $\omega_F = 1103.0 \text{ cm}^{-1}$.

In Fig. 6, the field frequency ω_F is turned to a two-photon resonance in band 2. The period of $P_{02}(t)$

Fig. 5 Time-dependent transition probabilities and the photon absorption at $\omega_F = 1103.0 \text{ cm}^{-1}$

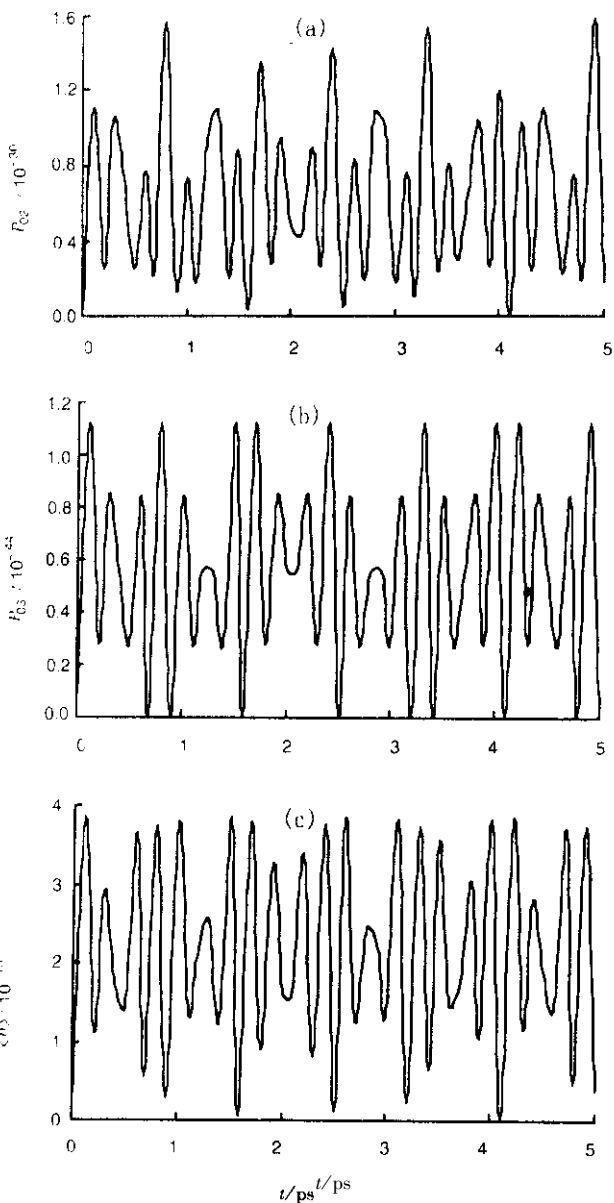


Fig. 6 Time-dependent transition probabilities and the photon absorption at $\omega_F = 1101.0 \text{ cm}^{-1}$

is about 0.2 ps, the amplitude is about 0.5×10^{-30} , the period of $P_{03}(t)$ is about 0.2 ps and the amplitude is about 0.3×10^{-44} .

In Fig. 7, the field frequency ω_F is turned to a three-photon resonance in band 3. The period of $P_{03}(t)$ is about 0.8 ps, and the amplitude is about 0.14×10^{-41} .

3.4 Energy absorption

Excitation in the molecules is measured by the average number of photons absorbed from the field.

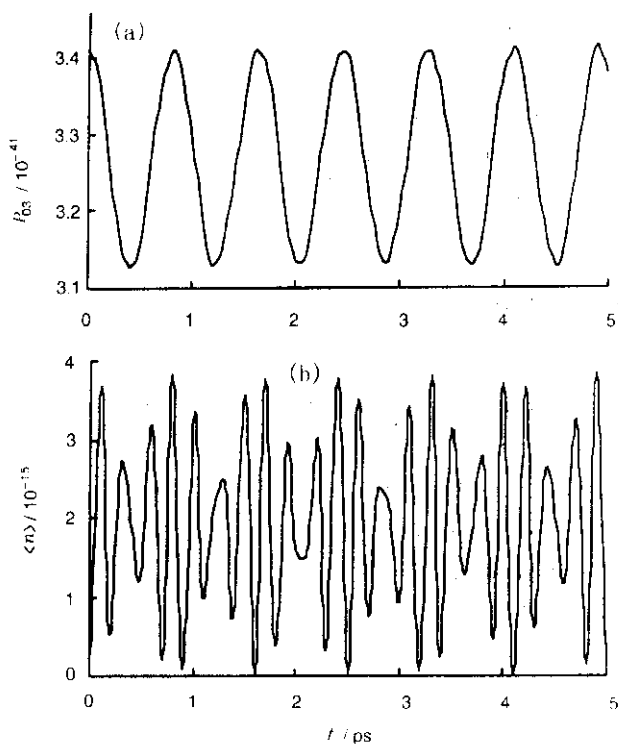


Fig. 7 Time-dependent transition probabilities and the photon absorption at $\omega_F = 1028.0 \text{ cm}^{-1}$

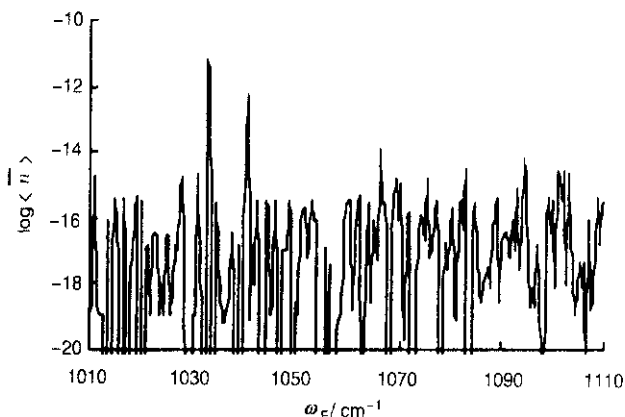


Fig. 8 Long-time-averaged number of photons absorbed from the ground state as function of field frequency

Fig. 5(d), 6(c) and 7(b) depict the flow of energy between molecules and the field as a function of time.

The long-time-averaged number of photons absorbed from the field (Eq. 15) is shown in Fig. 8. This is a portion of the absorbed spectrum which is accounted for the only bend-dressed stretch states of ozone. The peaks at 1042.5 and 1103.0 cm^{-1} are for absorption into the 1st and 2nd excited states of band 1. The

peaks at 1055.5 and 1101.0 cm^{-1} are for absorption into the 2nd and 3rd excited states of band 2. The peak at 1028.0 cm^{-1} is for absorption into the 2nd excited states of band 3. As the n -photon ($n \geq 4$) transition is too rare, there are not the peaks of band the 4, 5... in Fig. 8 and the other peaks need research in the future.

4 Discussion

This theoretical model can be used to discuss the multiphoton excitation for all of the molecules with the C_{2v} symmetry. But it is inadequate to calculate the n -photon ($n \geq 4$) transition.

Since the smaller Hamiltonian matrix can simplify the calculation, the intensity of the laser field is taken as $5 \times 10^{-2} \text{W}/\text{cm}^2$. In the computational process, we found the transition probability changed with the intensity of the laser field.

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